

Electronic Supplementary Information

pH-responsive Molecular Assemblies of Pyridylbutadiene Derivative with Cucurbit[7]uril

*Anuji K Vasu^a, Raman Khurana^{b,c}, Jyotirmayee Mohanty^{*b,c} and Sriram Kanvah^{*a}*

^aDepartment of Chemistry, Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar
382 355, India

^bRadiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.

^cHomi Bhabha National Institute, Training School Complex, Anushaktinagar, Mumbai 400 094,
India

Synthetic Details

Synthesis of 4-((1E,3E)-4-(4-(dimethylamino)phenyl)buta-1,3-dien-1-yl)-1-methylpyridin-1-ium

3 mmol of 1,4-dimethyl pyridinium iodide is dissolved in ethanol and into that 0.2 mol of piperidine and 30mg of zinc acetate was added. Into the reaction mixture, 3mmol 4-dimethyl cinnamaldehyde was added and allowed for reflux 60 min. The reaction mixture was turned

to deeply red coloured and allowed to cool down to RT and the precipitate filtered off. The crude mixture was washed with diethyl ether and crystallized from ethanol. Yield: 80-85%

$^1\text{H NMR}$ (D_2O , 500 MHz) δ (ppm) 8.32 (d, 2H, $J = 6$ Hz), 7.77 (d, 2H, $J = 6.5$ Hz), 7.53 (m, 1H), 7.45 (d, 2H, $J = 8.5$ Hz), 6.94 (t, 2H, $J = 6.5$ Hz), 6.86 (d, 2H, $J = 9$ Hz), 6.64 (d, 1H, $J = 15.5$ Hz), 4.09 (s, 3H,), 2.88 (s, 6H). $^{13}\text{C NMR}$ (DMSO, 125 MHz) δ (ppm) 153.23, 151.60, 144.96, 143.73, 142.51, 129.56, 124.01, 123.73, 123.54, 122.89, 112.51, 46.96, 40.52. [ESI] 265.1714

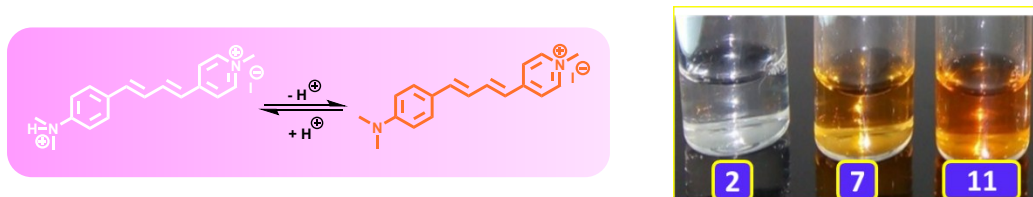


Fig. S1 Protonation and deprotonation process of DABP (a) Color changes observed for DABP in acidic (pH 2), neutral (pH 7) and in basic (pH 11) media (b).

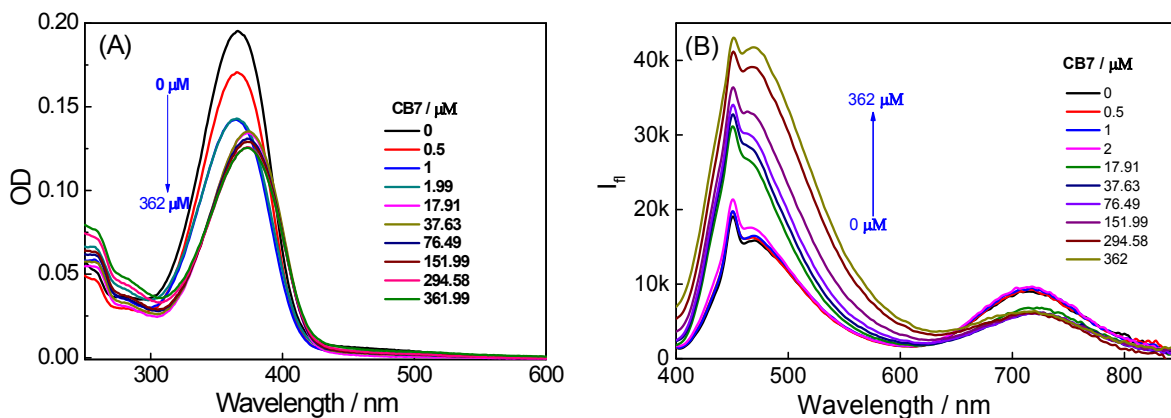
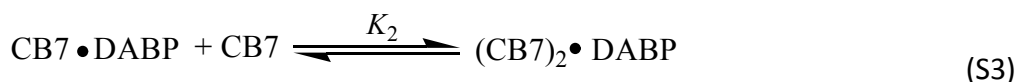


