Role of Aromatic Moiety in the Probe Property toward Picric Acid: Synthesis, Crystal Structure, Spectroscopy, Microscopy, and Computational Modeling of a Knoevenagel Condensation Product of D-Glucose

Sivaiah Areti,† Sateesh Bandaru,† Ravinder Kandi,† and Chebrolu Pulla Rao‡*,†

†Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
‡Beijing Computational Science Research Center, Zhongguancun, Software Park II, Beijing 100084, China

Supporting Information

ABSTRACT: Molecular probes for picric acid (PA) in both solution and solid states are important owing to their wide usage in industry. This paper deals with the design and development of a glucosyl conjugate of pyrene (L1) along with control molecular systems, possessing anthracenyl (L2), naphthyl (L3), and phenyl (L4) moieties, via Knoevenagel condensation of 2,4-pentanedione with d-glucose. The selectivity of L1 toward PA has been demonstrated on the basis of fluorescence and absorption spectroscopy, and the species of recognition by electrospray ionization mass spectrometry. The role of the aromatic group in the selective receptor property has been addressed among L1, L2, L3, and L4. The structural features of the {L1 + PA} complex were established by density functional theory computations. L1 was demonstrated to detect PA in solid state selectively over other nitroaromatic compounds (NACs). To study the utility of L1 in film, cellulose paper strips coated with L1 were used and demonstrated the selective detection of PA. The observed microstructural features of L1 and its complex {L1 + PA} differ distinctly in both atomic force microscopy and scanning electron microscopy, all in the support of the complex formation. Thus, L1 was demonstrated as a sensitive, selective, and inexpensive probe for PA over several NACs by visual, spectral, and microscopy methods.

INTRODUCTION

Excessive use of nitroaromatic compounds (NACs) in industries causes serious environmental concern, and hence is a sensitive global issue.1–4 This imposes the necessity of rapid detection of hazardous compounds, while their explosive character brings in the security issue.5 Among NACs, picric acid (PA) is a powerful explosive and a strong organic acid,6 as well as a main ingredient that is being used in the industrial preparation of explosives, pharmaceuticals, and dyes.7 Its contact causes skin and eye irritation and will also lead to chronic diseases and cyanosis.8–10 Due to these concerns, researchers were involved in the design and development of small molecular probes suitable for the detection of PA in both solution and solid states.11–13 Among these, low-molecular-weight fluorescent probes attracted the attention of scientists in the last decade owing to their higher sensitivity, selectivity, and real-time detectability.17–21 In this regard, the literature deals with the use of small to supramolecules,22–24 metal-organic frameworks,25–28 and nanoparticles29–32 as probes for the detection of PA. The topic of luminescence-based sensing of explosives has been reviewed recently.33 Several of the literature-known molecular probes for PA suffer from disadvantages such as interference from other NACs, poor aqueous solubility, and a high detection range.34–37 All of these aspects limit the practical utility of such probes for the detection of PA contamination in natural sources, including water and industrial effluents. All of this demands the development of a low-molecular-weight-based probe for PA with high water solubility and low detection range, which is still a challenging task.

Therefore, we have designed a molecule based on carbohydrate for its water solubility and tunable fluorescent aromatic moiety for imparting sensitivity and a linker to connect these two via a Knoevenagel condensation of 2,4-pentanedione with d-glucose.38–41 To our knowledge, such glycoconjugate has never been reported in the literature as a probe for PA. The present molecular system is an aromatic glycoconjugate that is being demonstrated for picric acid sensing effectively in solution, in the solid state, and on cellulose paper. All of this leads to the design of a glucosyl

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conjugate of pyrene (L_1) owing to its (i) water solubility, (ii) electron-transfer ability, (iii) ability to exhibit \( \pi \cdots \pi \) as well as H-bond interactions, and (iv) ability to emit in the visible region. The design for such a molecular probe (L_1) is given in Scheme 1.

