Electronic Supporting Information

On the Photophysics of 9-Amino-10-cyanoanthracene: Probing its Dual Absorption and Emission Behavior

Sharmistha Dutta Choudhury,*[,a] Sukumaran Muralidharan *[,b] and Haridas Pal[a]

[a] *Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India. E-mail: sharmidc@barc.gov.in*

[b] *Center for Biomedical Engineering and Technology, University of Maryland School of Medicine, 725 W. Lombard St., Baltimore, MD 21201, United States. E-mail: palakkadan@yahoo.com*

Note S1.

Preparation of 9-amino-10-cyanoanthracene (ACAN)

The compound, 9-amino-10-cyanoanthracene (ACAN) was prepared by the same procedure as outlined in a previous publication.[1] Briefly, the starting material, 9-nitroanthracene, was treated with three equivalents of sodium cyanide in dry DMF (under nitrogen) at room temperature. After 18 hours the solution was filtered and diluted with brine. The organic material was extracted from the solution, with CH_2Cl_2, followed by acidification of CH_2Cl_2 with dilute hydrochloric acid. The precipitated solid was treated with 5% sodium bicarbonate to yield the desired compound, ACAN.

Purification of ACAN

The crude material was recrystallized from toluene, twice. NMR analysis of this sample gave excellent agreement with the published results. For the present spectroscopic studies, the material was further purified by HPLC. The preparative HPLC was done with a Waters HPLC system with semi-preparative reverse phase column [MetaChem, Intersil 5µ ODS-3]. The monitoring system for the HPLC set-up was a diode array detector and the wavelength of this was set to 450 nm. The mobile phase used was a gradient with acetonitrile–water (with 0.1% TFA) and the fraction emerging at 19-20 minutes was collected and lyophilized. A small portion of the

lyophilized material was redissolved in acetonitrile and injected again in the HPLC (to ascertain the purity of the material). The HPLC trace thus obtained is shown below.

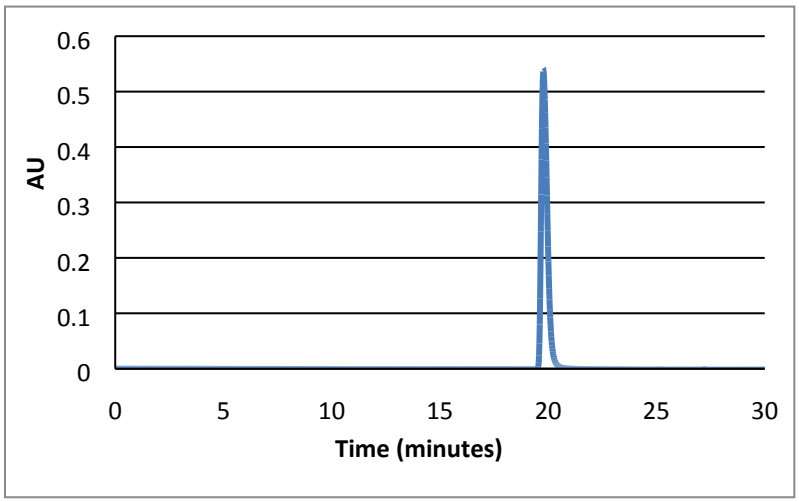

Figure S1. HPLC trace of the purified ACAN sample.

Note S2.

Stability of ACAN in highly acidic solutions

For the prototropic studies of ACAN, the absorption and fluorescence spectra have been recorded at very high H_2SO_4 concentrations. It is thus imperative to ascertain that there is no degradation of ACAN under these extreme conditions. Our concern was the stability of the cyano group of ACAN under strong acidic conditions. To allay our concern, we undertook a stability test of ACAN in the following manner: ACAN (10 mg) was dissolved in 2 mL DMSO-H_2O mixture (1:1 v/v). The solution was kept in ice/water bath, and 1 mL con. H_2SO_4 was added in small portions over 15 minutes. The mixture was stirred for 24 hours at room temperature (kept under argon and devoid of light) after which the acid was neutralized by the addition of solid $NaHCO_3$. This was followed by the addition of 10 mL of water, and the mixture was extracted with ethyl acetate (20 mL x 4 times). The extract was first dried with sodium sulfate, and then the organic solvent was evaporated to dryness under vacuum. Following this procedure, 7.8 mg of material was recovered. This material was then characterized using NMR analysis. The sample was dissolved in DMSO-d_6 and the ^{13}C NMR was recorded on a Varian 400 MHz NMR instrument with the DMSO-d_6 line at 39.51 ppm being used as reference. The ^{13}C NMR spectra thus obtained are shown below (Fig. S2A for the full and Fig. S2B for the expanded versions).