Fig. S2 Absorption (A) Emission spectra (B) of DABP in pH 3 solution at concentrations CB7 (0-362 μM).

Method M1

The binding constant values for 1:1 and 2:1 stoichiometries were evaluated by considering the following complexation equilibria;



where K_1 and K_2 are the binding constants for the formation of the respective 1:1 and 2:1 complexes. At any stage, the observed fluorescence intensity I_f corresponds to the sum of the fluorescence intensities arising from the free DABP, $\text{CB7} \bullet \text{DABP}$ and $(\text{CB7})_2 \bullet \text{DABP}$ and are directly proportional to their respective concentrations present in the solution. Therefore, one can write

$$I_f = I_f^0 \frac{[\text{DABP}]_{\text{eq}}}{[\text{DABP}]_0} + I_{\text{CB7} \bullet \text{DABP}} \frac{[\text{CB7} \bullet \text{DABP}]_{\text{eq}}}{[\text{DABP}]_0} + I_{(\text{CB7})_2 \bullet \text{DABP}} \frac{[(\text{CB7})_2 \bullet \text{DABP}]_{\text{eq}}}{[\text{DABP}]_0} \quad (\text{S4})$$

where I_f^0 is the fluorescence intensity in the absence of CB7, $I_{\text{CB7} \bullet \text{DABP}}$ is the fluorescence intensity when all DABP molecules are complexed with CB7 as 1:1 complex and $I_{(\text{CB7})_2 \bullet \text{DABP}}$ is the fluorescence intensity when all the DABP molecules are complexed with CB7 forming 2:1 complex. $[\text{DABP}]_0$ and $[\text{CB7}]_0$ are the total concentrations of DABP and the CB7 used. Equation S3 can be rearranged to a modified Benesi-Hildebrand equation as in equation S5,¹

$$I_f = \frac{I_f^0 + I_{\text{CB7} \bullet \text{DABP}} K_1 [\text{CB7}]_0 + I_{(\text{CB7})_2 \bullet \text{DABP}} K_1 K_2 [\text{CB7}]_0^2}{1 + K_1 [\text{CB7}]_0 + K_1 K_2 [\text{CB7}]_0^2} \quad (\text{S5})$$

In term of optical density (OD), one can write the equation S5 as

$$\text{OD} = \frac{\text{OD}^0 + \text{OD}_{\text{CB7} \bullet \text{DABP}} K_1 [\text{CB7}]_0 + \text{OD}_{(\text{CB7})_2 \bullet \text{DABP}} K_1 K_2 [\text{CB7}]_0^2}{1 + K_1 [\text{CB7}]_0 + K_1 K_2 [\text{CB7}]_0^2} \quad (\text{S6})$$

where OD^0 is the optical density in the absence of CB7, $\text{OD}_{\text{CB7} \bullet \text{DABP}}$ is the optical density when all DABP molecules are complexed with CB7 as 1:1 complex and $\text{OD}_{(\text{CB7})_2 \bullet \text{DABP}}$ is the optical density when all the DABP molecules are complexed with CB7 forming 2:1 complex.

