Supporting Information

meso-Tetrakis(3,5-dihydroxyphenyl)N-Confused Porphyrin: Influence of polar protic and aprotic solvents in tautomeric existence, exchange and morphology

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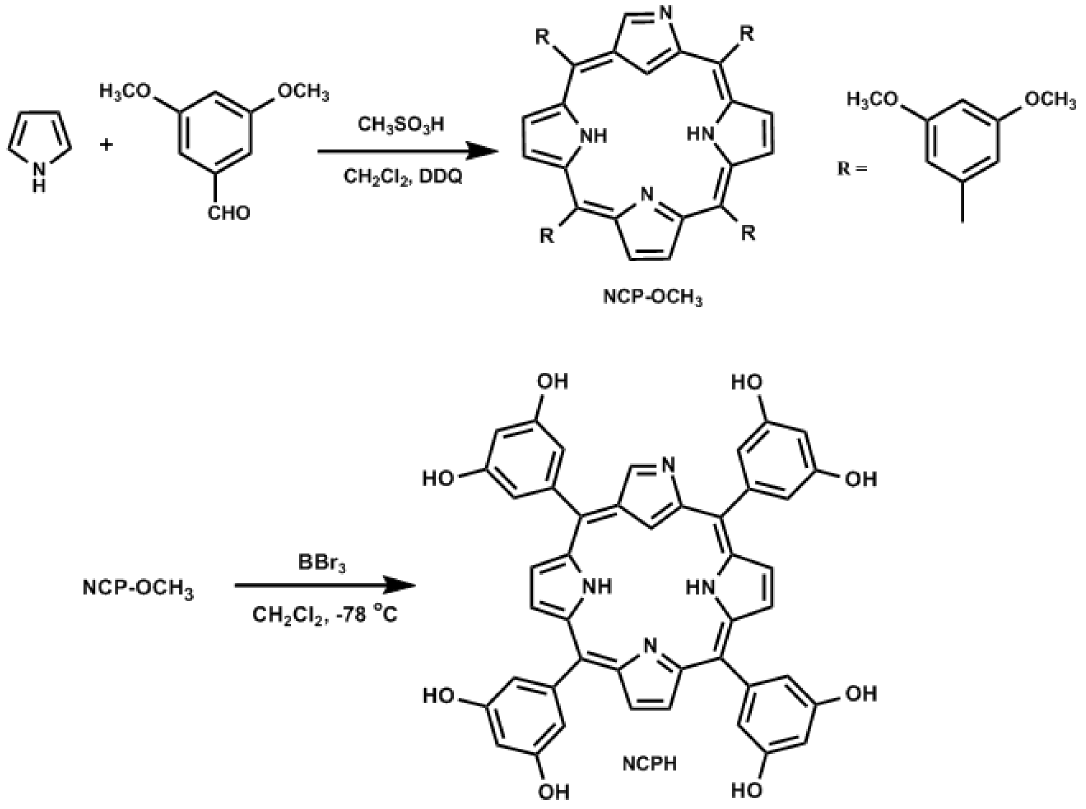
Table of contents:

Experimental Section

Materials and methods:

The reagents for the synthesis as well as photophysical studies were obtained from Sigma-Aldrich and Merck, India and used as such. All solvents were distilled and dried before use. Deionized water was from Millipore. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Biospin 400 MHz spectrometer. NMR experiments were done in DMSO-d_6 and CD_3OD. Spectra were referenced internally by using the residual solvent (1H, δ= 2.5 and 13C, δ = 39.4 for DMSO-D6) resonances relative to SiMe4 and the solvent peak were removed for clarity in the main text. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 KV, 10 mA) as the FAB gas. Infrared spectrum of the compound was recorded on a Perkin Elmer FT-IR spectrometer, spectrum RXI. Electronic absorption spectra and steady state fluorescence spectra were recorded on Perkin Elmer Lambda-750 UV-VIS Absorption spectrometer and Perkin Elmer LS55 Fluorescence spectrometer respectively. Time-resolved fluorescence measurements were carried out by using a time-correlated single photon counting (TCSPC) spectrometer (Edinburgh, OB920). A diode laser ($\lambda_{exc.}$= 445 nm, FWHM = 98 ps) was used to excite the compound and MCP photomultiplier (Hamamatsu R3809U-50) was used as the detector (response time 40 ps). The lamp profile was recorded by using a scatterer (dilute ludox solution in water) in place of the sample. Decay curves were analyzed by a nonlinear least-squares iteration procedure using F900 decay analysis software. The quality of the fit was judged by the χ^2, values and weighted deviation was obtained by fitting. SEM imaging was performed on a Zeiss EVO 18 Cryo Special Edn with variable pressure detector working at 20-30 kV. Atomic Force Microscopy images were recorded under ambient conditions using a NTEGRA (NT-MDT) operating with a use tapping mode regime. Micro-fabricated TiN cantilever tips (NSG10) with a resonance frequency of 299 kHz and a spring constant of 20-80 Nm^{-1} were used. AFM section analysis was done offline. Samples for the imaging were prepared by drop casting the solution on freshly cleaved mica surface at the required concentrations at ambient conditions.

Synthesis of NCPH:



Scheme S1: Synthetic route for **NCPH**.

Synthesis of **NCPH** was achieved through a two step synthetic strategy. In the first step, *meso*-Tetrakis(3,5-dimethoxyphenyl) N-Confused Porphyrin(NCP-OCH_3) was prepared by Lindsey's method[1]. In the second step, dry dichloromethane (15 ml) was taken in a 100 ml two neck RB flask at -78 °C under argon atmosphere and 0.5 ml boron tribromide (BBr_3) was added to this. Solution of NCP-OCH_3 (100 mg) in 15 ml dichloromethane was added slowly to the BBr_3 solution and allowed to stir for 2h at -78 °C and then gradually brought to RT. The mixture was refluxed at 65 °C for 8h and then room temperature for 12h. To the solution water was added and heated at 85 °C for 6h. The water layer was decanted and the compound recrystalised from dichloromethane and 2-propanol mixture. ^{1}H NMR (400MHz, DMSO-d6): δ 14.30 (s, 1H, exch. D2O, pyrrolic outer NH), 10.11 (s, 4H, exch. D2O, phenolic OH), 9.9 (s, 4H, exch. D2O, phenolic OH), 8.74−8.75 (d, J = 4.8 Hz, 1H, pyrrolic β H), 8.62−8.63 (d, J = 4.8 Hz, 1H, pyrrolic β H), 8.39 (s, 1H, pyrrolic α H), 8.29-8.39 (m, 2H, pyrrolic β H), 8.23-8.28 (m, 2H, pyrrolic β H), 7.27 (s, 4H, phenyl), 7.09 (s, 4H, phenyl), 6.90-6.91(d, 2H, phenyl), 6.77 (s, 2H, Phenyl), 2.14 (s, 1H, exch. D2O, pyrrolic inner NH), -1.82 (s, 1H, pyrrolic inner β H) ^{13}C{^{1}H}NMR (100 MHz, DMSO-d6): δ 167.29, 158.45, 157.83, 138.84, 138.57, 137.62, 128.82, 124.86, 124.47, 124.00, 115.34. IR (KBr): 3422(br), 2929, 2856, 1606, 1479, 1368, 1308, 1167 cm^{-1}. FAB-MS: m/z 743.83 ($C_{44}H_{30}N_4O_8$ + H, M + 1). Anal. Calcd for $C_{44}H_{30}N_4O_8$: C, 71.15; H, 4.07; N, 7.54. Found: C, 71.01, H, 4.02, N, 7.31.

