Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Fabrication of a GUMBOS-based acid-base indicator: smart probe for sensing acids and bases in any solvent

*Prabal Pramanik[a], Rajkumar Sahoo[a], Sudhir Kumar Das[b], and Mintu Halder[a]**

[a]Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India.

[b]Department of Chemistry, University of North Bengal, Darjeeling,734013, India.

Email: mintu@chem.iitkgp.ac.in

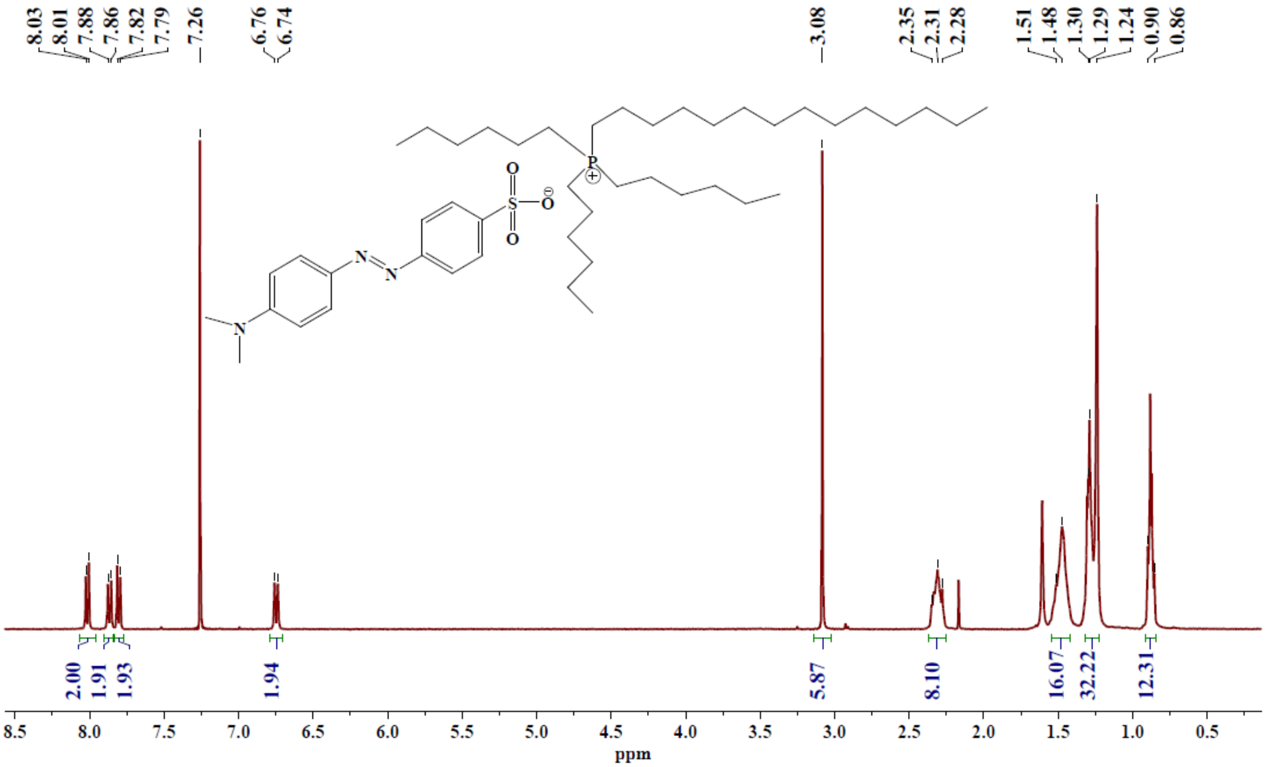


Fig. S1. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of MOIL.