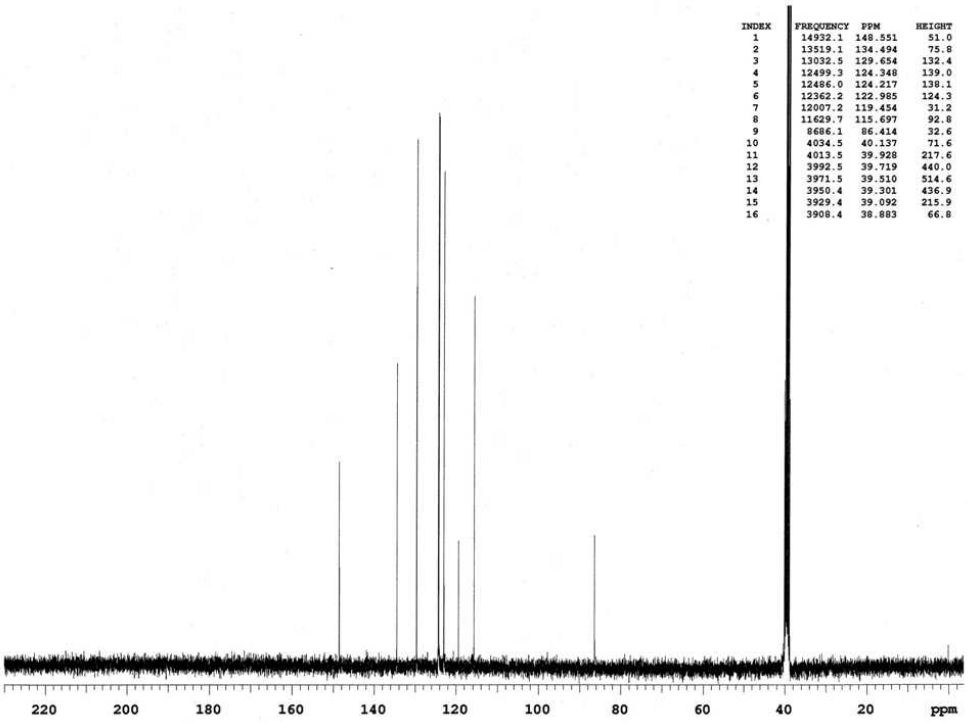

Figure S2A. ^{13}C NMR of ACAN sample after the treatment with acid (discussed above).

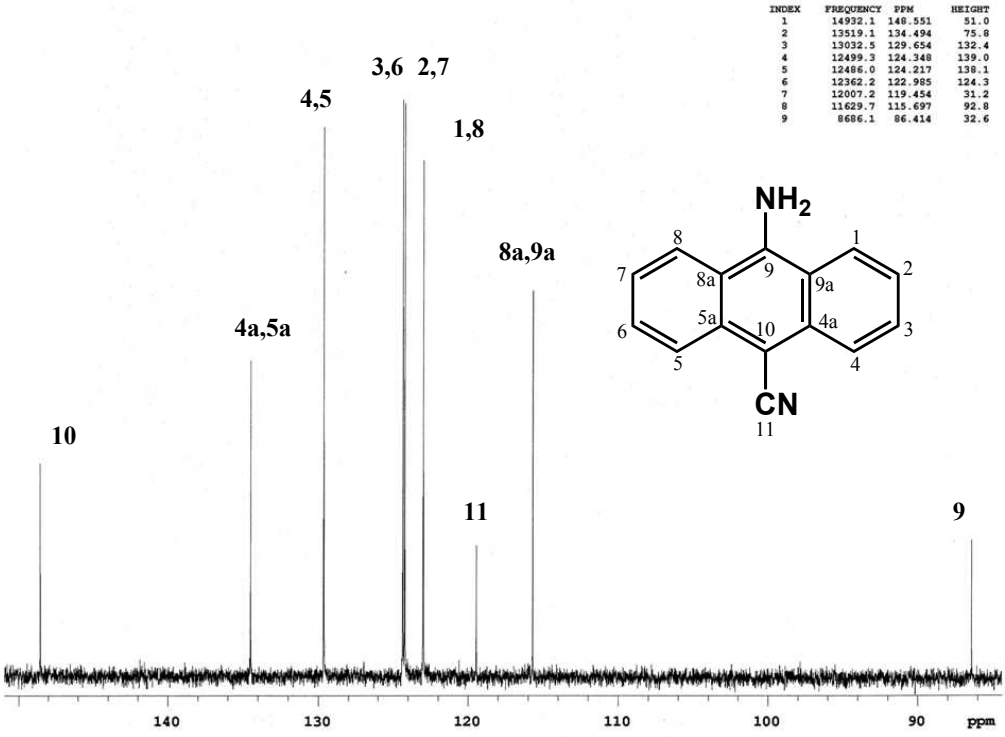

Figure S2B. ^{13}C NMR of ACAN sample after the treatment with acid (discussed above)-expanded from Fig. S2A.

The relevant ^{13}C line listings are as follows (in ppm): 148.551, 134.494, 129.654, 124.348, 124.217, 122.985, 119.454, 115.697, 86.414.

The ^{13}C line at 115.697 ppm is assigned to the cyano group, similar to benzonitrile.[2] There was no change in the ^{13}C NMR of the material before (Fig. S2C, Fig. S2D) and after the treatment with acid (i.e., no additional peaks appeared in the ^{13}C NMR of the recovered material, after the acid treatment). Thus, we are sure that the cyano group of ACAN is stable in the absorption/fluorescence experiments carried out at highly acidic conditions.