Scheme 1. Components Associated with the Design of L_1

The interaction between L_1 and PA was studied in solution by emission, and absorption spectroscopy, the binding by isothermal titration calorimetry (ITC), the complex formation by electrospray ionization mass spectrometry (ESI-MS), and the structural features of the complex by density functional theory (DFT) computations and thus shown to be selective for PA over 11 other NACs. The role of aromatic moiety in the molecular probe property has been explored by synthesizing molecules (L_2, L_3, and L_4) with different aromatic groups and studying all of those in comparison. Even the solid-state detection of PA by L_1 was demonstrated by fluorescence microscopy. The real-time applicability of L_1 in detecting the PA was demonstrated on Whatman cellulose paper strips. Thus, we report L_1 as an optimized aromatic glycoconjugate as probe for PA in solution, solid, and on cellulose paper.

Results and Discussion

Synthesis and Characterization. The probe molecule L_1 has been synthesized in two steps, as shown in Scheme 2, starting from \( \delta \)-glucose by going through a precursor, \( P_1 \), that is prepared by the Knoevenagel condensation of 2,4-pentanedione with \( \delta \)-glucose.\(^{42}\) To determine the role and importance of the aromatic moiety present in L_1 particularly in extending the \( \pi \cdots \pi \) interactions and the other control molecular derivatives, viz., L_2, L_3, and L_4 possessing anthracenyl, naphthyl, and phenyl moieties, respectively, were synthesized. All of the precursors and the final products were characterized by different techniques such as \( ^1\)H and \( ^{13}\)C NMR and ESI-MS (SI 01–04 and Figures S1–S4 in the Supporting Information). The three-dimensional structure of the anthracenyl derivative, viz., L_2 was established by single-crystal X-ray diffraction (XRD).

Single-Crystal X-ray Structure of L_2. Single crystals of good diffraction quality were obtained only in the case of L_2 from slow evaporation of its solution of H_2O/CH_3OH taken in 1:1 vol/vol ratio, although crystallization was attempted in the case of all of the derivatives. The L_2 crystallizes in monoclinic system with P_2_1 space group, and the crystal structure was solved using the diffraction data and was refined according to the parametric details given in this paper,\(^{43}\) and the metric data are given in the SI 05 as Tables S1–S3, Supporting Information. The single-crystal XRD structure of L_1 shows chair conformation for the glucose unit with \( \beta \)-anomeric form, wherein the anomeric form was already shown by the \( ^1\)H NMR spectra obtained in solution. Thus, the anomeric form present in the solution is retained even in the solid state. The centroid-to-centroid distance of anthracene units observed between the two neighbor molecules is 5.44 Å, suggesting that no \( \pi \cdots \pi \) interaction is expected to be present between the molecules in the lattice although the aromatic portions are stacked one over the other. The intermolecular distance between the C–H and the anthracenyl moiety in the lattice is 2.77 Å, supporting C–H–\( \pi \) interaction (Figure 1b). The lattice structure clearly shows four strong O–H–O intermolecular hydrogen bonds between the neighbor L_2 molecules (Table S1). Although the lattice structure is devoid of \( \pi \cdots \pi \) interactions, the molecules present in the lattice are stabilized by C–H–\( \pi \) as well as O–H–O type of interactions (Figure 1c).

Solvent Polarity-Dependent Aggregation of Probe Molecules. To demonstrate the solvent effect on the aggregation of L_1, absorption and fluorescence spectral titrations were carried out in different solvents varying in their polarity (Figure S6 in the Supporting Information). The L_1 exhibited an emission band, whose wavelength shifts to red with increase in the polarity on going from ethanol to water due to the aggregation-induced emission. This is further observed by the naked eye under UV light of wavelength 365 nm (inset of Figure S6b in the Supporting Information). However, in the presence of polar aprotic solvents, such as tetrahydrofuran and dimethyl sulfoxide (DMSO), the hydrogen-bonded structures break to result in monomeric species, leading to blue shift in the emission spectra (Figure S6a,b). Corresponding changes were observed even in the absorption spectra given in Figure S6e,f. It is known from the literature that the molecules possessing larger aromatic moieties, such as pyrene, undergo self-assembly in solution through \( \pi \cdots \pi \) interactions.