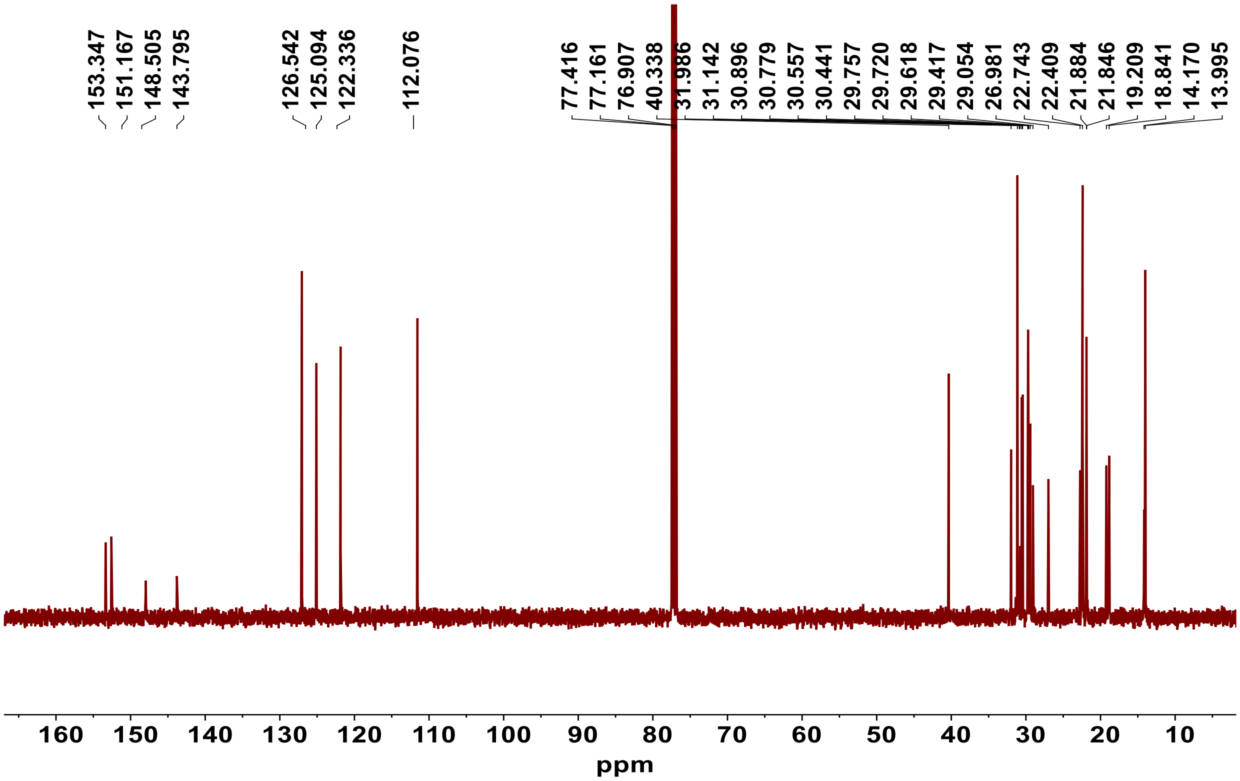


Fig. S2. ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of MOIL.