Applying equation S5 or S6 to fit the experimental data presented in Figs. S4 and S5, the K_1 and K_2 values were estimated to be $(2.25 \pm 0.5) \times 10^6 \text{ M}^{-1}$ and $(5.15 \pm 0.6) \times 10^3 \text{ M}^{-1}$ from the absorption study and $(1.8 \pm 0.6) \times 10^5 \text{ M}^{-1}$ and $(1.2 \pm 0.8) \times 10^3 \text{ M}^{-1}$ from the fluorescence study at pH 3. Similarly, at pH 9.5, the K_1 and K_2 values were estimated to be $(4.9 \pm 1.0) \times 10^5 \text{ M}^{-1}$ and $(4.3 \pm 0.7) \times 10^4 \text{ M}^{-1}$ from the absorption study and $(1.4 \pm 0.7) \times 10^5 \text{ M}^{-1}$ and $(1.6 \pm 0.7) \times 10^5 \text{ M}^{-1}$ from the fluorescence measurements. The high values for the first binding constant, K_1 , in both the pHs suggest a strong ion-dipole interaction among the carbonyl laced portals of CB7 and the positive charge center (methyl pyridinium group) on the DABP dye, in the formation of the 1:1 complex. Similarly, slightly lower K_2 values indicate that the second interaction of CB7 with DABP is mainly attributed to the combination of both ion-dipole and hydrophobic interactions.

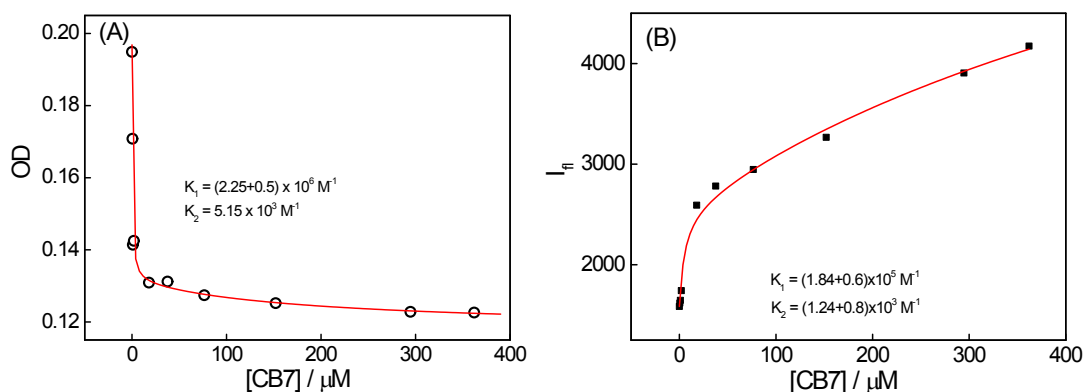


Fig. S3 Optical density monitored at 367 nm (A) and fluorescence intensity monitored at 470 nm (B) versus CB7 concentration plots for DABP:CB7 complex formation at pH 3.

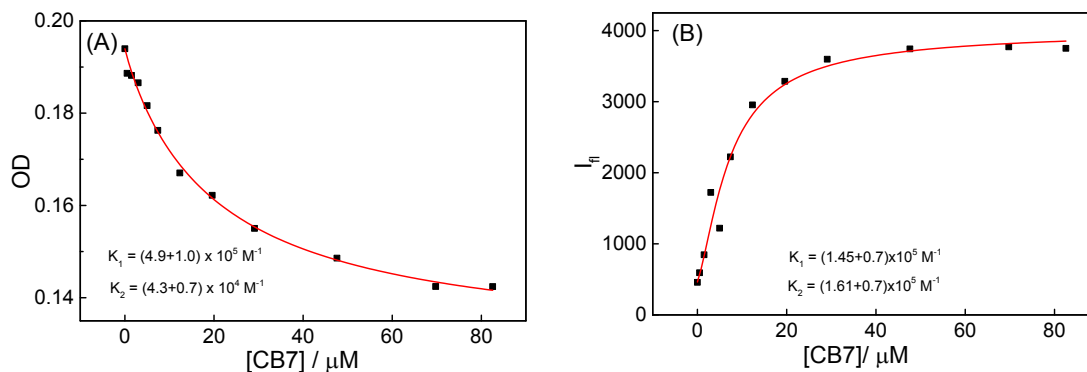


Fig. S4 Optical density monitored at 448 nm (A) and fluorescence intensity monitored at 713 nm (B) versus CB7 concentration plots for DABP:CB7 complex formation at pH 9.5.