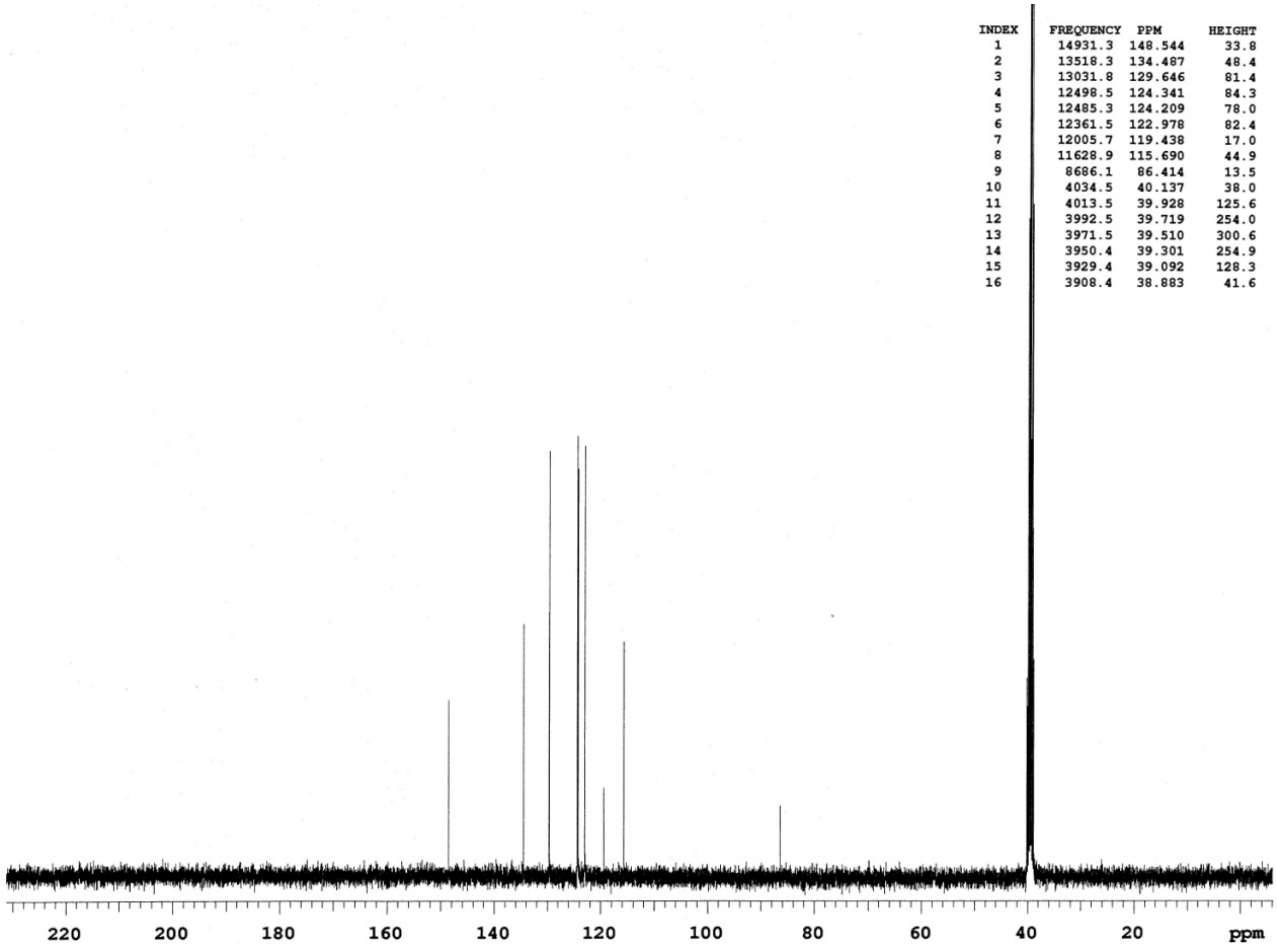

Figure S2C. ^{13}C NMR of ACAN sample prior to the treatment with acid.