Scheme 2. Synthesis of L_1 and the Control Molecules via Knoevenagel Condensation of 2,4-Pentanedione with \( \delta \)-Glucose

\(^{42}\) Pentane-2,4-dione, NaHSO_4, 90 °C, 12 h; (b) corresponding aromatic aldehyde (i.e., 1-pyrene aldehyde/9-anthraldehyde/1-naphthaldehyde/benzaldehyde), pyrrolidine (30 mol %), CH_2Cl_2, 30 °C, 3 h.
interaction. L1 exhibited an emission band in the range of 545–575 nm, whose intensity increases with an increase in the concentration from 2.5 to 100 μM (Figure S6c in the Supporting Information). All of this clearly supports the formation of aggregates (580 nm) at higher concentrations, while it is not aggregated (380 and 397 nm) at lower concentration of L1.

Interaction and Binding of L1 with NACs by Emission, Absorption, and ITC Titrations. Upon titrating L1 with PA, the emission intensity is gradually quenched to a maximum extent (∼96%) due to the electron transfer between L1 and PA, which results in the formation of nonfluorescent complex (Figure 2b,c). All of the other NACs studied (Figure 2a) did not show any appreciable change in the fluorescence intensity of L1, which leads to a selective detection of PA among all of the 11 NACs studied (Figures 2d and S7). The fluorescence study provided a lowest detection limit of 12 ± 1 ppb or (0.5 ± 0.1) × 10^{-7} M for PA (Figure S8 in the Supporting Information). The probe L4 showed a much lower detection limit compared to other recently developed fluorescent probes in the literature for picric acid in aqueous medium (SI 09 in the Supporting Information).

The Stern–Volmer quenching constant (KSV) derived for L1 with PA is (6.4 ± 0.4) × 10^3 M^{-1} and the nonlinear plot indicates the presence of energy transfer when larger equivalents of PA are added (Figure S10 in the Supporting Information). The fluorescence quenching that occurred in the presence of PA can be identified by the naked eye due to color change when the vials containing solutions of {L1 + NAC} were kept under a 365 nm UV lamp (inset of Figure 2d). The competitive fluorescence titration studies indicate that L1 can recognize PA even in the presence of excess amount of other nitroaromatic derivatives, and none of these NACs interfere in the detection efficiency of L1 toward PA.

The absorption spectrum of L1 exhibit strong bands at 346 and 276 nm (Figure 2e). Among all of the 11 NACs studied, only PA exhibited considerable absorption spectral changes in L1 and no other NAC showed any significant change. As can be seen from Figure 2e, upon addition of increasing equivalents of PA, the spectra showed increase in the absorbance of both the 346 and 275 nm bands. In the presence of other NACs, the absorption spectra exhibited only marginal (or no) change supporting that the interaction of other NACs with L1 is rather weak (Figures 2f and S11 in the Supporting Information). Job plot yielded 1:1 stoichiometry between L1 and PA in the complex (Figure S12 in the Supporting Information), and the complex formed was further supported by ESI-MS, where the molecular ion peak was observed at m/z = 662.68 ([L1 + PA] + H^+ ) (Figure S13 in the Supporting Information). To understand the thermodynamic aspects of the interaction of PA with L1, ITC titration was performed and the corresponding thermogram is shown in Figure 2g. The interaction of PA with L1 is exothermic with large change in the heat of enthalpy (ΔH = −390 kcal). The greater ΔH observed for this goes well with a stronger interaction between L1 and PA, which was supported by absorption and emission studies. The negative ΔS further supports the formation of a complex between PA and L1. All of this reflected in a greater sensitivity of interaction of PA with L1.

Size of the Aromatic Moiety vs Detection Sensitivity of PA among L1, L2, L3, and L4. To understand the importance of the size of the aromatic moiety in sensing PA, other molecules containing anthracenyl (L2), naphthyl (L3), and phenyl (L4) having lower aromatic surface area were used for the study (Figure 2h–j). The control molecules, viz., L2, L3, and L4, exhibited their emissions at considerably lower wavelengths, viz., ∼450, ∼400, and ∼350 nm, respectively, while L1 shows emission at 560 nm. The fluorescence emission of L2, L3, and L4 was quenched by PA. However, the number of equivalents of PA required to bring the same level of quenching follows a trend L4 > L3 > L2 > L1, suggesting that the sensitivity to PA is greater with the probe molecule compared to the control ones. This is further reflected in their
Thus, the sensitivity of $L_1$ toward PA is at least 3.5 times greater than that of $L_2$, 7 times than that of $L_3$, and 10 times than that of $L_4$, supporting that the size of the aromatic moiety plays a positive role in contributing to greater sensitivity when the surface area of the moiety is larger; hence, $L_1$ possessing pyrene moiety is a sensitive probe for PA.

