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

Electronic Supplementary Information

Cylcodextrin-assisted Modulation in the Photophysical Properties and Acidity Constant of Pyrene-armed Calix[4]arene

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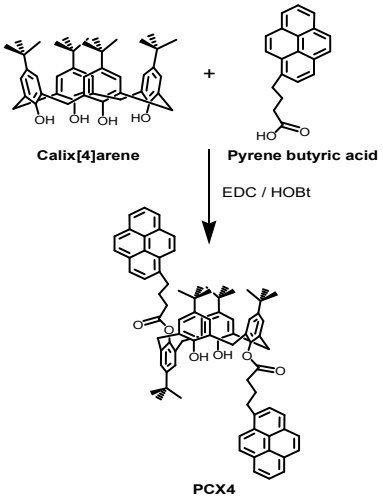

Scheme S1: Synthetic route for the synthesis of PCX4.

Experimental methods

Absorption spectra were recorded with a Jasco V-650 UV-vis spectrophotometer (Tokyo, Japan). Steady-state fluorescence spectra were recorded using a Hitachi F-4500 spectrofluorometer (Tokyo, Japan). The samples were excited at 345 nm, where the changes in the optical density were nominal in the absorption spectra. The time-resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) set-up from Horiba Scientific (UK). In the present work, a 339 nm LED (<1ns, 1 MHz repetition rate) was used for excitation. A reconvolution procedure was used to analyze the observed decays,[1] which could be satisfactorily fitted by mono- or biexponential decay functions. The fluorescence decays [I(t)] were analyzed in general as a sum of exponentials,[1]

$$I(t) = \sum B_i \exp(-t/\tau_i) \quad \text{(S1)}$$

where, B_i and τ_i are the pre-exponential factor and fluorescence lifetime for the i^{th} component, respectively. Reduced chi-square (χ^2) values (within 1.00-1.20) and random distribution of the weighted residuals among data channels were used to judge the acceptance of the fits.

For anisotropy measurements, samples were excited with a vertically polarized excitation beam and the vertically and horizontally polarized fluorescence decays were collected with a large spectral bandwidth of ~32 nm. Using these polarized fluorescence decays, the anisotropy decay function, $r(t)$, was constructed as follows:[1]

$$r(t) = \frac{I_V(t) - GI_H(t)}{I_V(t) + 2GI_H(t)} \quad \text{(S2)}$$

$I_V(t)$ and $I_H(t)$ are the vertically and horizontally polarized decays, respectively, and G is the correction factor for the polarization bias of the detection setup. The G factor was determined independently by using a horizontally polarized excitation beam and measuring the two perpendicularly polarized fluorescence decays.

Method M1:

In the present study, the binding constants (K_{eq}) for the β-CD:PCX4 complex was determined by using the fluorescence titration method, according to a 1:1 binding model (eq. S3).[2, 3]

$$\beta\text{-CD} + \text{PCX4} \underset{}{\overset{K_{eq}}{\rightleftharpoons}} \beta\text{-CD:PCX4} \quad \text{(S3)}$$

Taking $[PCX4]_0$ and $[\beta\text{-CD}]_0$ as the total concentrations of PCX4 and β-CD, respectively, eq. S4 applies for the concentration of free (uncomplexed) PCX4 in equilibrium:

$$[PCX4]_{eq} = \{K_{eq}[PCX]_0 - K_{eq}[\beta - CD]_0 - 1 + \sqrt{(K_{eq}[PCX4]_0 + K_{eq}[\beta - CD]_0 + 1)^2 - 4K_{eq}^2[PCX4]_0[b - CD]_0}\}/2K_{eq} \quad \text{(S4)}$$

where K_{eq} represents the binding constant for the PCX4 with the host. Since the interconversion of the free and complexed dye in solution (*cf.* equilibrium 1) occurs at a much slower rate (in microseconds)[2, 3] than the excited-state lifetimes of the dyes (subnanosecond to nanoseconds), it can be safely assumed that during the fluorescence measurements there is effectively no ex-

change between the free and complexed dyes. Thus, the observed results in the fluorescence measurements can be attributed simply to the excited-state processes, assuming that the initial populations of the excited free and complexed dyes are determined by the binding constant of the dye as given by equilibrium 1 and the absorption coefficients of the two species at the excitation wavelength. The total fluorescence intensity can be expressed as

$$I_{\text{Total}} = I_{\text{PCX4}} \frac{[\text{PCX4}]_{\text{eq}}}{[\text{PCX4}]_0} + I_{\beta\text{-CD:PCX4}} \frac{[\beta\text{-CD} : \text{PCX4}]_{\text{eq}}}{[\text{PCX4}]_0} \quad \text{(S5)}$$

where, I_{PCX4} is the fluorescence intensity in the absence of β-CD and $I_{\beta\text{-CD:PCX4}}$ is the fluorescence intensity of the complex when all the PCX4 molecules in the solution are complexed.