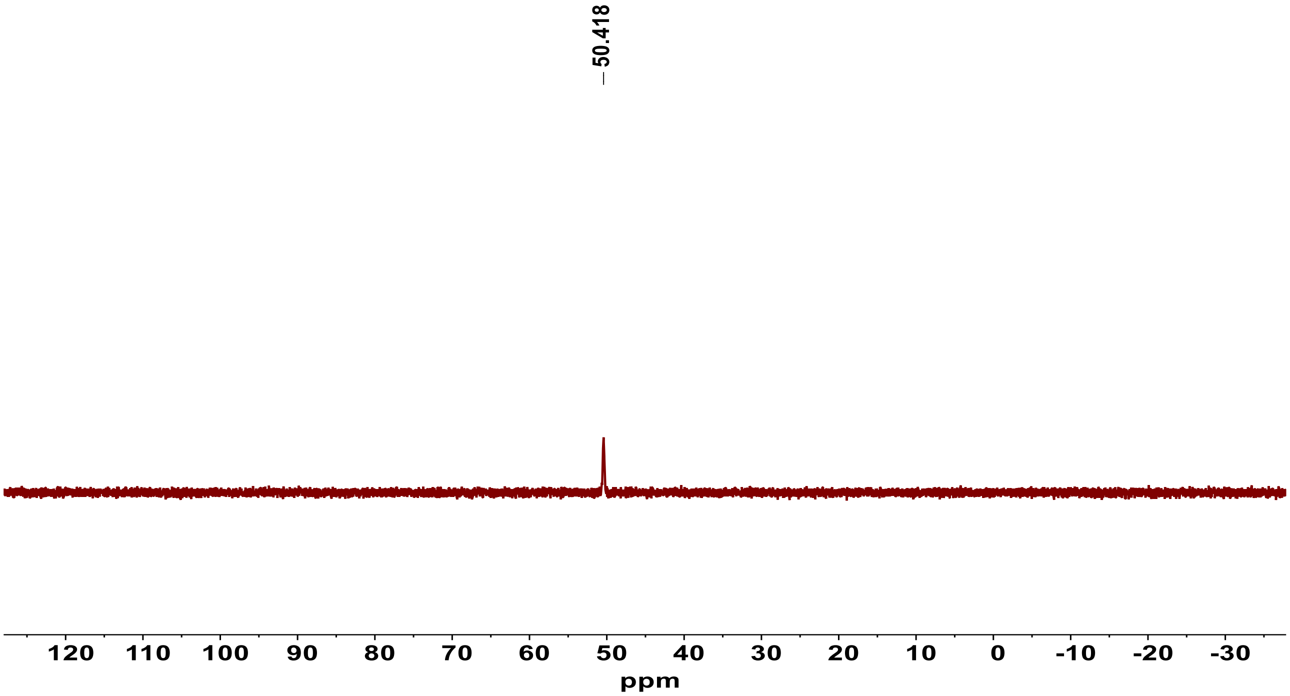


Fig. S3. ^{31}P NMR (CDCl$_3$, 202 MHz) spectrum of MOIL.

NMR data of MOIL:

^{31}P NMR (CDCl$_3$, 202 MHz): δ (ppm) 50.418; **^{1}H NMR** (CDCl$_3$, 400 MHz): δ (ppm) 8.03 (d, *J*(H,H) = 8.0 Hz, 2H, phenyl), 7.88 (d, *J*(H,H) = 8.0 Hz, 2H, phenyl), 7.82 (d, *J*(H,H) = 12.0 Hz, 2H, phenyl), 6.76 (d, *J*(H,H) = 8 Hz, 2H, phenyl), 3.08 (s, 6H, methyl), 2.35-2.28 (m, 8H, methylene), 1.51-1.48 (m, 16H, methylene), 1.30-1.24 (m, 32H, methylene), 0.90-0.086 (m, 12H, methyl); **^{13}C NMR** (CDCl$_3$, 125 MHz): δ (ppm) 153.3, 151.2, 148.5, 143.8, 126.5, 125.1, 122.3, 112.1, 40.3, 32.0, 31.1, 30.9, 30.8, 30.6, 30.4, 29.8, 29.7, 29.6, 29.4, 29.1, 27.0, 22.7, 22.4, 21.9, 21.8, 19.2, 18.8, 14.2, 14.0.

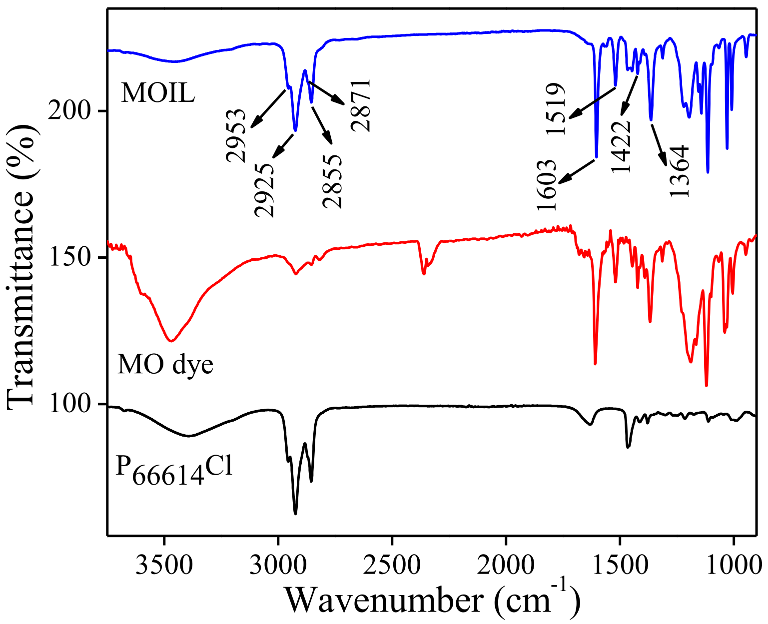
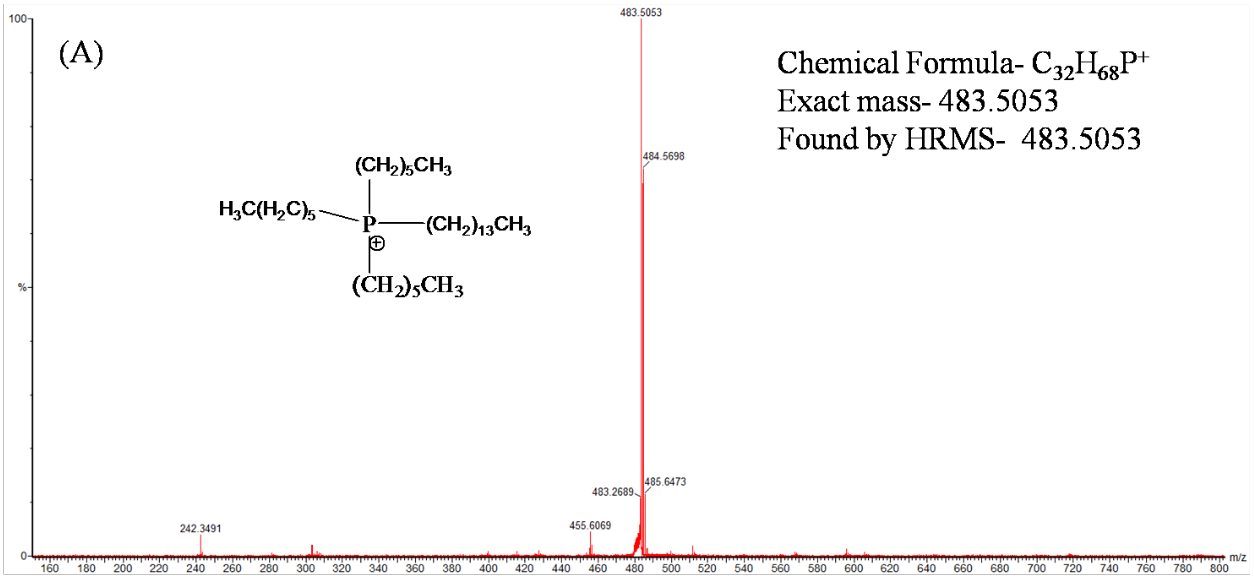