Note S1

From the ITC measurements the enthalpy, entropy and free energy changes ($\Delta G = \Delta H - T\Delta S$) for the 1:1 and 2:1 CB7:DABP complexation processes (at both pH 3 and 9.5) were evaluated and the values are:

$\Delta H_1 = 14.7 \text{ kcal mol}^{-1}$, $-T\Delta S_1 = -19.91 \text{ kcal mol}^{-1}$, $\Delta G_1 = -5.2 \text{ kcal mol}^{-1}$ for 1:1 CB7:DABP complex and $\Delta H_2 = -19.2 \text{ kcal mol}^{-1}$, $-T\Delta S_2 = 9.9 \text{ kcal mol}^{-1}$, $\Delta G_2 = -9.3 \text{ kcal mol}^{-1}$ for 2:1 CB7:DABP complex at pH 3.

$\Delta H_1 = -1.7 \text{ kcal mol}^{-1}$, $-T\Delta S_1 = -4.77 \text{ kcal mol}^{-1}$, $\Delta G_1 = -6.5 \text{ kcal mol}^{-1}$ for 1:1 CB7:DABP complex and $\Delta H_2 = -1.13 \text{ kcal mol}^{-1}$, $-T\Delta S_2 = -5.51 \text{ kcal mol}^{-1}$, $\Delta G_2 = -6.6 \text{ kcal mol}^{-1}$ for 2:1 CB7:DABP complex at pH 9.5.

Table S1. Fluorescence decay parameters for DABP (20 μM , pH ~ 9.5) monitored at 700 nm at different CB7 concentrations.

Dye 20 μM pH ~ 9.5 [CB7] / μM	Life time	
	* τ_1 / ps	τ_2 / ps
0.5	~ 40 (68%)	923 (32%)
1.5	~ 40 (43%)	912 (57%)
3.0	~ 40 (27%)	923 (73%)
5.0	~ 40 (17%)	907 (83%)
7.4	~ 40 (10%)	935 (90%)
12.3	~ 40 (5%)	928 (95%)
19.6	~ 40 (3%)	938 (97%)

* The lifetime of the fast decay component has kept fixed ($\sim 40\text{ps}$, which is beyond the time resolution of our TCSPC instrument) during analysis. For all the decay fitting, c^2 values were obtained within 1.0-1.2.

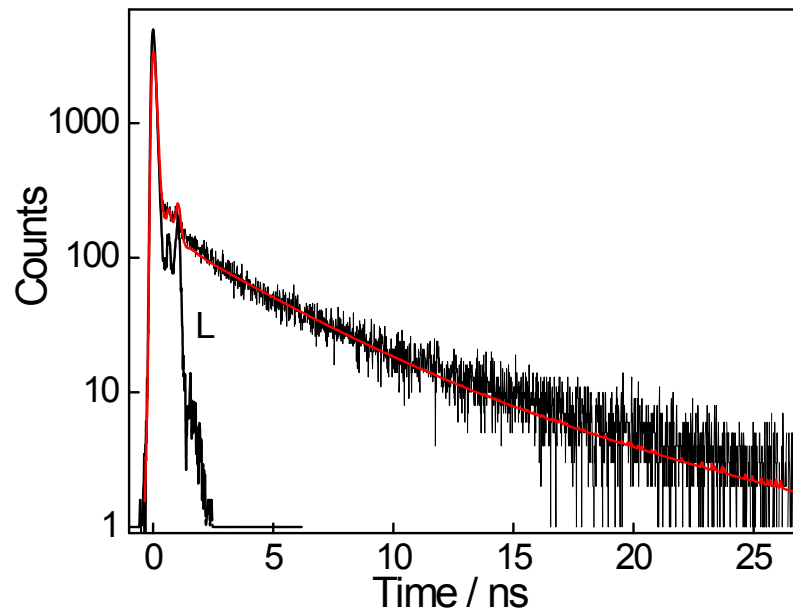


Fig. S5 Fluorescence decay trace of DABP (20 μ M) in water with 350 μ M of CB7 at pH \sim 3. λ_{ex} = 374 nm and λ_{mon} = 470 nm. L represents the lamp profile.