Rearranging eq. S5, the changes in fluorescence intensity can be written as,

$$\Delta I = \left(1 - \frac{[\text{PCX4}]_{\text{eq}}}{[\text{PCX4}]_0}\right)\left(I_{\beta\text{-CD:PCX4}} - I_{\text{PCX4}}\right) \quad \text{(S6a)}$$

In the absorption titrations, we have employed the changes in the optical density of PCX4 with the β-CD host which can be written as[3]

$$\Delta OD = \left(1 - \frac{[\text{PCX4}]_{\text{eq}}}{[\text{PCX4}]_0}\right)\left(OD_{\beta\text{-CD:PCX4}} - OD_{\text{PCX4}}\right) \quad \text{(S6b)}$$

The K_{eq} values were obtained by non-linear curve fittings according to eq. S6(a&b).

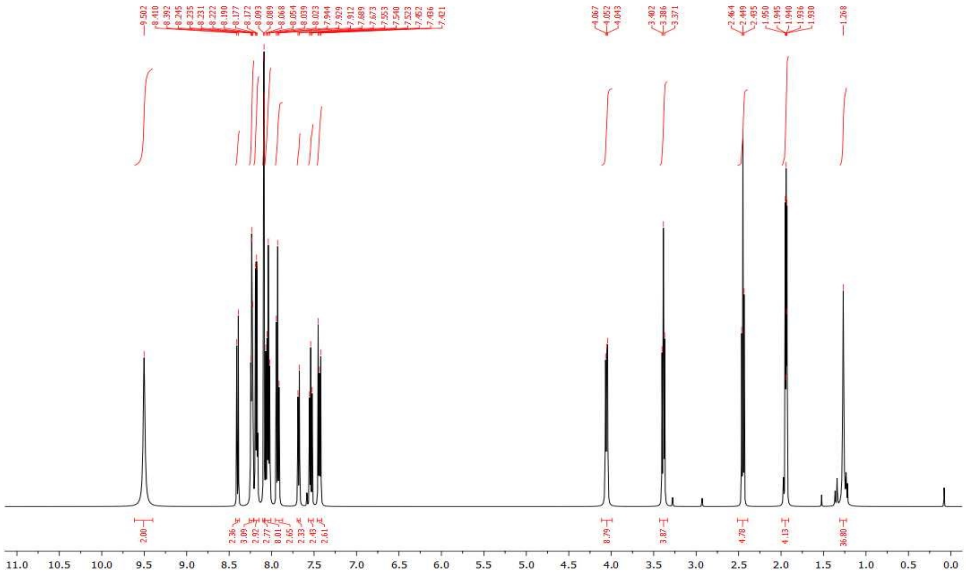

Figure S1: ^{1}H-NMR of PCX4 in $CDCl_3$.