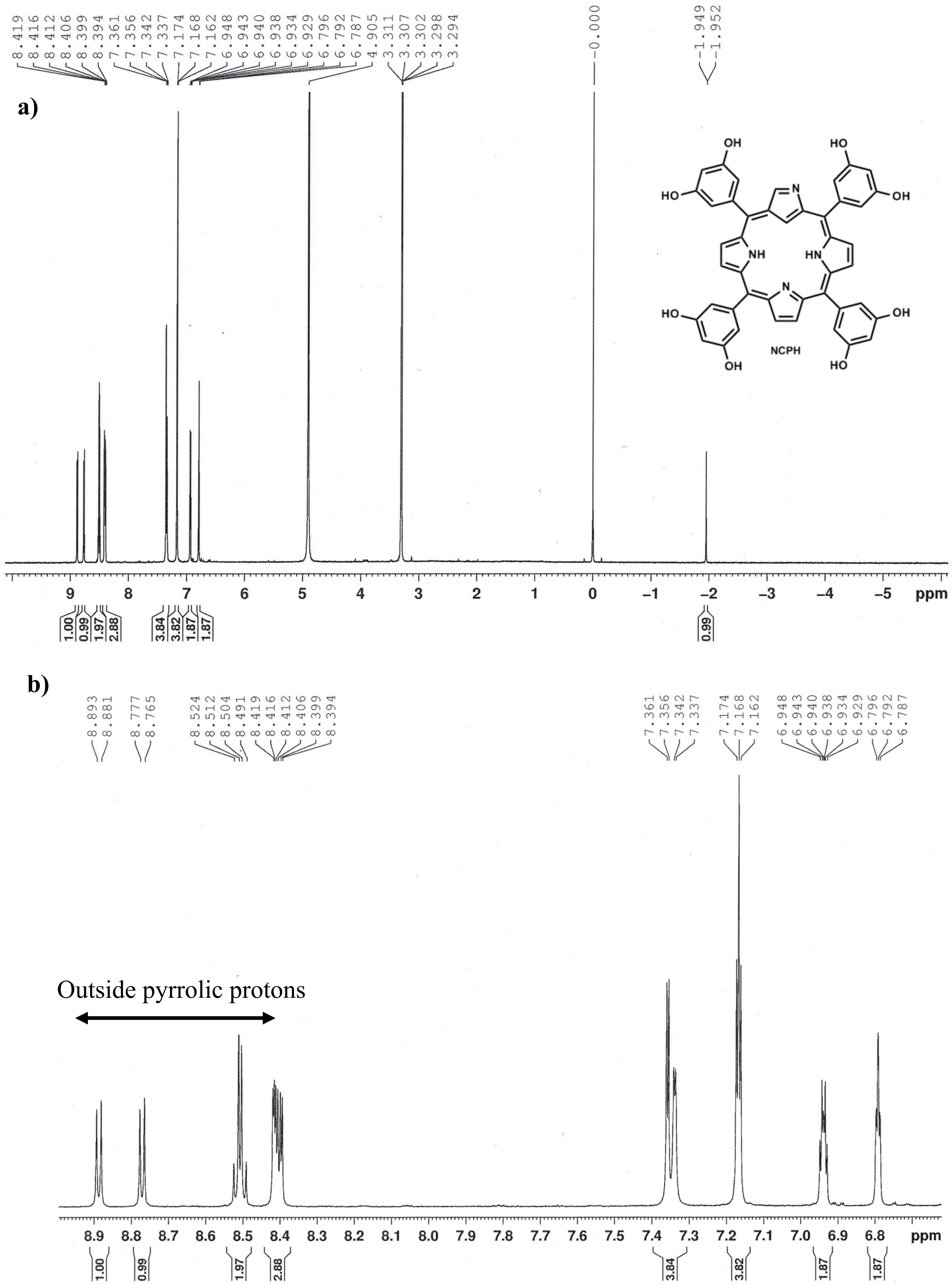


Fig. S1 a) ^{1}H NMR spectrum of **NCPH** in CD_3OD; b) Expansion in the aromatic region.