Fig. S4. FTIR spectra of $P_{66614}Cl$ IL, MO dye and MOIL.



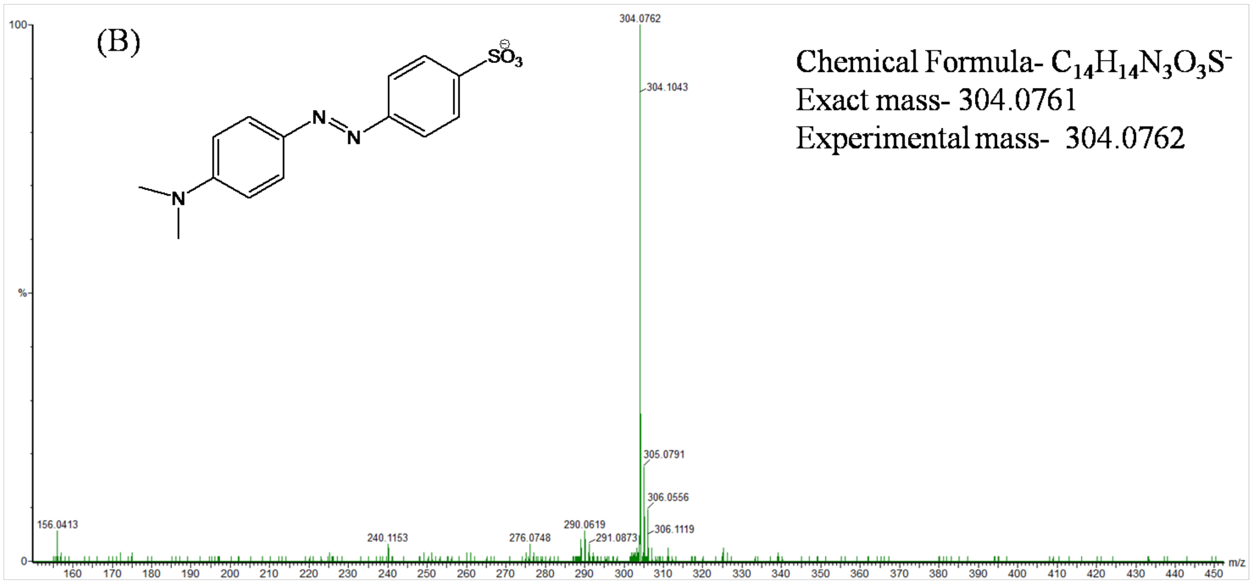


Fig. S5. HRMS spectra of MOIL, (A) positive ion mode and (B) negative ion mode.

