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N-alkyl derivative of 1,9-pyrazoloanthrone as a sensor for picric acid

Karothu Durga Prasad and Tayur. N. Guru Row*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India.
E-mail: ssctng@sscu.iisc.ernet.in; Fax: +91-080-23601310

Supporting Information

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General Procedures: All chemical reagents were purchased from commercial sources (Sigma Aldrich & Alfa Aesar, Bangalore) and were, unless otherwise noted, used without further purification. Analytical grade solvents were used for synthesis and purification. All reactions were carried out under a dry nitrogen atmosphere. Column chromatography was performed on silica gel, Acme grade 100-200 mesh and TLC plates were visualized either with UV or iodine chamber. HRMS was obtained using a micromass-QTOF spectrometer using electron spray ionization. ^{1}H and ^{13}C NMR were recorded on Bruker 400 MHz NMR machine in $CDCl_3$ solvent with TMS as a internal reference. The UV-Vis spectra were recorded using a Perkin–Elmer (Lambda 35) UV-Vis spectrophotometer. Steady-state fluorescence emission studies were carried out using a Spex FluoroLog-3 spectrofluorometer (Jobin–Yvon Inc). Single crystal X-ray diffraction data sets were collected on an Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector using MoKα radiation (λ= 0.71073 A). The temperature on crystal was maintained using the Oxford Instruments Cryojet-HT controller during data collection. All structures were solved by direct methods using SHELXS-97 and refined against F2 using SHELXL-97.[1] H-atoms were located geometrically and refined isotropically. The WinGX[2] package and OLEX2 (version 1.2)[3] was used for refinement and production of data tables and ORTEP-3[4] for structure visualization and making the molecular representations. Analysis of the H-bonded and $\pi\cdots\pi$ interactions were carried out using PLATON[5] for all the structures. Packing diagrams were generated by using MERCURY.[6]

2-hexyldibenzo[cd,g]indazol-6(2H)-one (1): The compound was synthesized by N- alkylation of 1,9-pyrazoloanthrone with excess 1-bromohexane.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 7.9 Hz, 2H), 8.22 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 6.9 Hz, 2H), 8.57 – 7.10 (m, 15H), 7.79 – 7.58 (m, 6H), 7.52 (t, *J* = 7.6 Hz, 2H), 4.51 (t, *J* = 7.1 Hz, 4H), 2.20 – 1.93 (m, 4H), 1.54 – 1.16 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 6H).;^{13}C NMR (100 MHz, $CDCl_3$): *δ* 183.6, 138.8, 138.3, 133.1, 131.8, 129.0, 128.0 (2C), 126.2, 123.3, 120.4, 114.7, 50.0, 31.2, 30.2, 26.4, 22.4, 13.9; HRMS: m/z calcd for $C_{20}H_{20}N_2O$ +Na calcd 327.1473; found 327.1474.