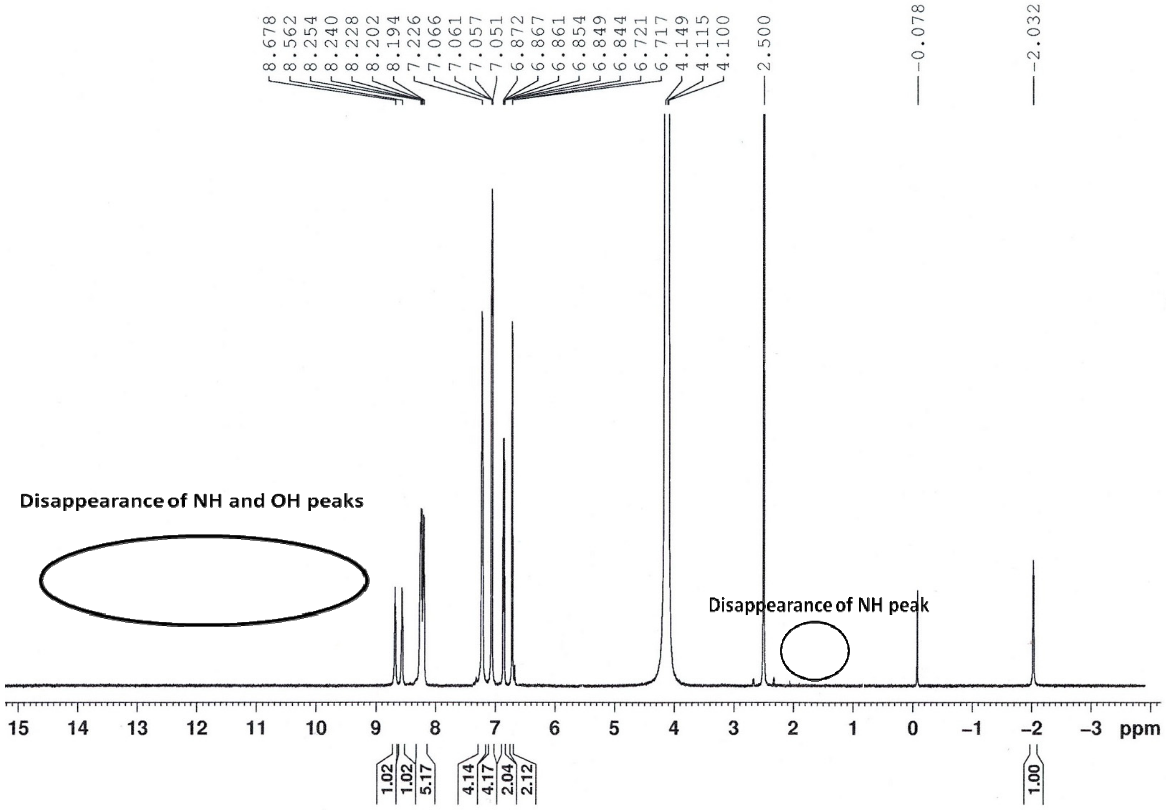


Fig. S2 ^{1}H NMR spectrum of **NCPH** after D_2O shake

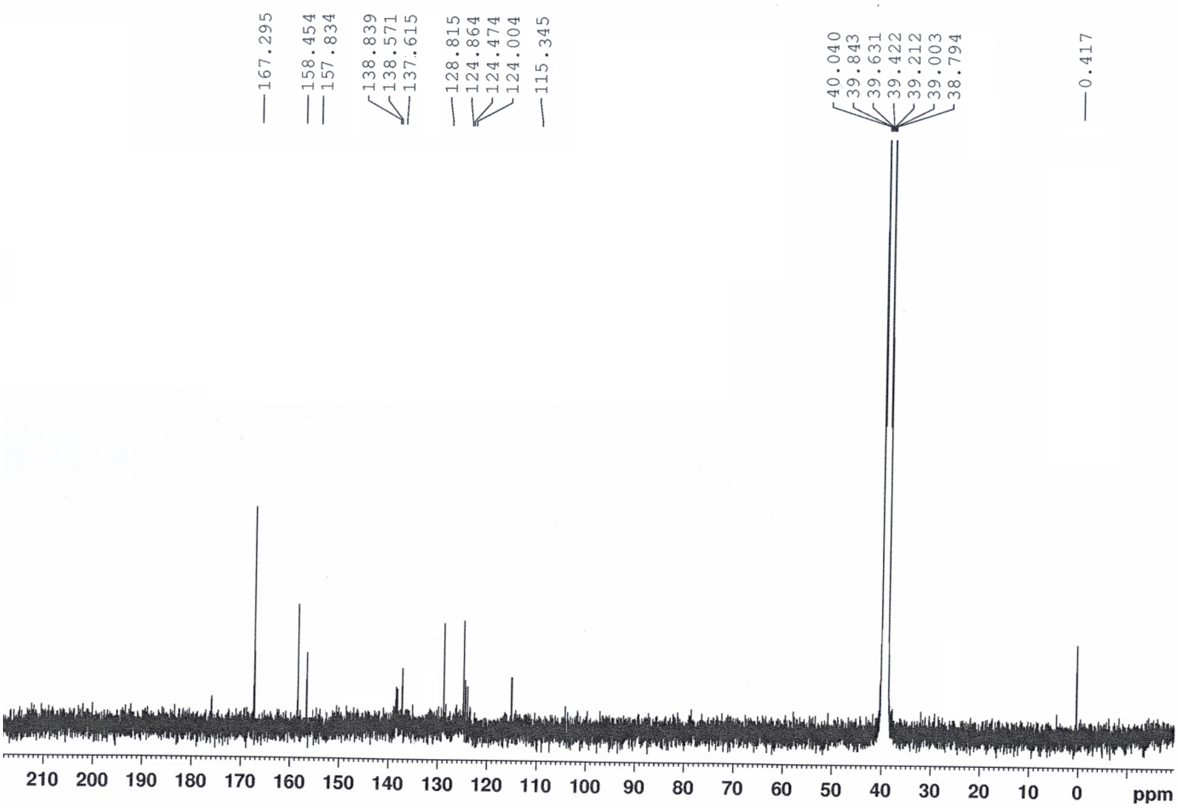


Fig. S3 ^{13}C NMR spectrum of **NCPH**.

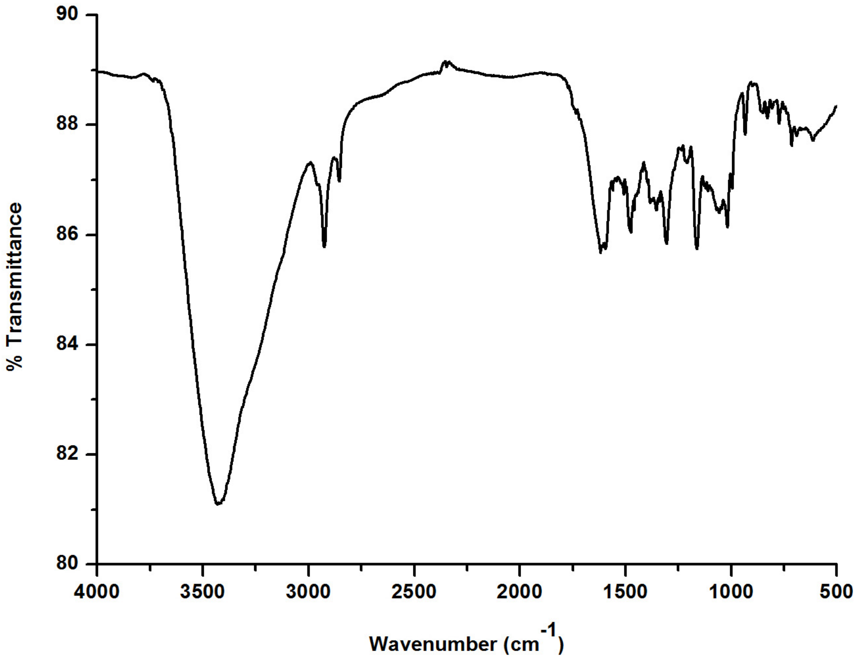


Fig. S4 FT-IR spectrum of **NCPH**.