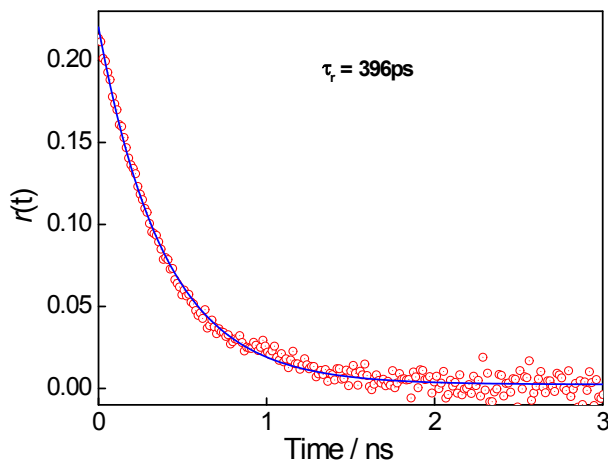


Fig. S6 Time-resolved fluorescence anisotropy decay of CB7:DABP system at pH \sim 9.5. λ_{ex} = 445 nm and λ_{mon} = 700 nm.

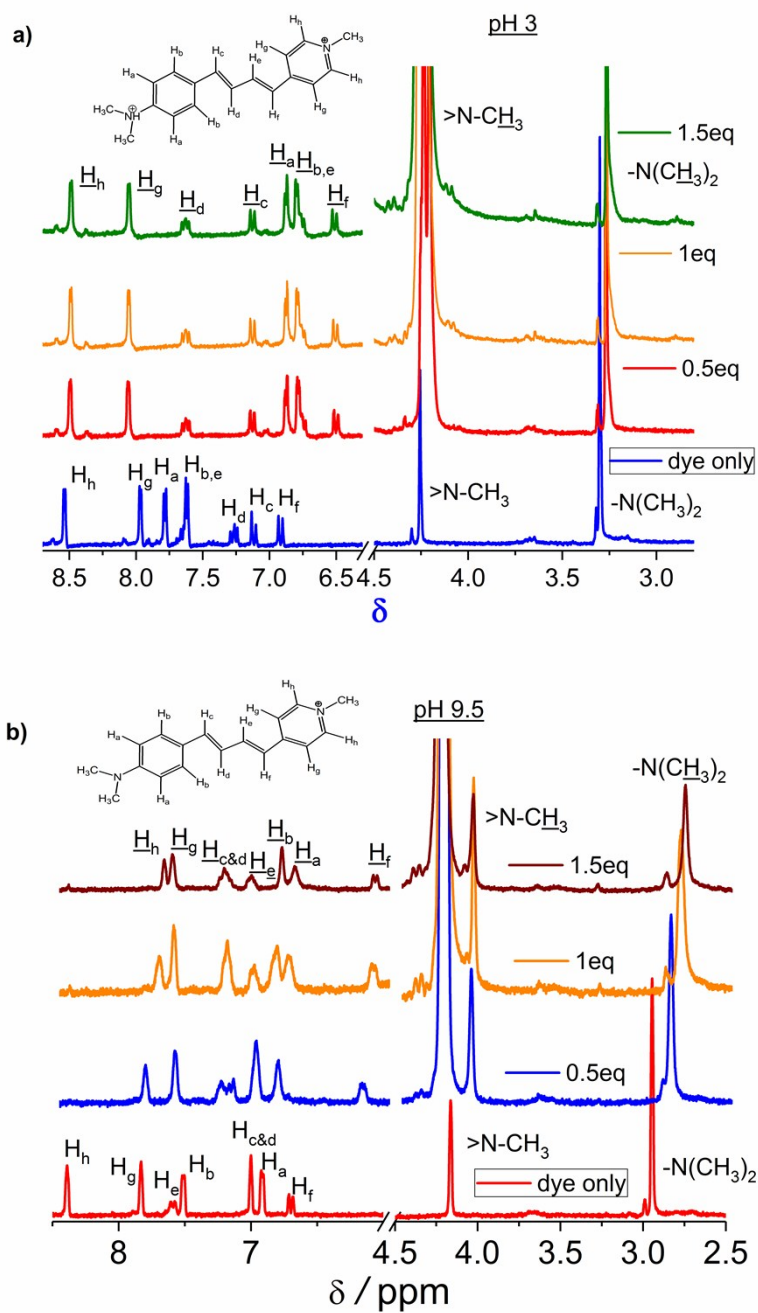


Fig. S7 ^1H NMR signals for DABP at pH 3.0 (above, **a**) and pH 9.5 (below, **b**) in the presence of CB7.