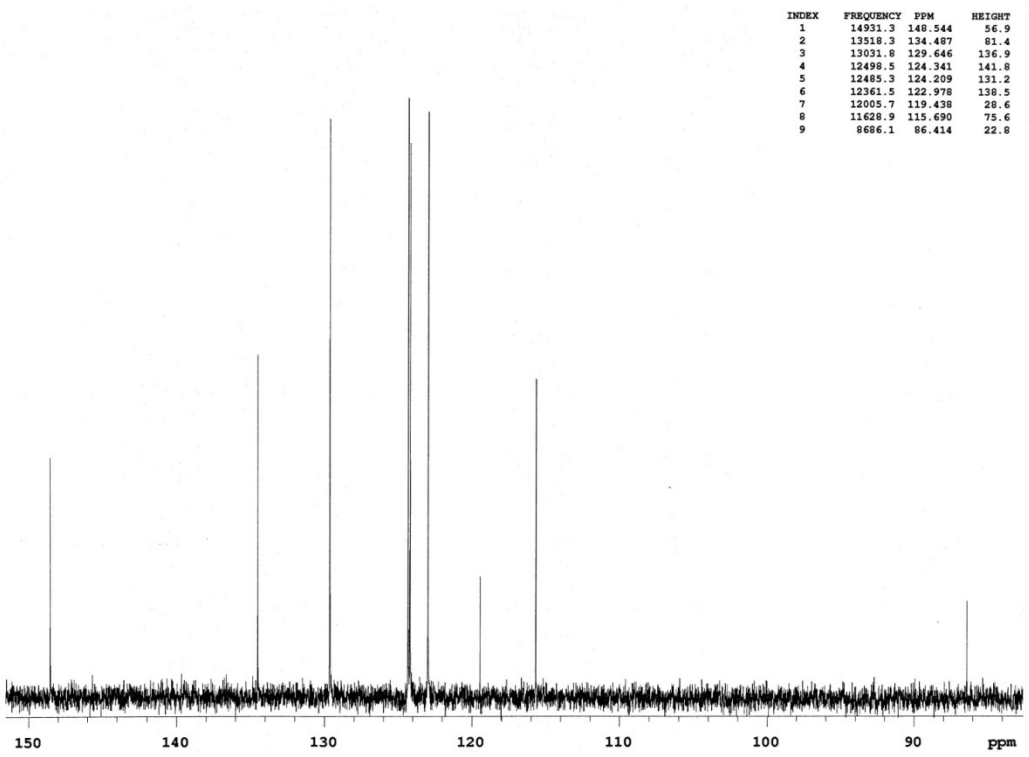

Figure S2D. ^{13}C NMR of ACAN sample prior to treatment with acid- expanded from Fig. S2C.

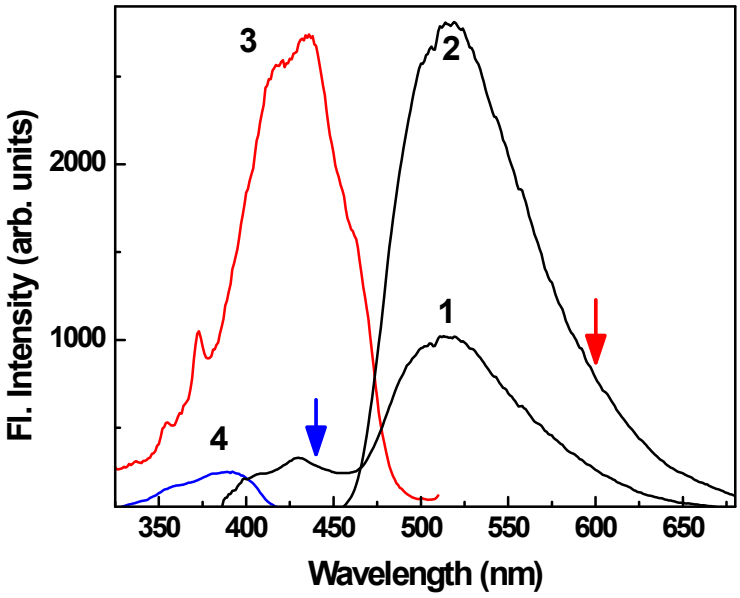

Figure S3. Emission spectra of ACAN in cyclohexane on excitation at (1) 350 nm and (2) 435 nm and the corresponding excitation spectra for emission monitored at (3) 600 nm and (4) 450 nm (These wavelengths are also indicated with arrows).

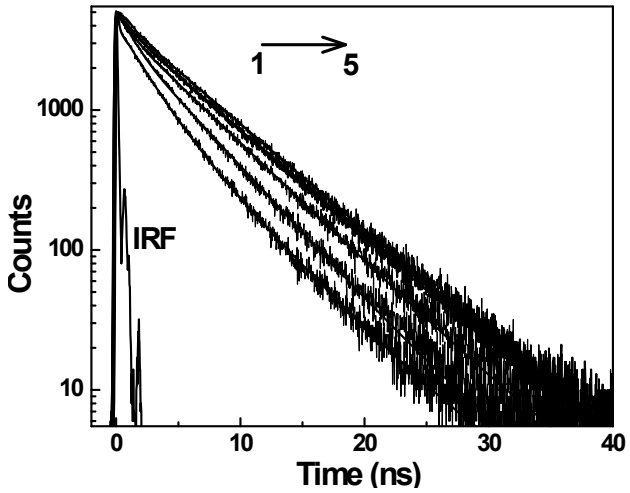

Figure S4. Fluorescence decay traces of ACAN at 435 nm in Cyclohexane-Ethylacetate (CH-EA) solvent mixtures; (1) CH_{100}-EA_0, (2) $CH_{99.5}$-$EA_{0.5}$, (3) CH_{98}-EA_2, (4) CH_{90}-EA_{10}, (5) CH_0-EA_{100}. The subscripts show the volume percentage of each solvent. Excitation wavelength = 375 nm.

Table S1. Fluorescence decay parameters[a] of ACAN at 435 nm in cyclohexane-ethylacetate (CH-EA) solvent mixtures; (1) CH_{100}-EA_0, (2) $CH_{99.5}$-$EA_{0.5}$, (3) CH_{98}-EA_2, (4) CH_{90}-EA_{10}, (5) CH_0-EA_{100}. The subscripts indicate the volume percentage of each solvent in the mixture.