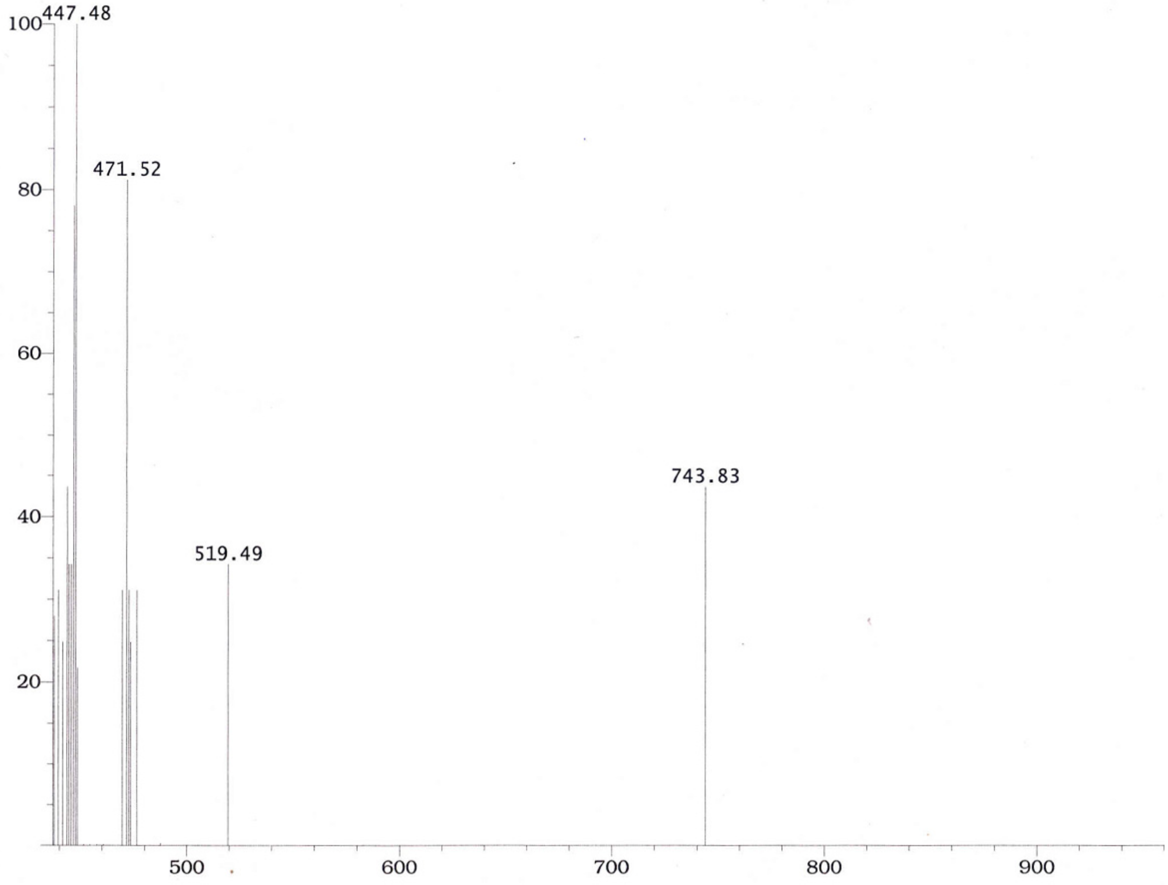


Fig. S5 FAB MS spectrum of **NCPH**

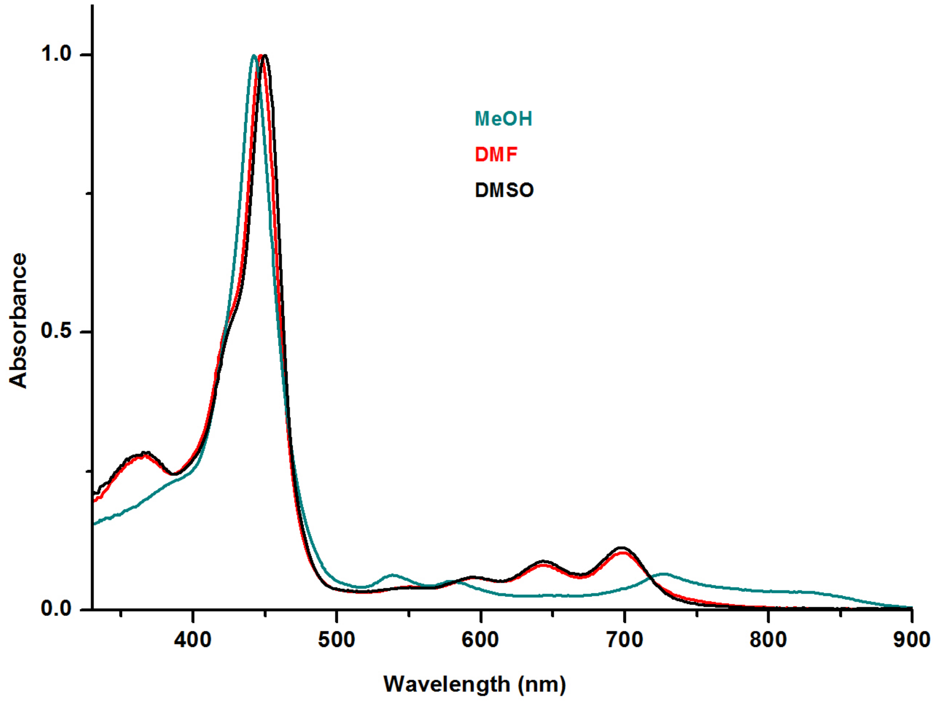


Fig. S6 Absorption spectra of **NCPH** in different solvent systems.