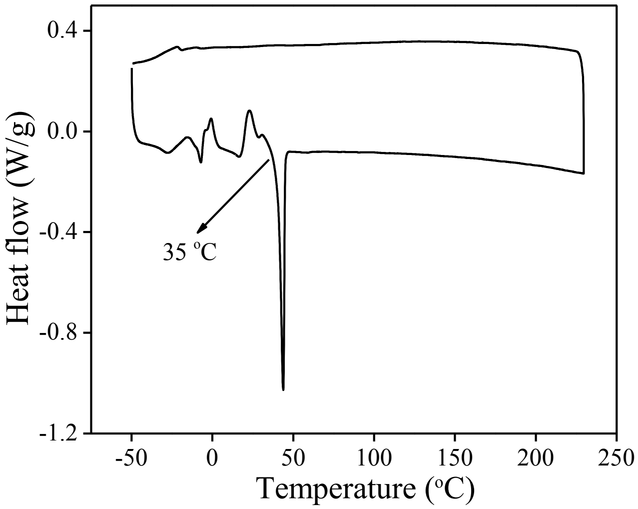


Fig. S6. DSC trace of MOIL under nitrogen atmosphere. Scanning rate is 2 ºC min^{-1}.

Decanol-Water Partition Coefficient ($K_{o/w}$)

To determine the hydrophobicity of MOIL, we have estimated its partition coefficient spectrometrically according to the following procedure.[1] Briefly, requisite amount of MOIL was dissolved in water-saturated 1-decanol solvent in order to prepare a 1 mM stock solution. This stock solution was then used to prepare four different diluted solutions in decanol and the absorbance of each solution was recorded. From these data, a calibration curve was made by plotting the best fitted line. An arbitrary concentration from this calibration curve was then selected and the corresponding solution was mixed with equal volume of water. This diluted solution was stirred for 24 h followed by nightstand for the complete separation of the two immiscible phases. Absorbance of the decanol phase was then recorded. Now, from the calibration curve, one can determine the concentration of the compound present in decanol and water phase. From the following equation, we have determined the partition coefficient of MOIL.

$$K_{(o/w)} = [\mathrm{MOIL}_{\ decanol\ layer}] \ / \ [\mathrm{MOIL}_{\ water\ layer}]$$

Water solubility determination

The phase diagram of the ternary system, [MOIL] / [Benzene] / [Water] was constructed by mixing of those three components at room temperature (25 ºC) and the appearance of turbidity was observed carefully.[2] Different concentrated stock solutions were prepared by dissolving different amount of MOIL in benzene. Then, to each solution, water was added gradually until turbidity appeared due to phase separation. At the point of phase separation, transparent solution will become turbid in naked eyes and this is further confirmed by UV-vis measurements. From these data, weight fraction of each component was calculated and a ternary phase diagram was plotted. The molar fraction of each component and the molar fraction of the binary solution (X_{IL}) for [IL]/[Benzene] in the absence of water were estimated following the eqn (1). From the plot of x_{water}/x_{IL} vs. X_{IL}, one may estimate water solubility within the compound (material).[3]

$$X_{IL} = \frac{x_{IL}}{x_{IL} + x_{Benzene}} \qquad (1)$$

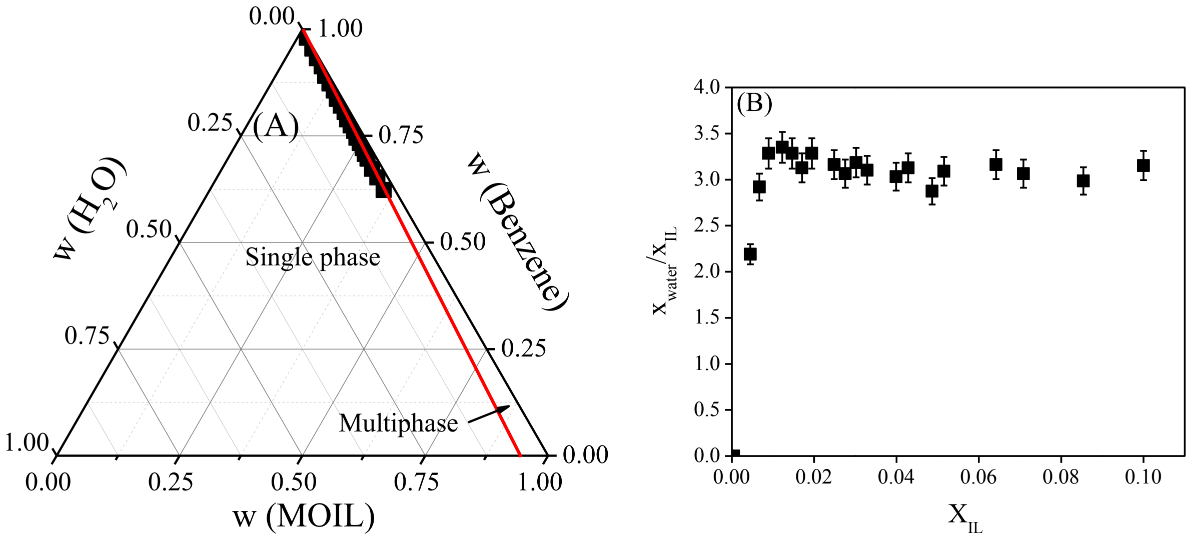


Fig. S7. (A) Phase diagram of the MOIL/Benzene/water ternary systems at 25 ºC. The concentrations of the components are expressed as weight fractions. (B) Dependence of water/MOIL molar fractions ratio on the relative molar fraction of IL in the solvent.