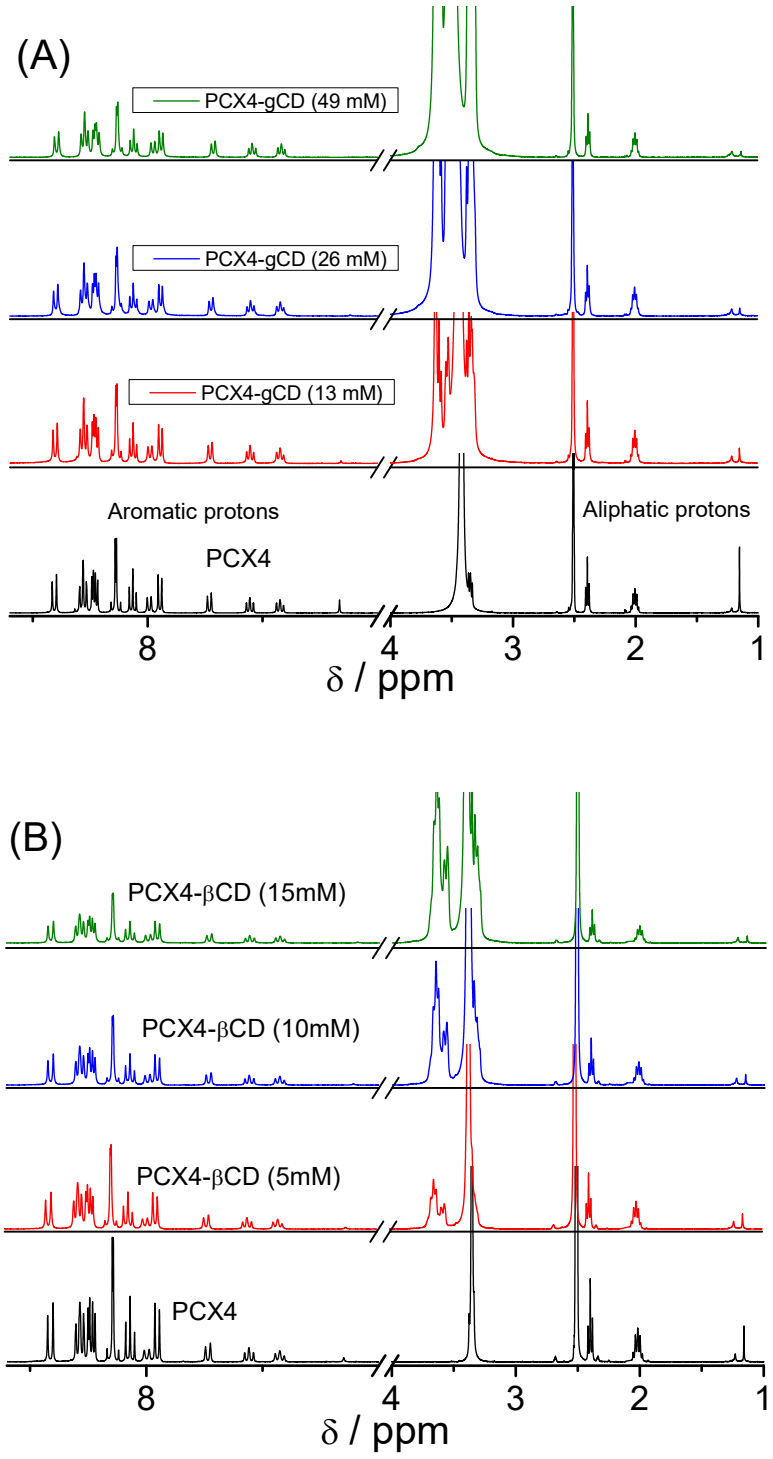

Figure S2. ^{1}H NMR titrations of PCX4 at different concentrations of γ-CD (A) and β-CD (B) in DMSO-d6.

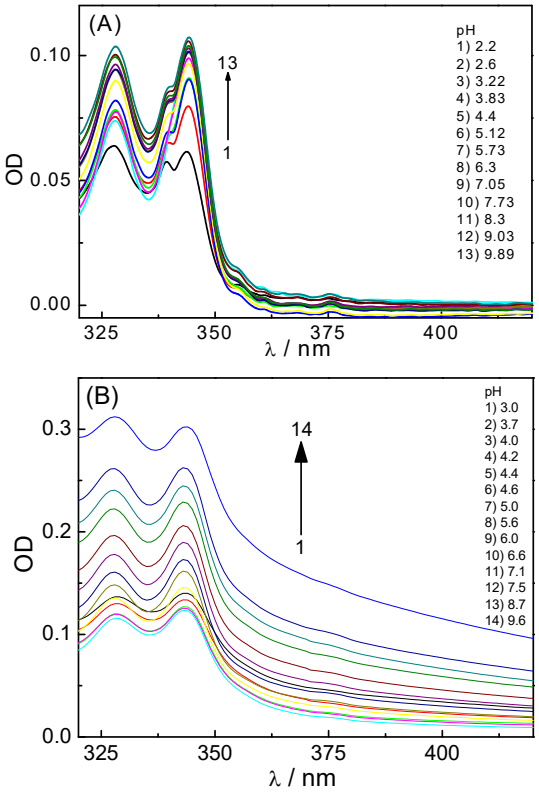

Figure S3. Absorption spectra of PCX4 in water containing 1.5 mM β-CD (A) and 18 mM γ-CD at different pHs.