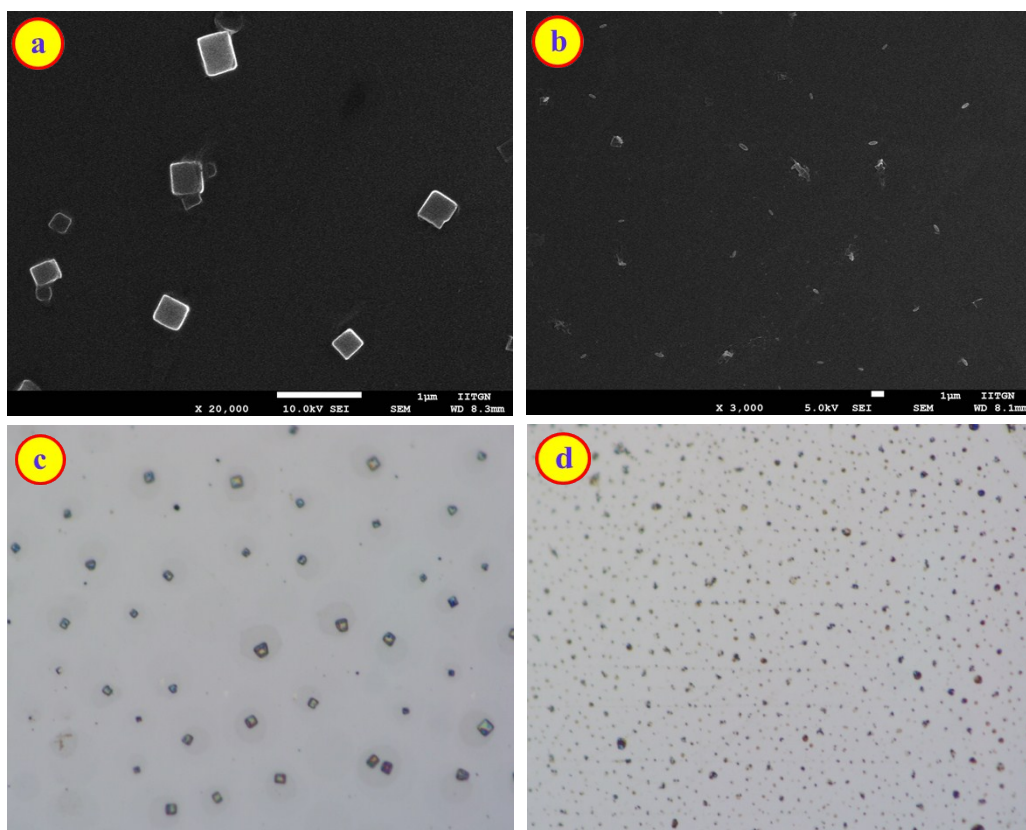


Fig. S8 Scanning electron microscopy images of a: CB7 b: dye c: optical microscopy images of CB7 and d: dye at pH 3. * Dye concentration used is 10µM.