Solvent	**435 nm**			
	A_1(%)	**τ_1 (ns)**	**A_2 (%)**	**τ_2 (ns)**
CH_{100}-EA_0	43	2.2	57	4.8
$CH_{99.5}$-$EA_{0.5}$	16	1.3	84	4.8
CH_{98}-EA_2	9	1.1	91	5.1
CH_{90}-EA_{10}	6	0.7	94	5.5
CH_0-EA_{100}	5	0.7	95	5.6

[a]The fluorescence decays were fitted by considering a bi-exponential function;

$$I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \;;\; A_1(\%) = \frac{a_1\tau_1}{a_1\tau_1 + a_2\tau_2} \times 100 \text{ and } A_2(\%) = \frac{a_2\tau_2}{a_1\tau_1 + a_2\tau_2} \times 100$$

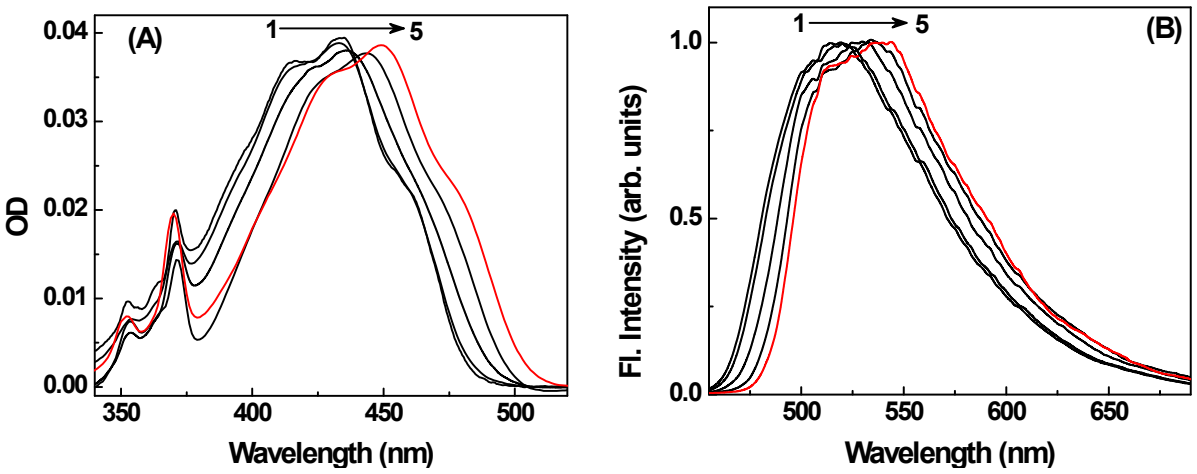

Figure S5. (A) Absorption spectra and (B) emission spectra (excitation wavelength = 435 nm) of ACAN in Cyclohexane-Ethylacetate (CH-EA) solvent mixtures; (1) CH_{100}-EA_0, (2) $CH_{99.5}$-$EA_{0.5}$, (3) CH_{98}-EA_2, (4) CH_{90}-EA_{10}, (5) CH_0-EA_{100}. The subscripts show the volume percentage of each solvent.

Note S3

Exchange of amino hydrogen atoms of ACAN with deuterium

We have carried out photophysical experiments in H_2O and D_2O. It is postulated that the -NH_2 group of ACAN gets converted to –ND_2 in D_2O solution. The support for this assertion comes from the NMR analysis of ACAN in $CDCl_3$, with and without the addition of D_2O. The compound was dissolved in $CDCl_3$ and the ^{1}H NMR was recorded on a Varian 400 MHz NMR instrument (with TMS as an internal reference, at 0.0 ppm). The ^{1}H NMR spectra are shown below (Fig. S6A and S6B, full & expanded versions, respectively). The broad peak appearing at 5.54 ppm is assigned to the –NH_2 hydrogen atoms. On shaking the NMR sample with 2 drops of D_2O, the peak at 5.54 ppm disappears and a new peak at 4.77 ppm (corresponding to D-O-H) appears (Fig. S6C and S6D).