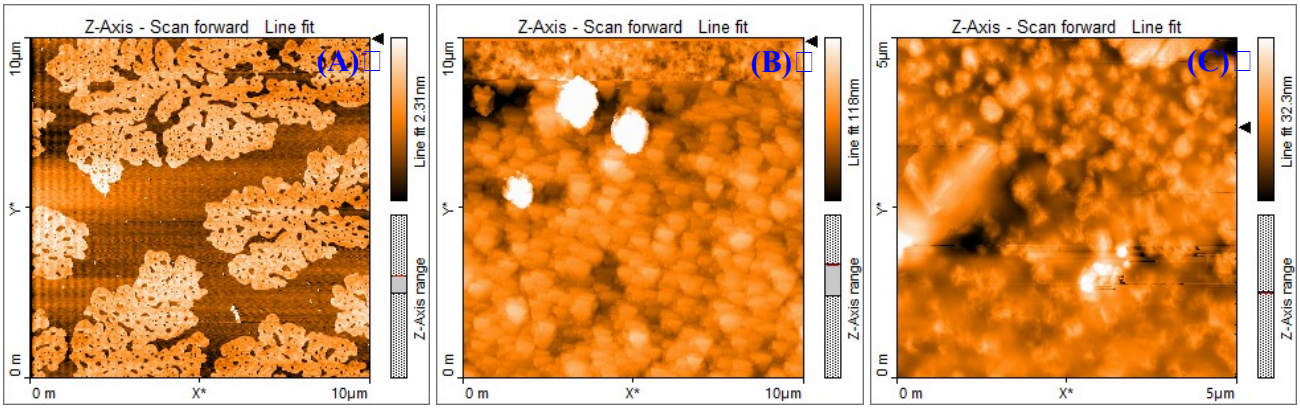

Figure S4. AFM images of PCX4 in the presence of 3.0 mM γ-CD (A), 1.5 mM of γ-CD (B) and 1.5 mM β-CD (C).

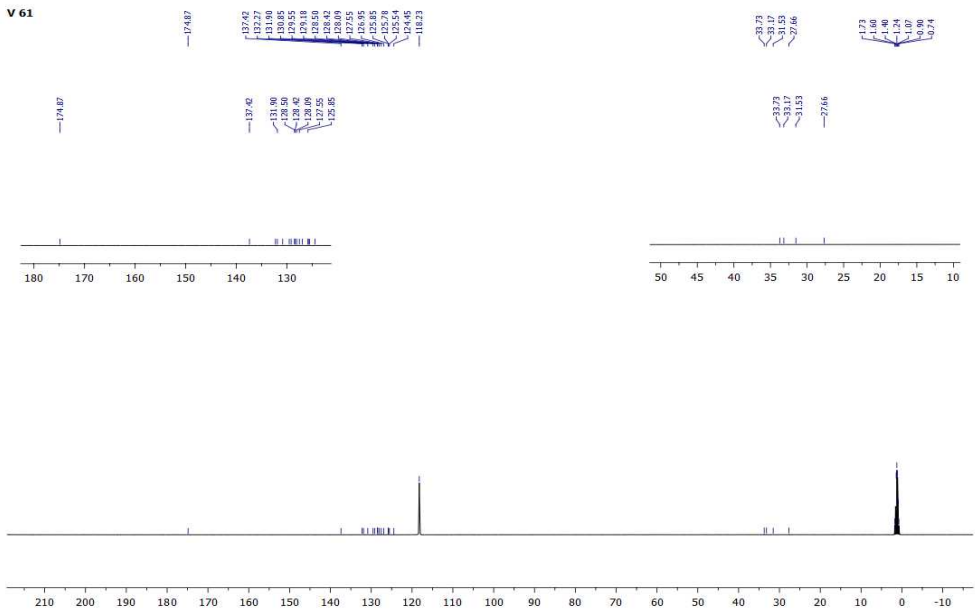

Figure S5: ^{13}C-NMR Spectra of PCX4.