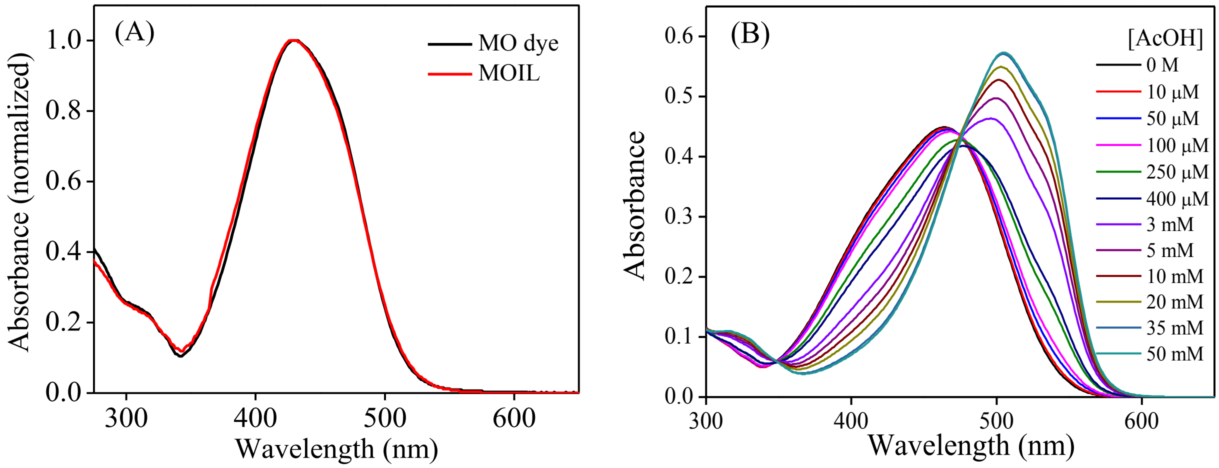


Fig. S8. (A) Absorption spectra of free MO dye and MOIL in DMSO. (B) Absorption spectra of free MO dye in water in the presence of acetic acid.

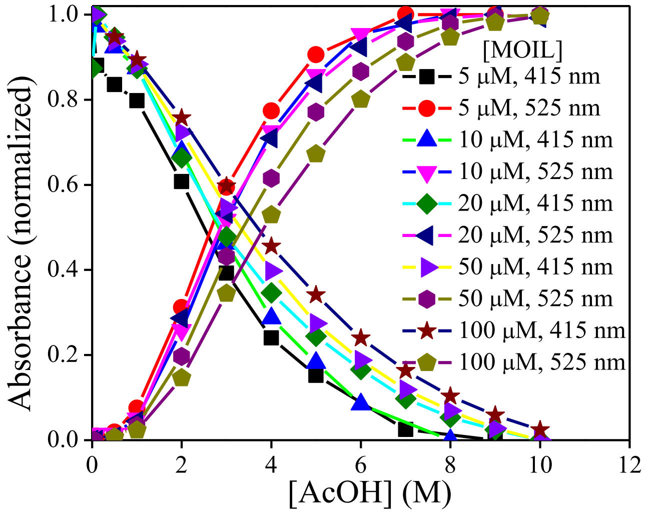


Fig. S9. The change in absorbance of MOIL solution of different concentrations as a function of AcOH concentration in DCM.