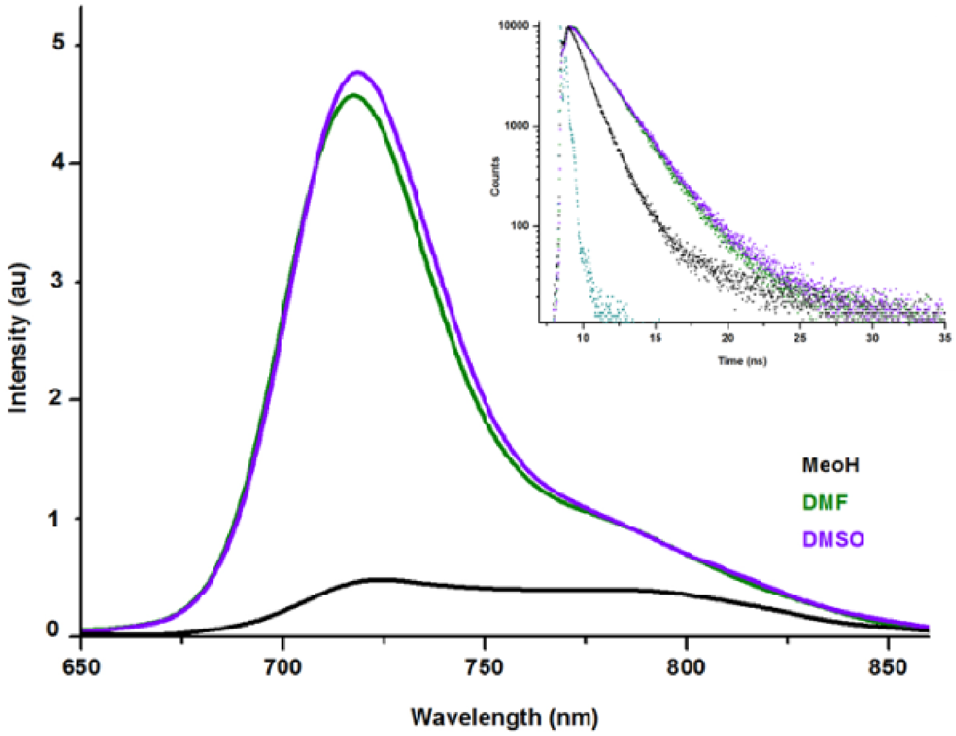


Fig. S7 Emission spectra of **NCPH** in different solvent systems. Inset shows the decay profile in different solvents.

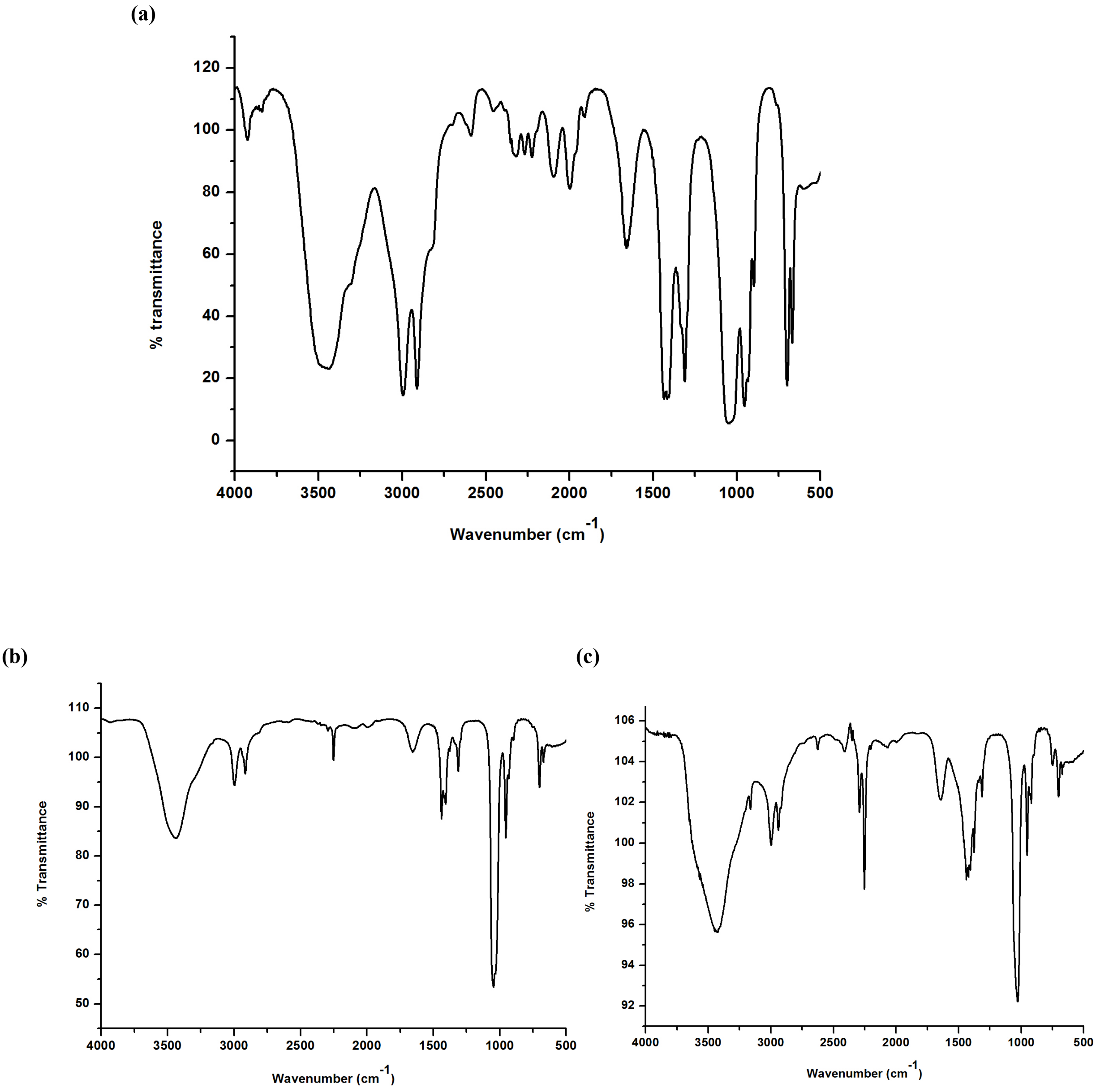


Fig. S8 FT-IR specta of **NCPH** in DMSO solution (a), 1:1 mixture of DMSO/ ACN (b) and 1:9 mixture of DMSO/ACN (c).