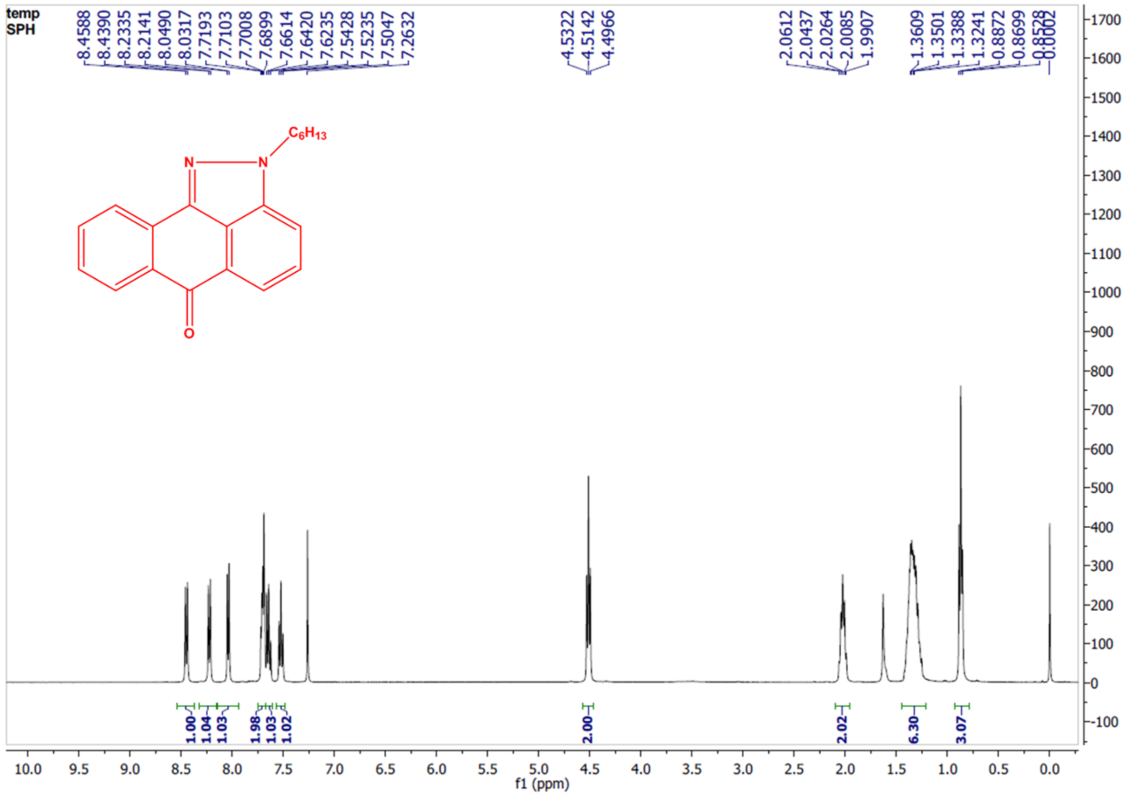

Fig. S1 ^{1}H NMR spectra of compound **1** in $CDCl_3$.

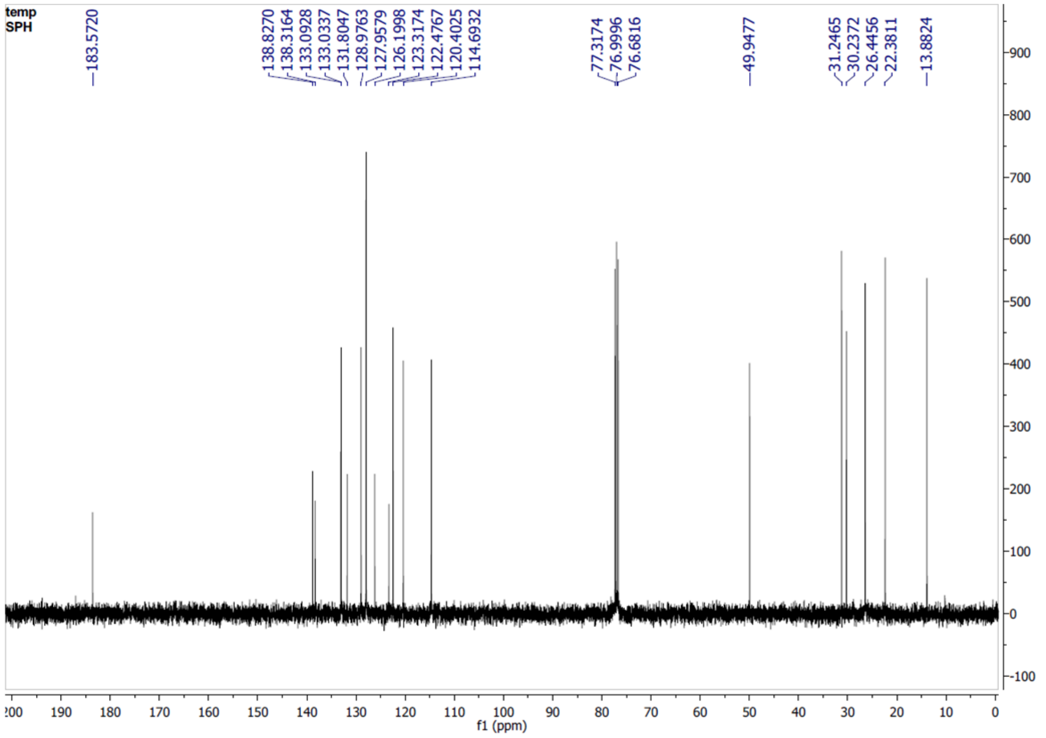

Fig. S2 ^{13}C NMR spectra of compound **1** in $CDCl_3$.