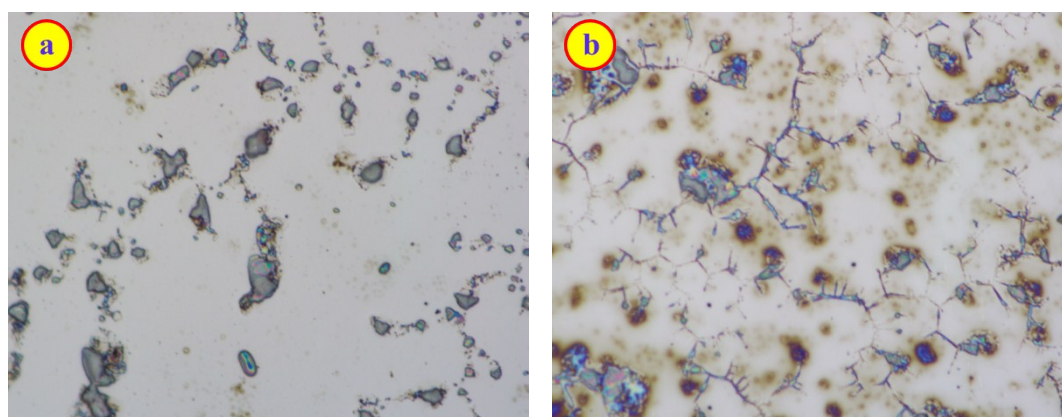


Fig. S9 Optical microscopy images of dye+10µM CB7 (a) dye+200µM CB7 (b) at pH 3. *Dye concentration used is constant at 10µM.

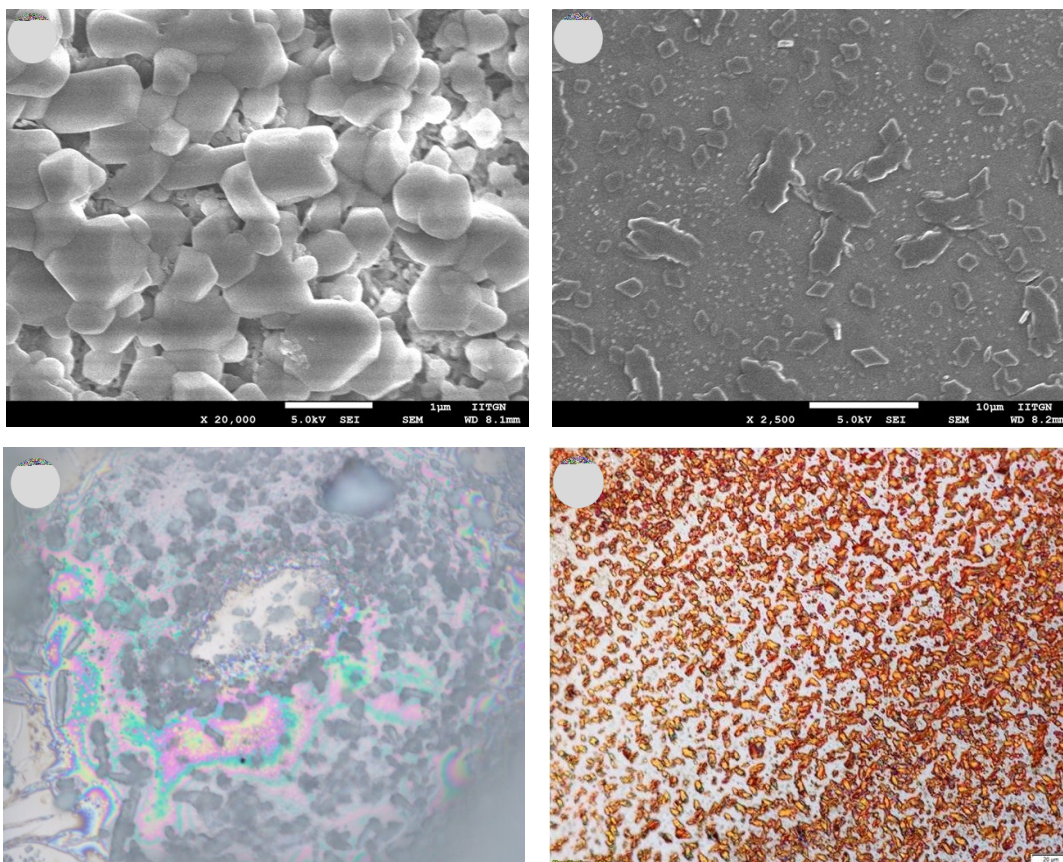


Fig. S10 Scanning electron microscopy images of a) CB7 b) dye and optical microscopy images of c) CB7 d) dye at pH 9.5. * Dye concentration 10 μ M.