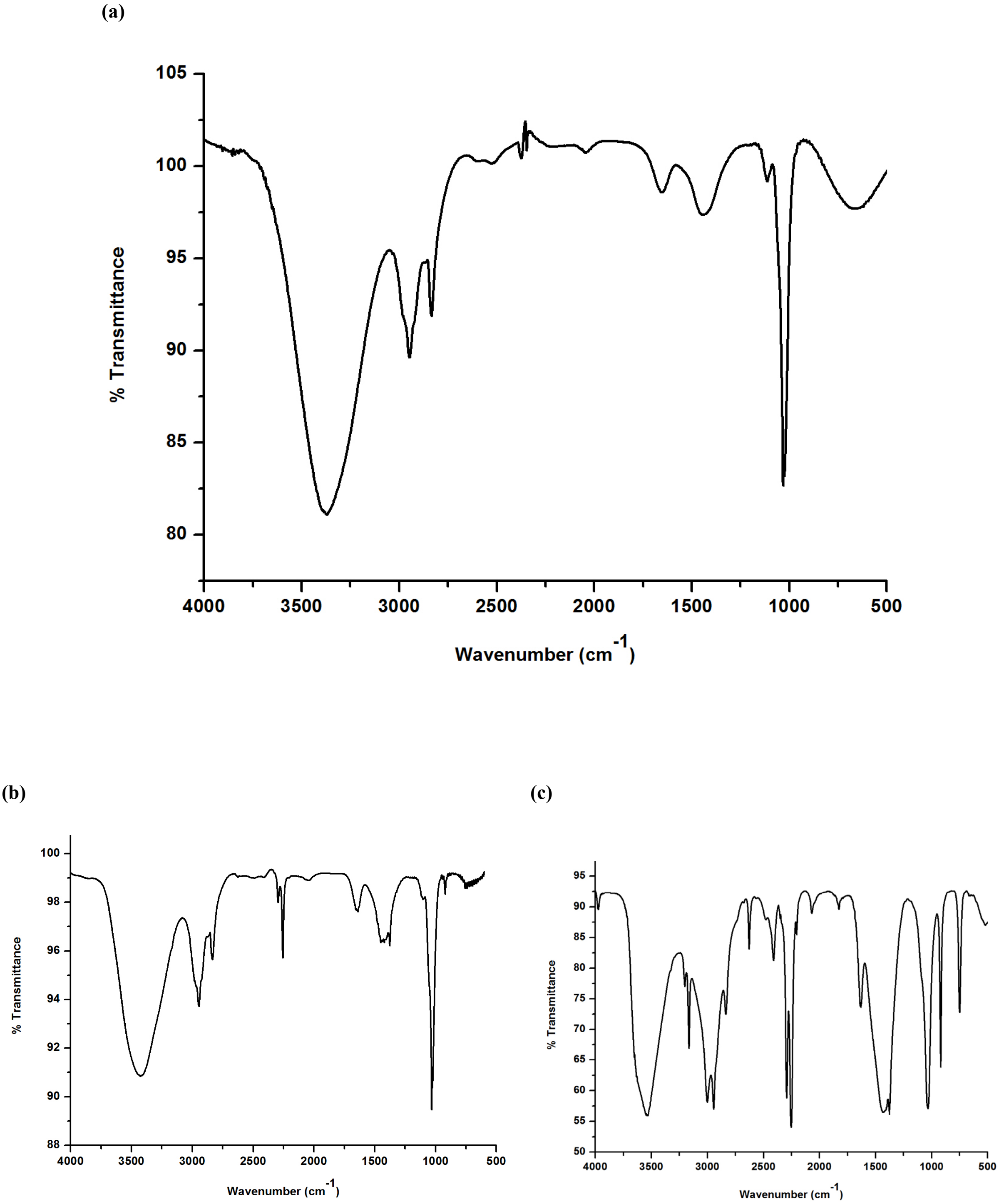


Fig. S9 FT-IR spectra of **NCPH** in MeOH solution (a), 1:1 mixture of MeOH/ ACN (b) and 1:9 mixture of MeOH/ACN (c).

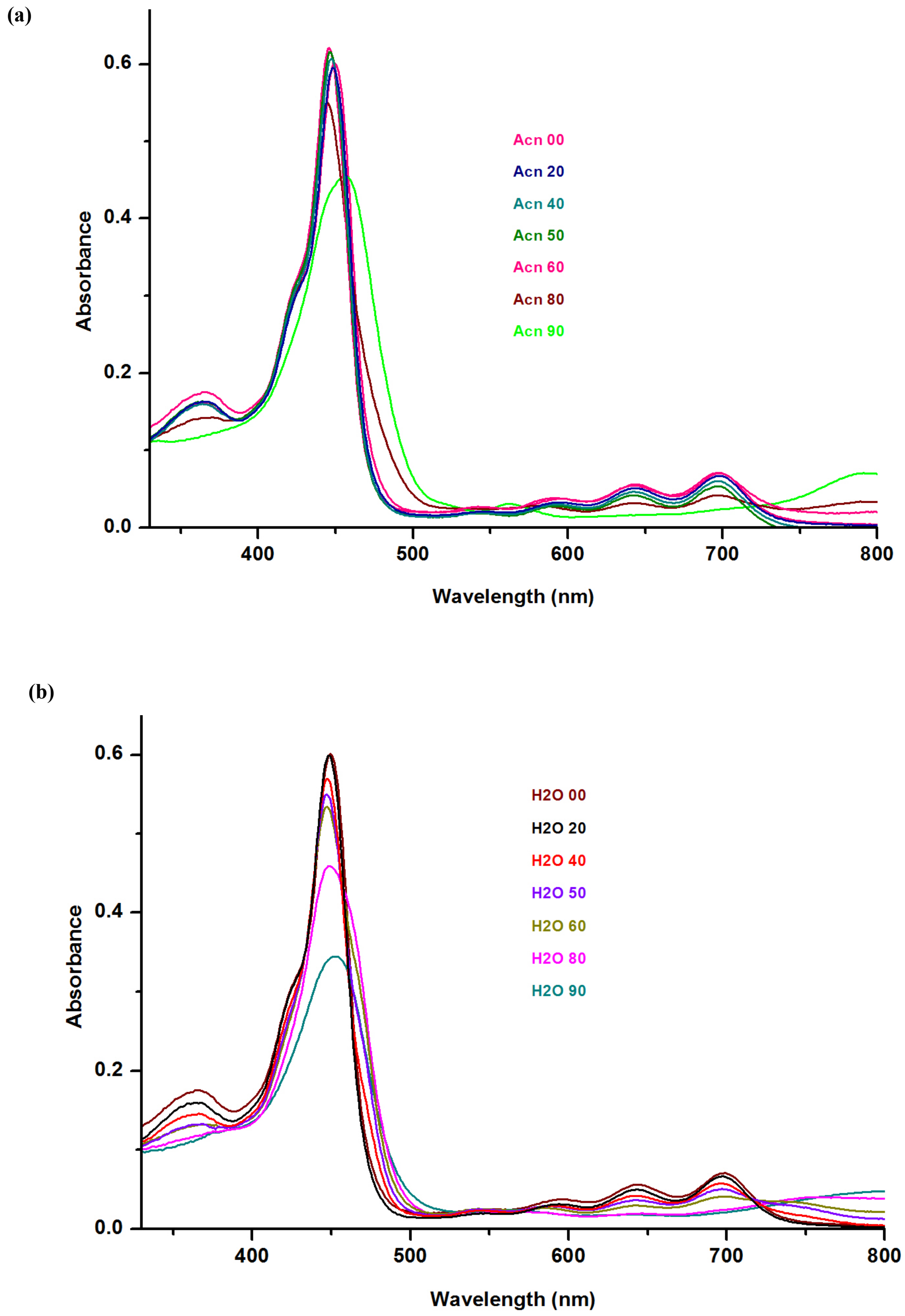
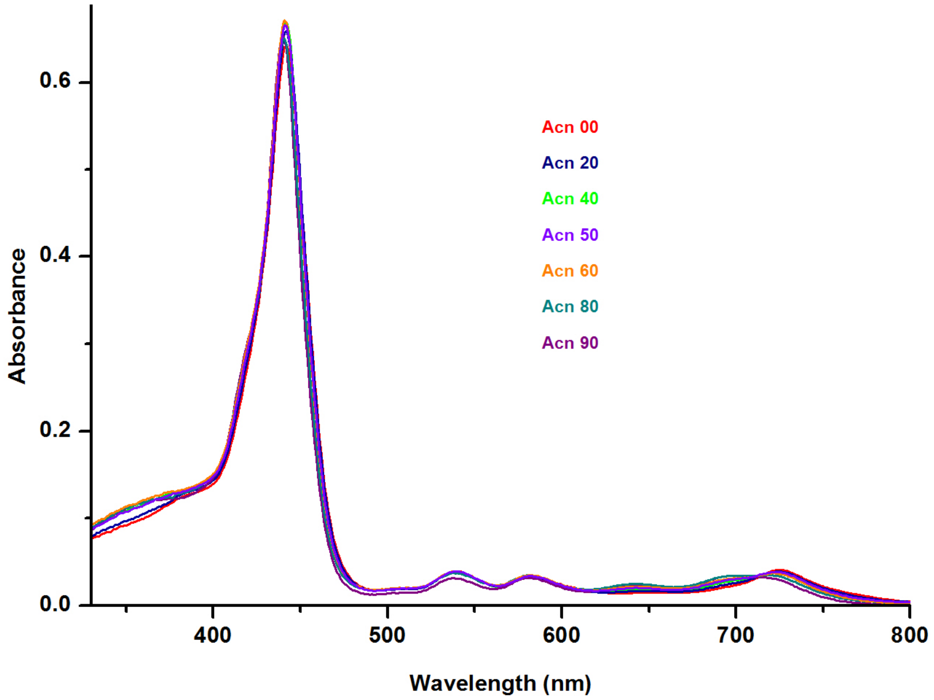