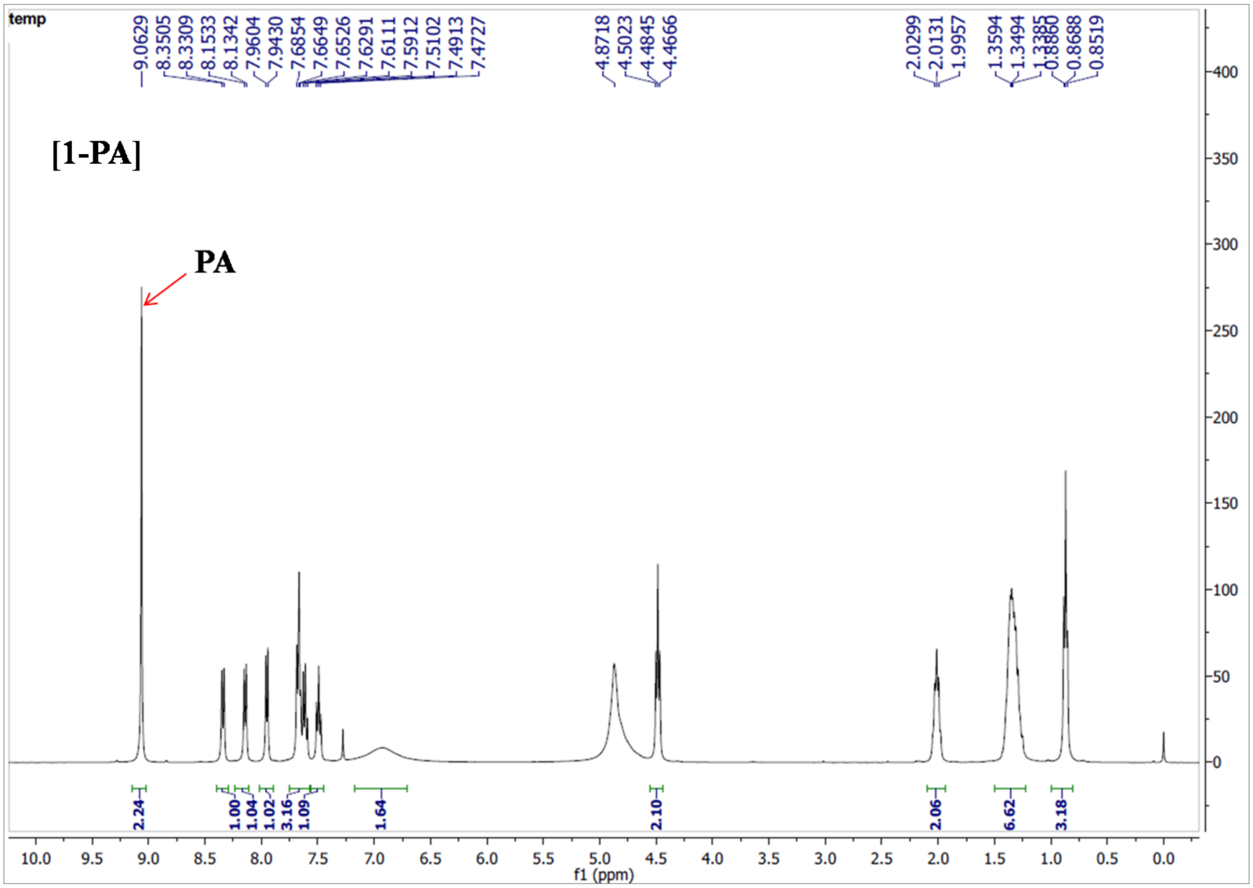

Fig. S3 ^{1}H NMR spectra of sensor compound **1** with PA in $CDCl_3$.

Table S1 Crystallographic parameters.

Compound	**1**
Formula	$C_{20}H_{20}N_2O$
Formula weight	304.4
system	Monoclinic
Space group	$P2_1/n$
a (Å)	4.804(4)
b (Å)	14.203(1)
c (Å)	23.132(1)
β	91.57(8)
Volume (Å^3)	1577.8(4)
Z	4
Density (gcm^{-3})	1.28
μ (mm^{-1})	0.080
F (000)	647.9
$h_{min, max}$	-5, 5
$k_{min, max}$	-16, 16
$l_{min, max}$	-27, 27
No. of measured reflections	16392
No. of unique reflections	2779
No. of reflections used	2212
$R_{\_all}$, $R_{\_obs}$	0.078, 0.062
wR_{2_all}, wR_{2_obs}	0.201, 0.191
$\Delta\rho_{min,max}$ (e Å^{-3})	-0.188, 0.235
GOOF	1.284

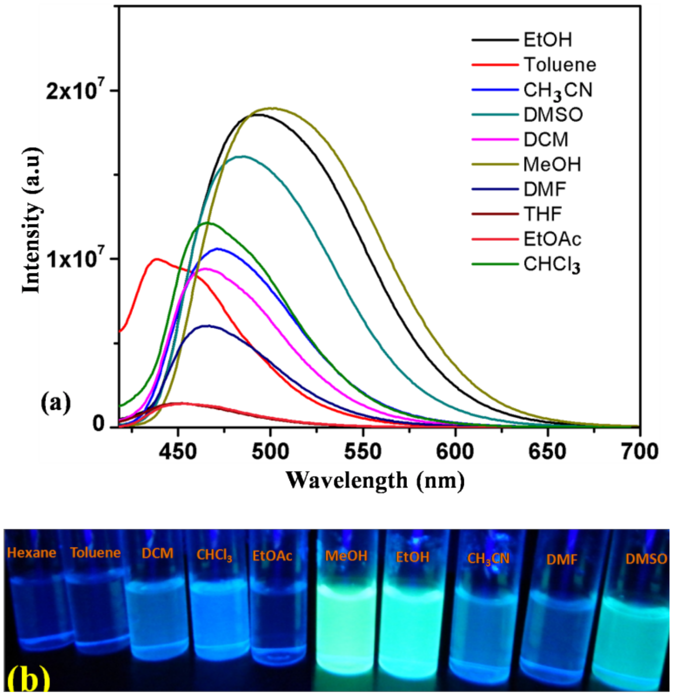

Fig. S4 Fluorescence spectrum of compound **1** in different solvents. **b** Compound **1** in different solvents under UV light (λex = 365 nm).