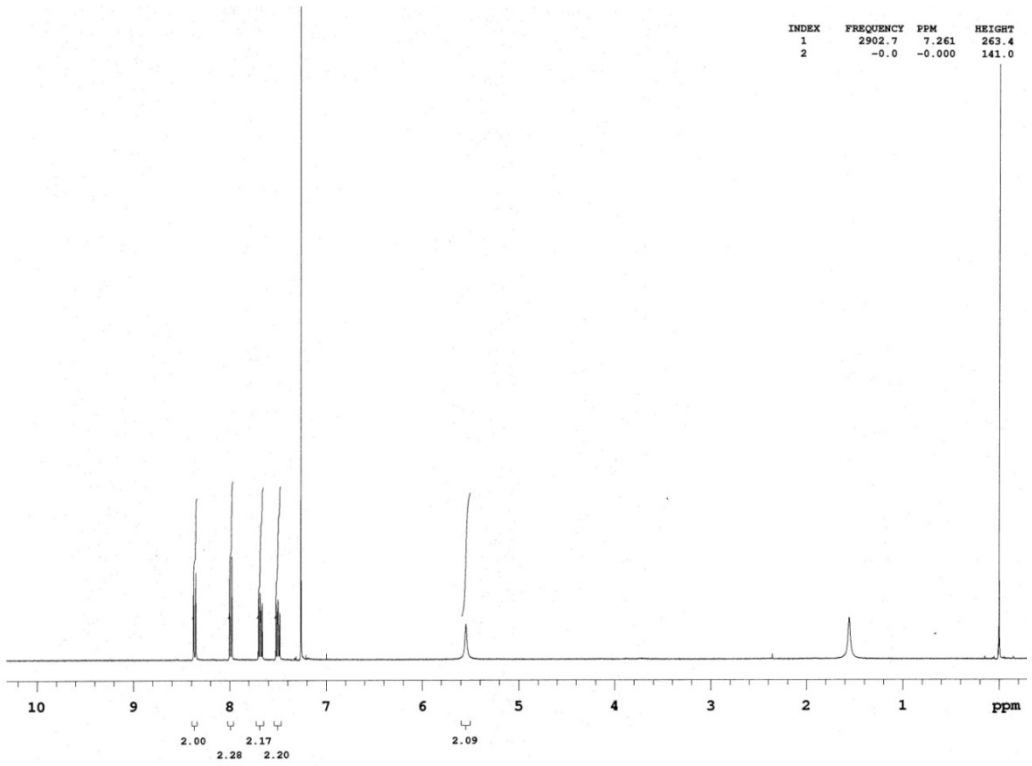

Figure S6A. ^{1}H NMR of ACAN in $CDCl_3$.

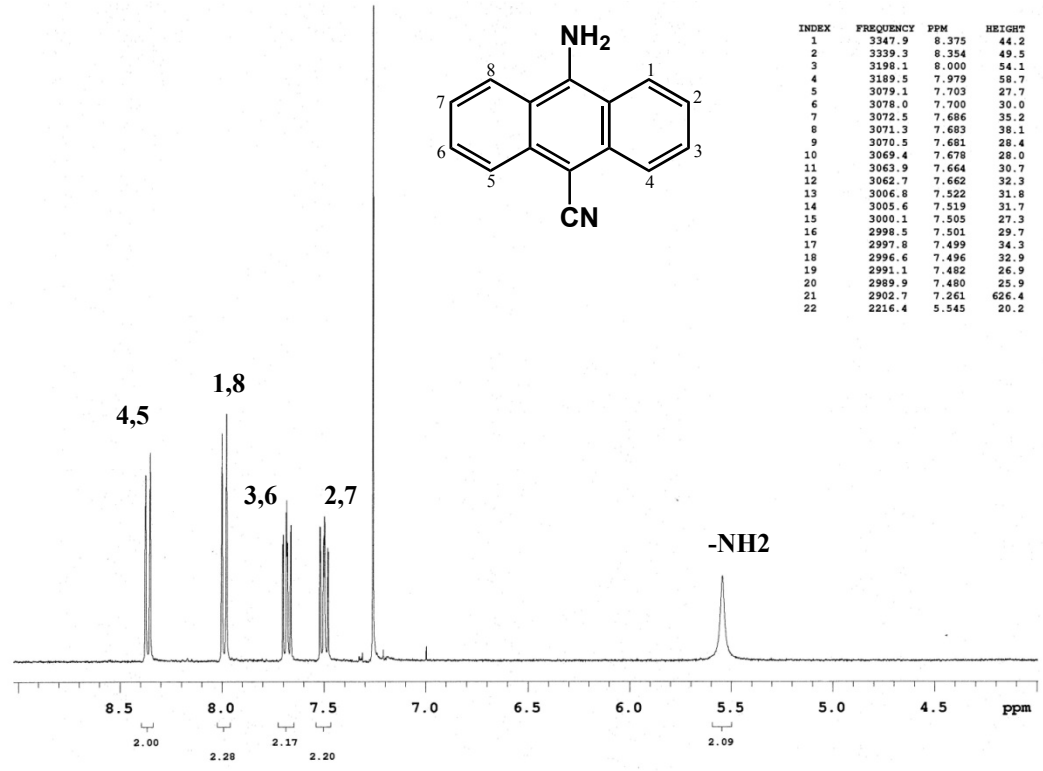

Figure S6B. ^{1}H NMR of ACAN in $CDCl_3$ – expanded from Fig. S6A.