Fig. S10 Change in the absorption profile of **NCPH** on aggregation in DMSO/ACN mixture (a) and DMSO/H_2O mixture (b).

(a)



(b)

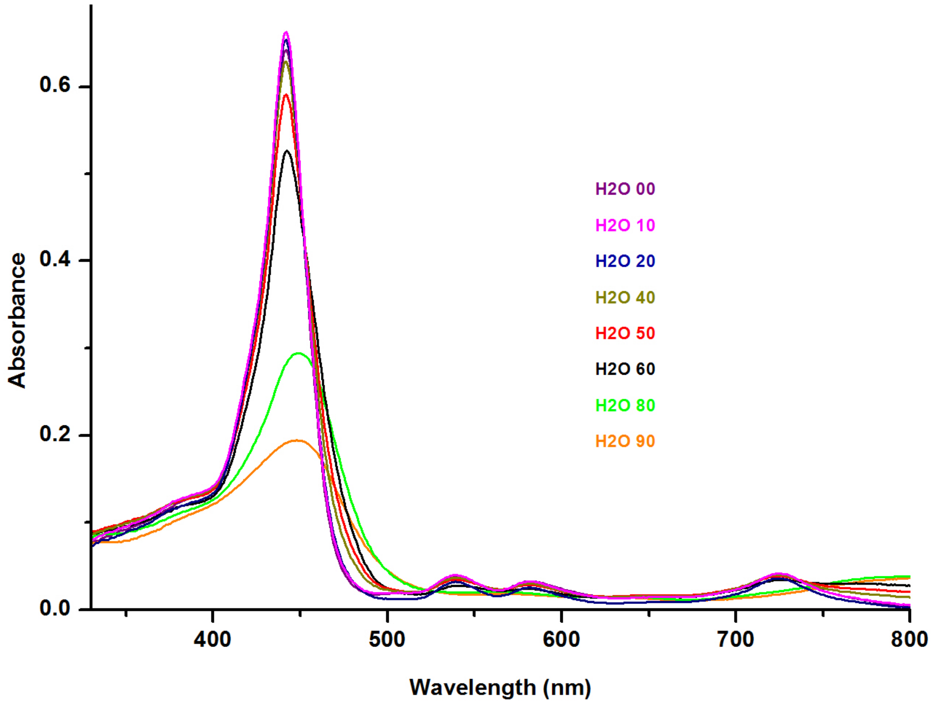
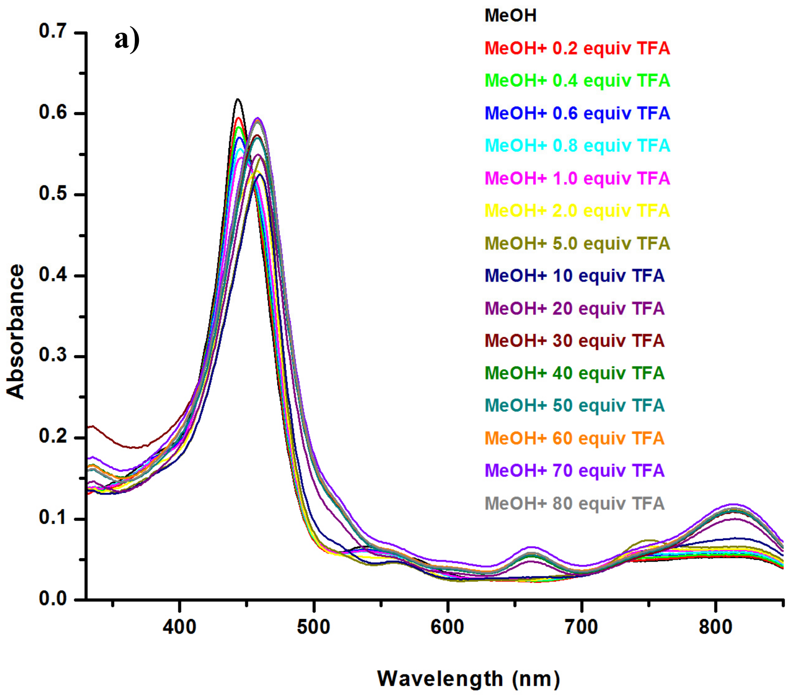


Fig. S11 Change in the absorption profile of **NCPH** on aggregation in MeOH/ACN mixture (a) and MeOH/H_2O mixture (b).