Fluorescence quenching titration: Fluorescence quenching efficiency of compound **1** towards picric acid was calculated by following equation

$\eta = (I_0\text{-}I)/I_0 \times 100\%$

where, I_0 is the initial intensity of the sensor compound **1** and I is the intensity after addition of a fixed volume of analytes. Stern-Volmer constants (KSV) were obtained for sensor compound **1** from I_0/I vs [PA] plot by fitting using Stern-Volmer equation.

$I_0/I = 1 + K_{SV}[PA]$

Calculation of detection limit for picric acid

The detection limits were calculated from fluorescence titration experiments. The intercept to X-axis (here log[PA]) was obtained by linear fitting of the (Imax-I)/(Imax-Imin) vs log[PA], where Imax, I and Imin are the initial fluorescence intensity, intensity at particular concentration and intensity at saturation point respectively. Detection limit were calculated by the formula, [PA] × MWPA)/1000 (multiplied by 10^6 to get the values in ppm), where MWPA is the molecular weight of either picric acid (PA). The detection limit of compound 1 for picric acid (PA) is calculated to be 1 ppm.

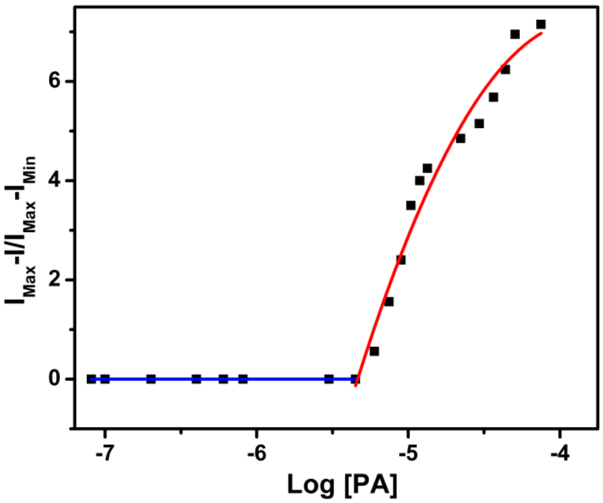

Fig. S5 Detection limits of picric acid (PA) with compound **1** obtained from fluorescence titration.

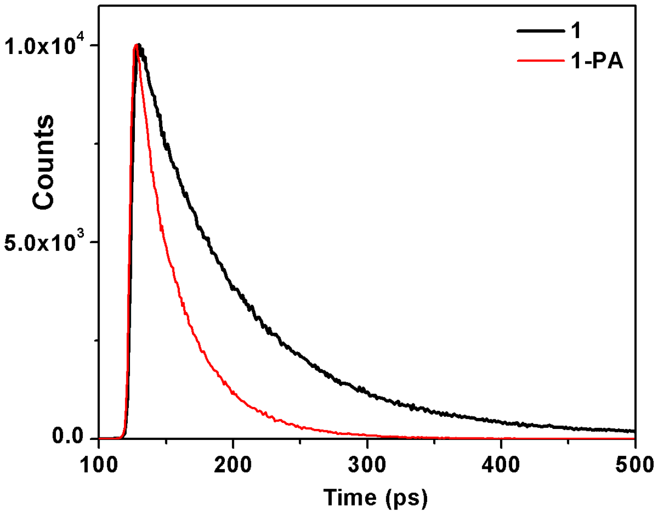

Fig. S6 Comparison of fluorescence lifetime decay profile of compound **1** with [**1-PA**] in solution state. The excited state of the complex decay faster than bare sensor compound **1** and this confirms the involvement of dynamic quenching mechanism.

References:

(1) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 2008, **64**, 112.

(2) L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, **32**, 837.

(3) O. V. Dolomanov, A. J. Blake, N. R. Champness and M. Schröder, *J. Appl. Crystallogr.*, 2003, **36**, 1283.

(4) Farrugia, L. *J. Appl. Crystallogr.,* 1997, **30**, 565.

(5) A. Spek, *J. Appl. Crystallogr.,* 2003, **36**, 7.

(6) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. Streek, *J. Appl. Crystallogr.,* 2006, **39**, 453.

(7) Organic Syntheses, Coll. Vol. 6, p.75 (1988); Vol. 53, p.13 (1973).