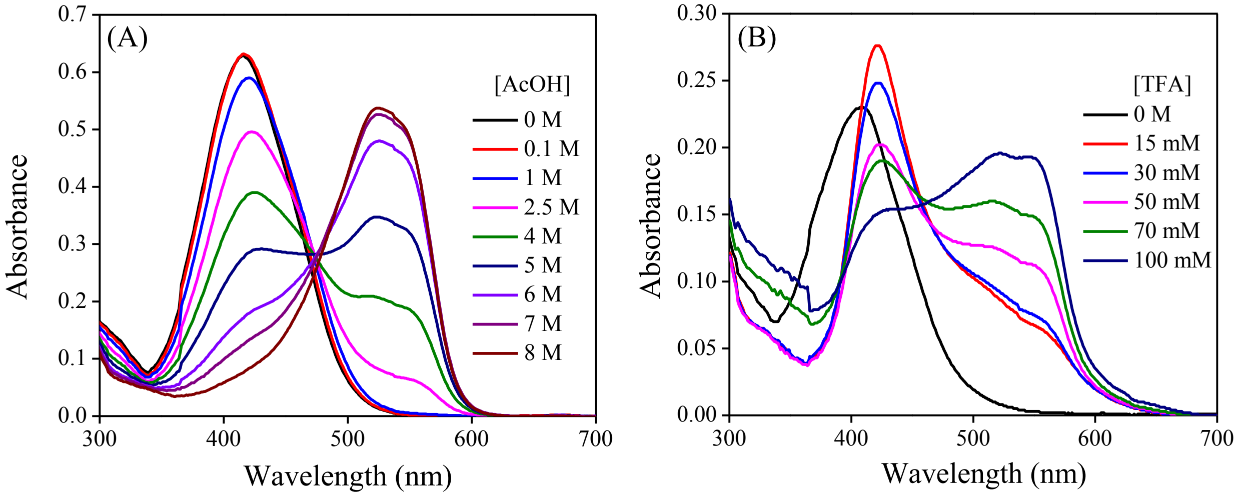


Fig. S10. Absorption spectrum of MOIL as a function of acid concentration in (A) chloroform, and (B) benzene.

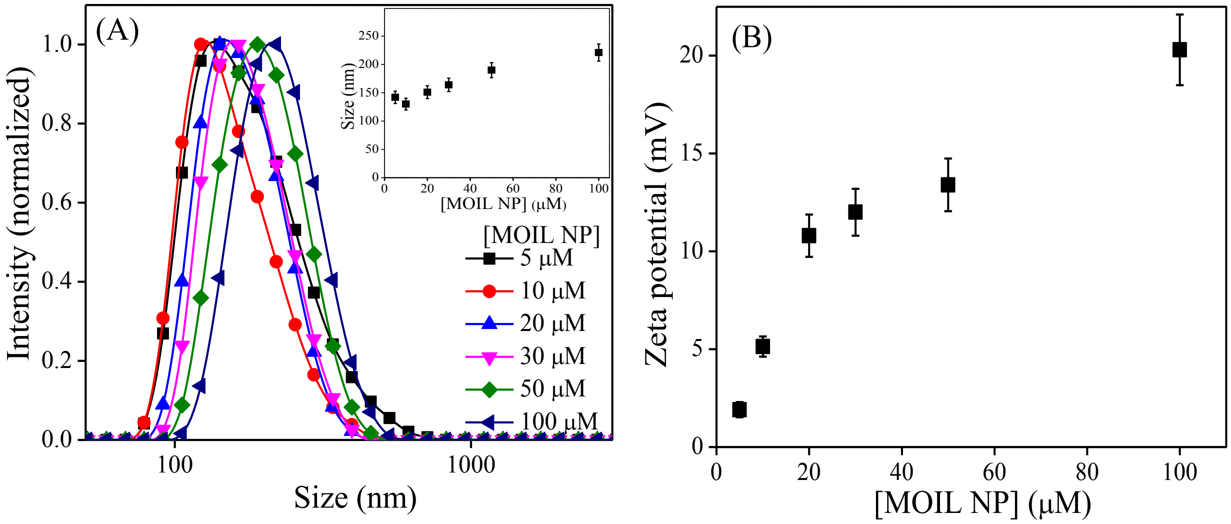


Fig. S11. The variation of (A) hydrodynamic size and (B) zeta potential of MOIL NP as a function of nanoparticle concentration.

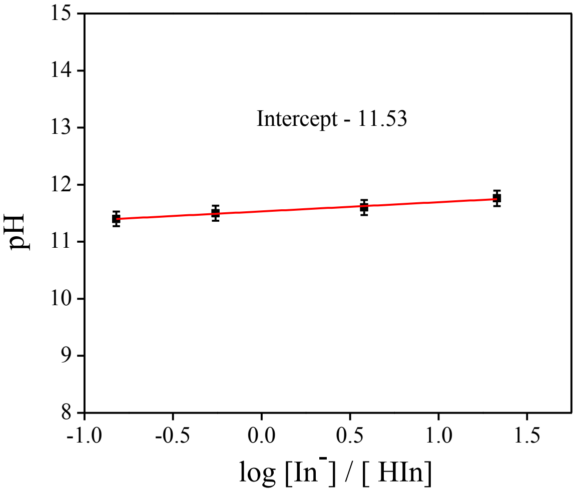


Fig. S12. Plot of pH vs log ([In$^-$] / [HIn]) of MOIL in acetonitrile.