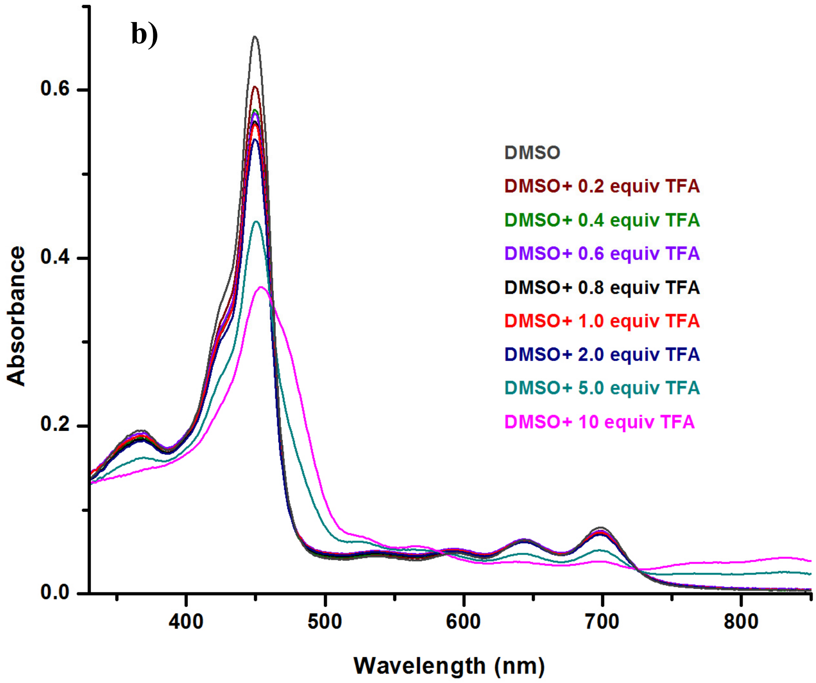


Fig. S12 Change in the absorption spectra of **NCPH** during acid titration in a) MeOH b) DMSO.

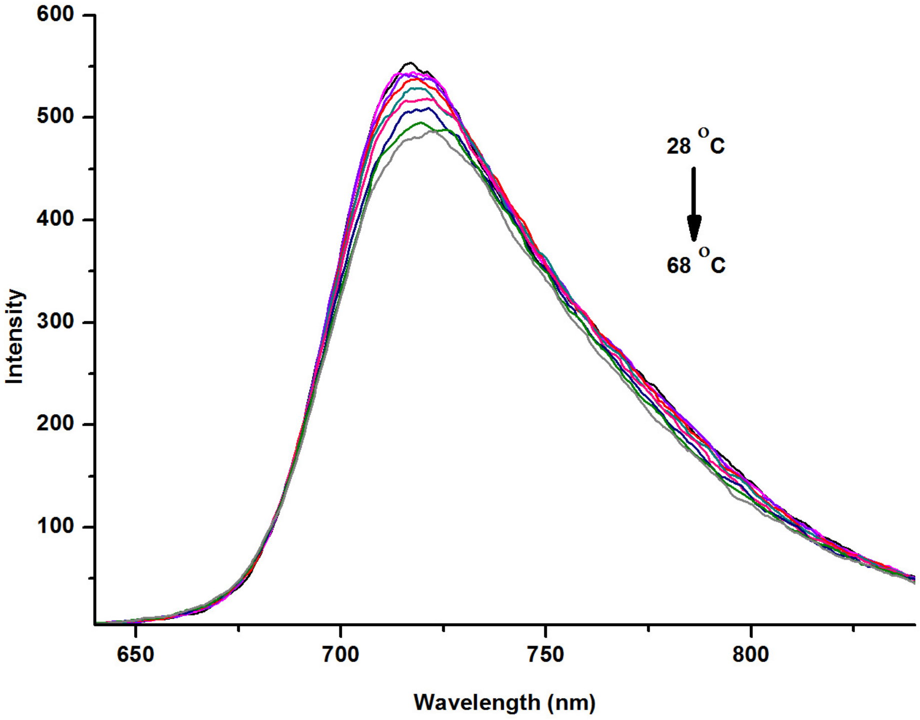


Fig. S13 Temperature dependent emission spectra of **NCPH**.

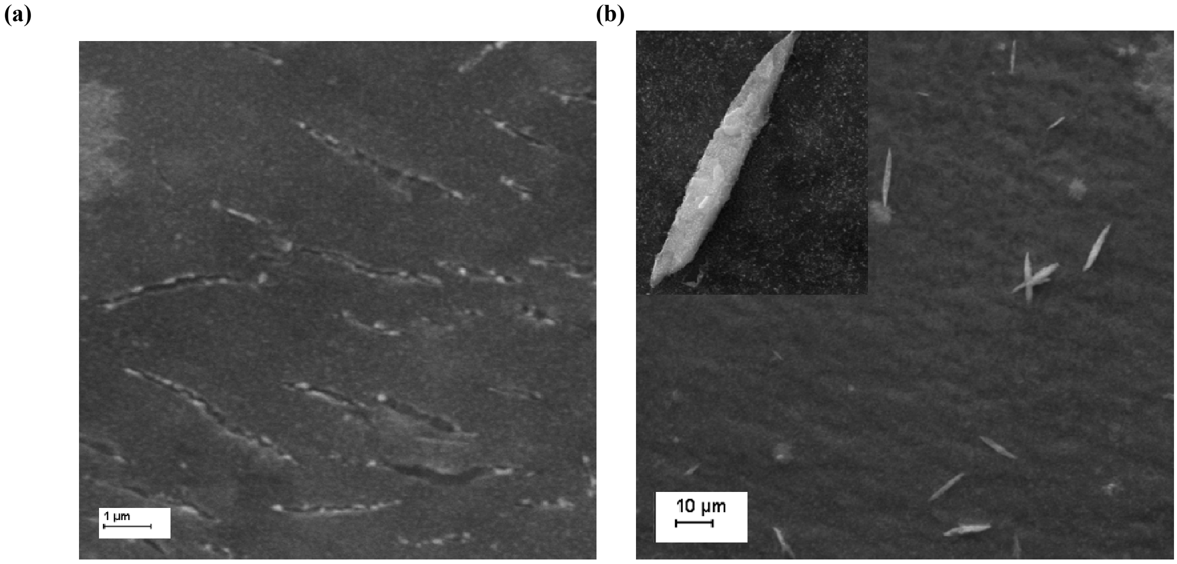


Fig. S14 SEM images of **NCPH** in DMSO/ACN (a) and DMSO/H_2O (b) mixture.

Reference

1 G. R. Geier III, D. M. Haynes and J. S. Lindsey, *Org. Lett.,* 1999, **1**, 1455.