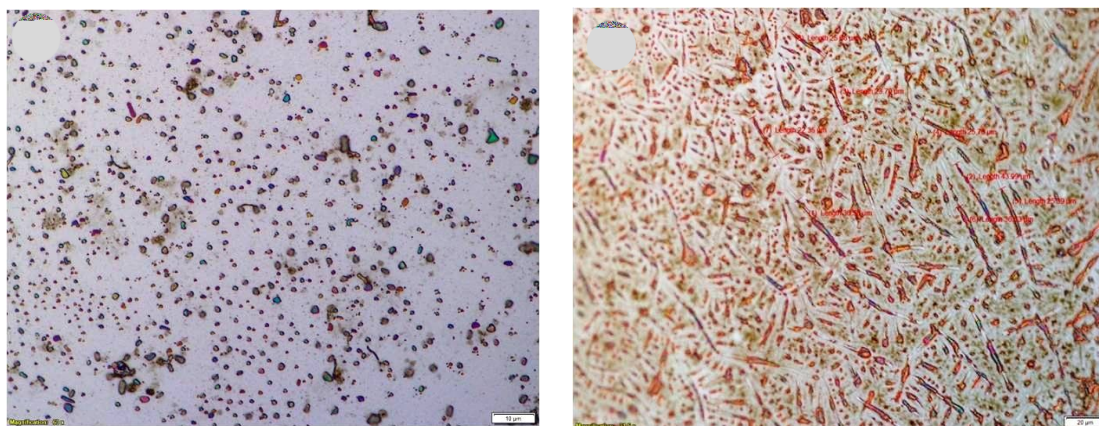


Fig. S11 Optical microscopy images of dye+10 μ M CB7 (a) dye+200 μ M CB7 (b) in pH 9 solution. *Dye concentration 10 μ M.

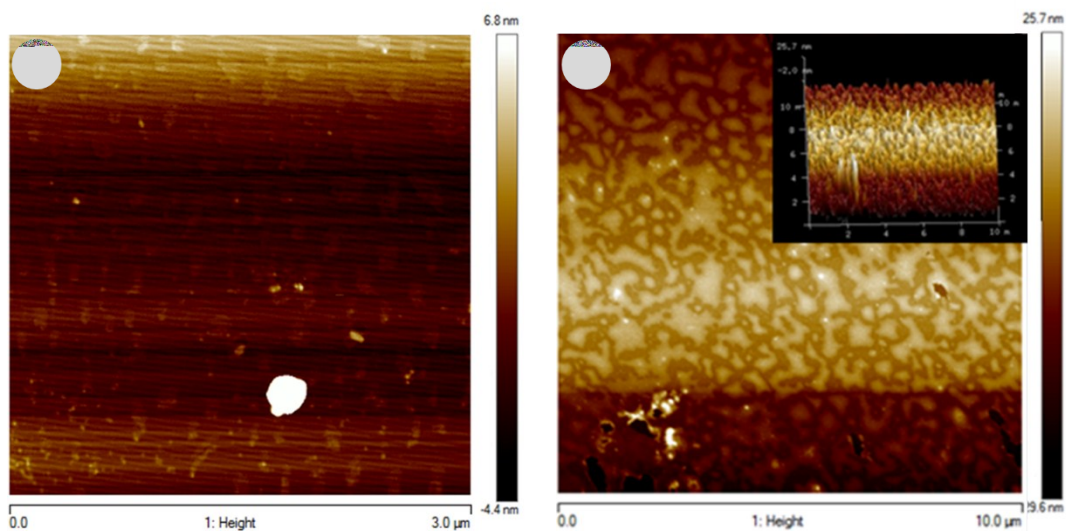


Fig. S12 Atomic force microscopy images of dye in pH 3 (a) and pH 9 (b) solution. *Dye concentration 10 μ M.

Reference

1. S. Dutta Choudhury, J. Mohanty, H. P. Upadhyaya, A. C. Bhasikuttan and H. Pal, *J. Phys. Chem. B* 2009, **113**, 1891-1898.