Acidity measurements

The absolute acidities of several acids in non-polar solvent (acetonitrile) were determined following overlapping indicator method developed by Bordwell and his groups with some modifications.[4, 5] The procedure is given below: (i) The molar extinction coefficient (ε) of the protonated (HIn) form of MOIL indicator was determined in acidic condition. Several aliquots of the MOIL indicator were added in the pure deoxygenated solvents in the presence of excess acid (TFA) and the absorbance was recorded at the corresponding wavelength. We may expect that in the presence of excess acid, all the indicator molecules should remain as the protonated (HIn) form. Hence, from the plot of absorbance vs concentration, ε of HIn can be determined. The correlation coefficient for the Beer's plot is found to be nearly unity. (ii) Several aliquots of an acid were added to a definite concentrated indicator solution and the absorbance was recorded each time. The concentration of the HIn can be estimated from corresponding ε–value and the concentration of the remaining species (In^-) can be determined using the eqn (2).

$$C_{In^-} = C_0 - C_{HIn} \tag{2}$$

Here C_0 is the initial concentration of the indicator taken; C_{In^-} and C_{HIn} are the concentration of the azo (In^-) and quinonoid (HIn) forms after the addition of acids, respectively. (iii) Due to the absence of any other proton source, we might assume that the change in absorbance spectrum of the indicator is only due to the addition of acids. Hence we can apply the following equations.

$$HA + In^- \rightleftharpoons A^- + HIn \tag{3}$$

$$\Delta[HIn] = \Delta[HA] \tag{4}$$

With the known initial concentration of the indicator and acid added, one can calculate the equilibrium constant (K_{eq}) and also the pK_{a} of the acid using the following equations.

$$HA + In^- \rightleftharpoons A^- + HIn\,; \quad K_{eq} = \frac{[A^-][HIn]}{[HA][In^-]} \tag{5}$$

$$\mathrm{p}K_{HA} = \mathrm{p}K_{HIn} - \log K_{eq} = \mathrm{p}K_{HIn} - \log \frac{[A^-][HIn]}{[HA][In^-]} \tag{6}$$

We have estimated at least five pK_a values during titration by an acid and considered the average value as the result. One selected example is given below (Table S1).

Table S1. Estimated and average pK_a of TFA in acetonitrile at 25 ºC.

Acid	pK_a (Estimated)					pK_a (average)
TFA	13.61	13.46	13.39	13.33	13.26	13.41

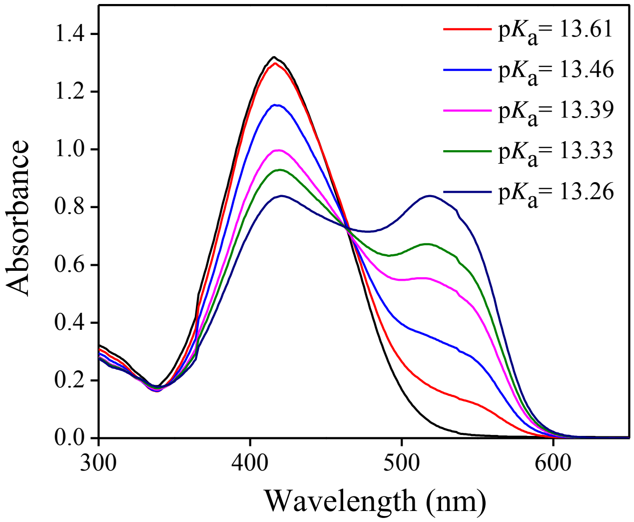


Fig. S13. Absorption spectrum of MOIL during titration by TFA in acetonitrile at 25 ºC.

References

1. W. I. S. Galpothdeniya, F. R. Fronczek, M. Y. Cong, N. Bhattarai, N. Siraj, and I. M. Warner, *J. Mater. Chem. B*, 2016, **4**, 1414.

2. V. G. Rao, S. Ghosh, C. Ghatak, S. Mandal, U. Brahmachari, and N. Sarkar. *J. Phys. Chem. B*, 2012, **116**, 2850.

3. M. Blahusiak and S. Schlosser, *J. Chemi. Thermodyn*., 2014, **72**, 54.

4. W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. Mccallum, G. J. Mccollum, and N. R. Vanier, *J. Am. Chem. Soc.*, 1975, **97**, 7006.

5. G. Jakab, C. Tancon, Z. G. Zhang, K. M. Lippert, and P. R. Schreiner, *Org. Lett.*, 2012, **14**, 1724.