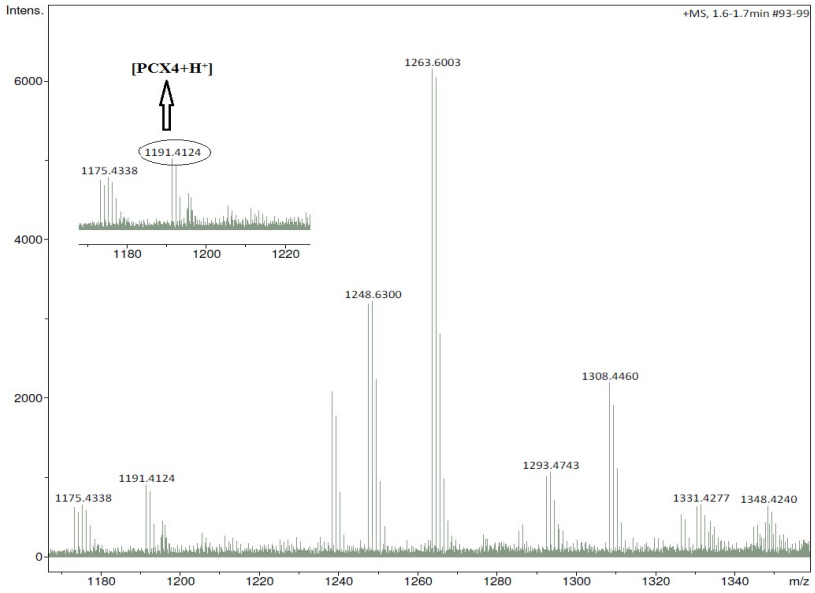

Figure S6: HR-MS spectra of PCX4.

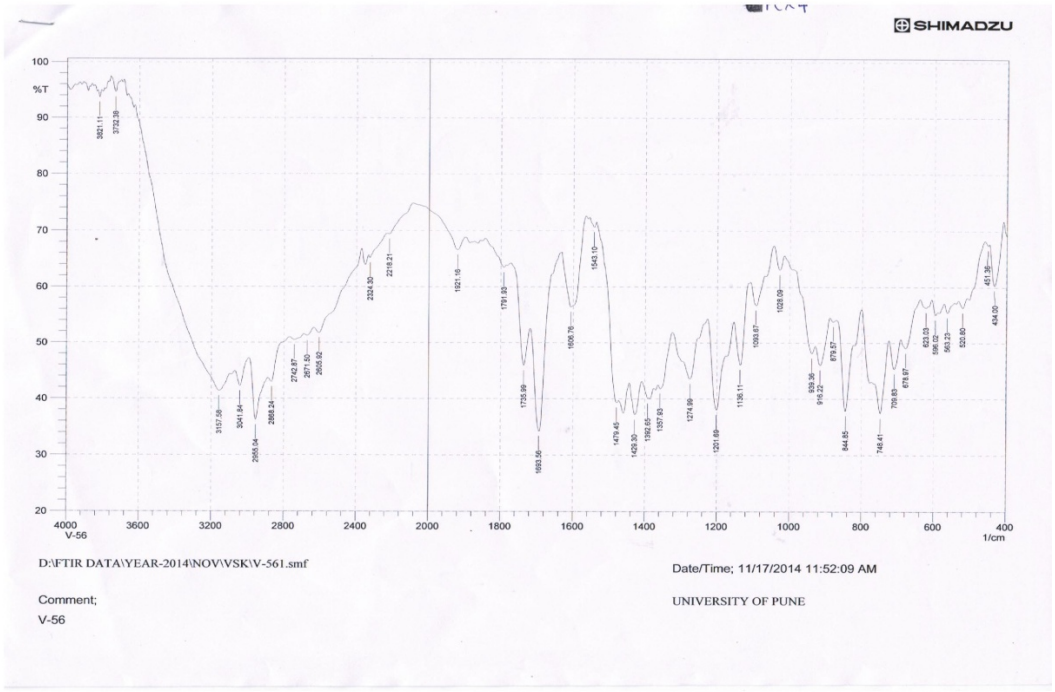

Figure S7: FT-IR spectra of PCX4.

References

1. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, 2006.
2. J. Mohanty, A. C. Bhasikuttan, W. M. Nau and H. Pal, *J. Phys. Chem. B*, 2006, **110**, 5132-5138.
3. W. M. Nau and X. Zhang, *J. Am. Chem. Soc.*, 1999, **121**, 8022-8032.