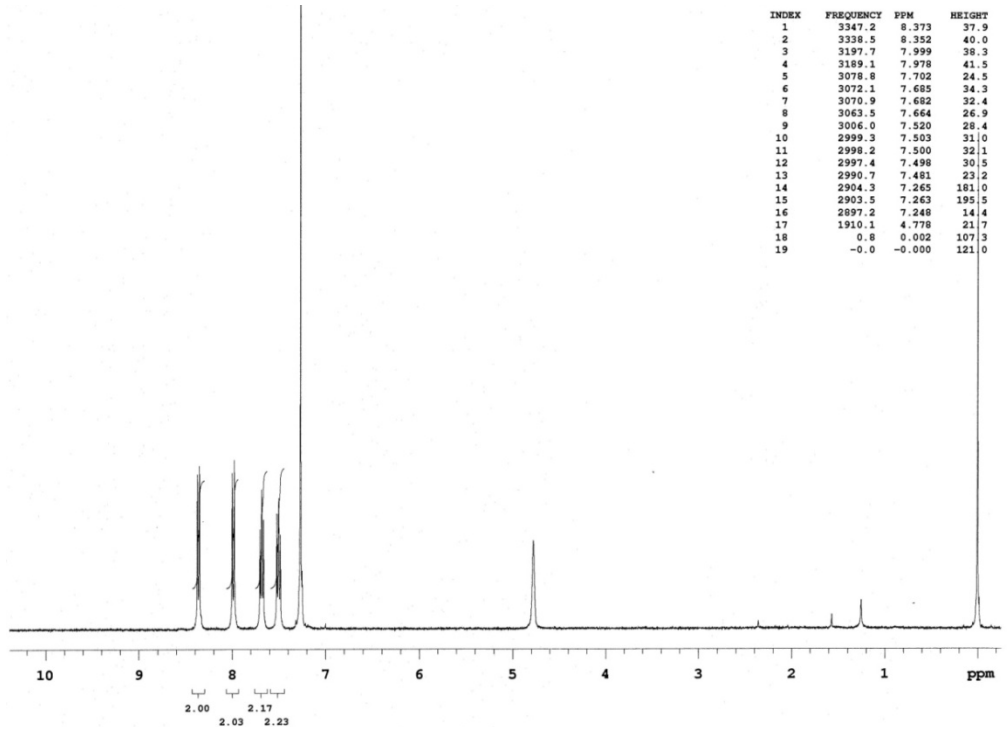

Figure S6C. ^{1}H NMR of ACAN in $CDCl_3$ (sample shaken with 2 drops of D_2O).

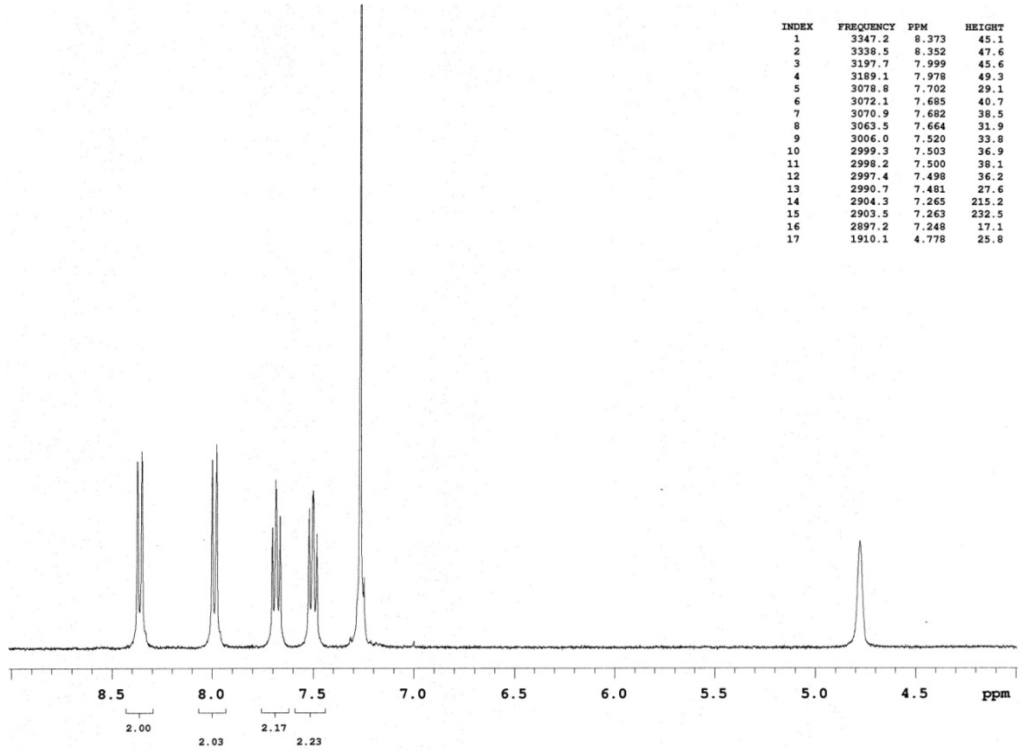

Figure S6D. ^{1}H NMR of ACAN in $CDCl_3$ (sample shaken with 2 drops of D_2O) – expanded from Fig. S6C.

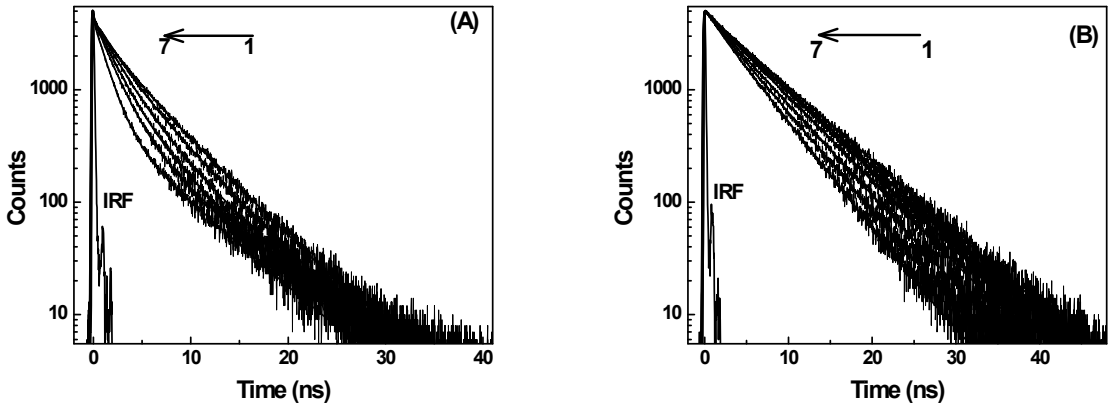

Figure S7. Fluorescence decay traces of ACAN at 435 nm in (A) cyclohexane and (B) acetonitrile at 10, 20, 30, 40, 50, 60 and 70°C (1-7).

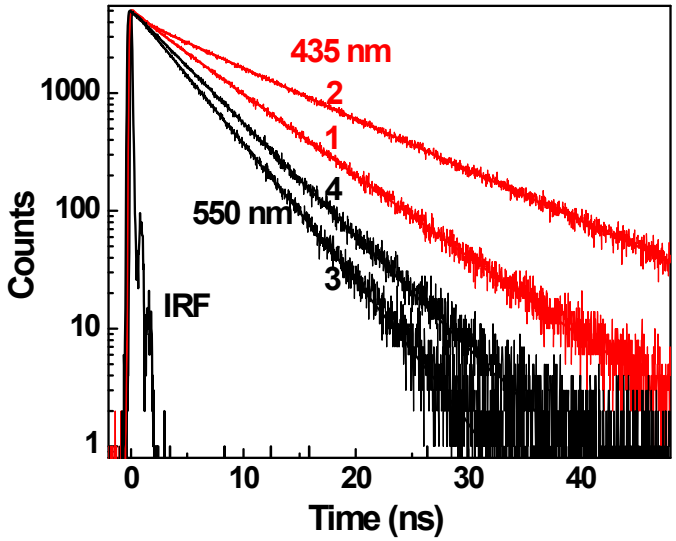

Figure S8. Fluorescence decay traces of ACAN at 435 nm (red lines) before (1) and after (2) purging with N_2. Fluorescence decay traces of ACAN at 550 nm (black lines) before (3) and after (4) purging with N_2.

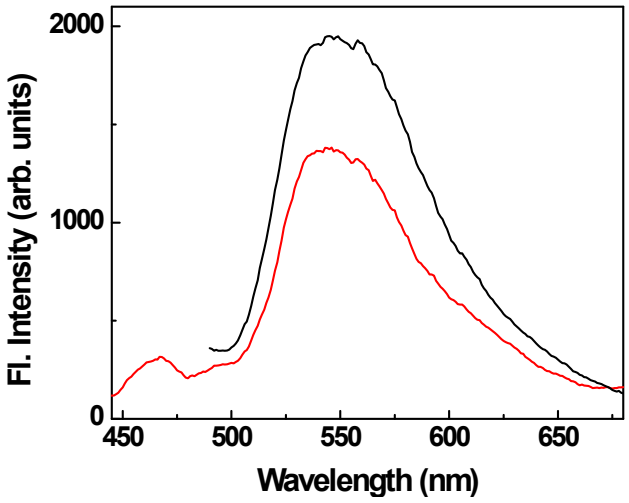

Figure S9. Emission spectra from ACAN film deposited on quartz slide on excitation at (1) 350 nm and (2) 435 nm.

Note S4.

A thin film of ACAN was obtained by depositing drops of acetonitrile solution of ACAN on a clean quartz slide and allowing the solvent to dry off slowly at ambient conditions. The fluorescence spectra were recorded with front face geometry using suitable emission filters to minimize the scattered light.

Note S5.

To determine the pK_a value of $ACANH^+$ we recorded the absorption spectra of ACAN in aqueous medium (5% methanol in water) with gradually increasing H_2SO_4 concentrations. These spectra were used to construct a plot of the optical density (OD, at 465 nm) versus the Hammett acidity function, H_0 (inset in Fig. 8). According to the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\frac{[ACAN]}{[ACANH^+]} \qquad (1)$$

Since the acid concentrations in the present cases are very high, we used the Hammett acidity function, H_0, instead of the pH scale. From the above plot of OD vs. H_0, the inflection point where $[ACAN]/[ACANH^+] = 1$, is obtained at $H_0 = -1.3$. This H_0 value at the inflection point was

further adjusted for proton activity based on the data reported by Dixon et al.[4] The proton activity corrected pK_a for $ACANH^+$ was thus estimated to be -0.9.[3, 4]

The excited state acidity constant, pK_a^*, was estimated using the Förster cycle method, which correlates the ground- and excited-state acidity constants (i.e. pK_a and pK_a^*, respectively) as,

$$pK_a^* = pK_a + \frac{hc\Delta\bar{\nu}}{2.303RT} \quad (2)$$

where, $\Delta\bar{\nu} = \bar{\nu}_{ACAN} - \bar{\nu}_{ACANH^+}$, $\bar{\nu}_{ACAN}$ and $\bar{\nu}_{ACANH^+}$ being the 0-0 absorptions of the base (ACAN) and conjugate acid ($ACANH^+$) forms, respectively.[5] The energy of the 0-0 transition was determined from the intersection point of the excitation and emission spectra of the corresponding forms.

References

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