The sensitivity of $L_1$ is much below the tolerable levels of the nitroaromatics in drinking water (i.e., 0.1 mg/m$^3$) as reported by EPA.1

**Solid-State Detection of PA by $L_1$.** The molecular probe $L_1$ was shown to sense PA in water via fluorescence quenching. To demonstrate the utility of $L_1$ in detecting PA in the solid state, the corresponding solid systems were viewed under UV light that clearly differentiates $L_1$ from {[$L_1$ + PA]} and even simple PA, as can be noted from Figure 3a,b. This cannot be differentiated under visible light. Since the visual appearance under UV light gave positive result, a detailed fluorescence microscopy study was carried out for demonstrating the advantage of solid-state detection of PA by $L_1$. While the control solid $L_1$ alone showed green and red fluorescence, both these components of fluorescence was quenched when PA is mixed in the solid and the extent to which the quenching take place is dependent on the mole ratio of the PA added to $L_1$ (Figure 3c–w). The component of red fluorescence is completely quenched when the mole ratio is 1:20. However, the component of green emission diminishes as a function of the ratio of PA added and a 20% intensity of green emission was still remaining even at 1:50. The fluorescence intensities were quantitatively measured for both the green and red emission components, and the corresponding plots (Figure 3x–z) clearly show that both these emissions were quenched, and among these, the red emission was quenched to a greater extent compared to the green emission. As a negative control, when 4-nitrophenol (4-NP) was used in place of PA, no significant fluorescence quenching was observed in the
corresponding microscopy images, supporting that even in the solid state, the PA selectively reacts with L1. Thus, the solid-state sensing of PA by L1 provides an advantage to monitor both the fluorescence components independently. All of these results suggest that PA is responsible for quenching the fluorescence intensity of L1 in the solid state and hence the probe is suitable for detection of PA even in the solid state. Both the components showed a linear relation between the fluorescence intensity and [PA/L1] mole ratio in the range of 1–6.

Detection of PA by L1 on Whatman Cellulose Paper Strip. To use the molecular probe L1 for the detection of PA in different samples routinely, an inexpensive, rapid, and use-and-throw method is required; one such method is developed by coating the Whatman No. 1 cellulose filter paper strips with L1 (10 μM). Increasing concentrations of PA were added to the strips coated with L1, resulting in [PA]/[L1] mole ratios of 0–10 (Figure 4), and this exhibited gradual quenching up to a maximum of ~90% (Figure 4a,b). The fluorescence intensity ratio plot is linear in 2–30 μM PA, and the minimum

Figure 3. (a, b) Photographs of solid samples under visible and UV lights, respectively. (c–w) Fluorescence micrographs of the solid samples; the scale bar is 100 μm in all of the cases. The first column corresponds to the bright-field images, the second column corresponds to the images taken using green filter; and the third column corresponds to the red filter measurements. The micrographs present in each row are for the same sample. The L1/PA mole ratios of the solid samples are: 1:0 for (c–e); 1:2 for (f–h); 1:4 for (i–k); 1:6 for (l–n); 1:10 for (o–q); 1:20 for (r–t); and 1:50 for (u–w). (x, y) Bar diagrams for the intensities of green and red emissions, respectively, at the corresponding L1/PA mole ratios in the solid state. (z1, z2) The corresponding plots of intensity vs [PA/L1] mole ratio. The insets show the linear regions.
detection of PA by $L_1$ is $6 \pm 0.4 \mu M$ on a Whatman cellulose paper strip. Among all of the NACs studied, only PA exhibited significant fluorescence color change in $L_1$ on the cellulose paper strip under UV light and no other NACs showed any change in the fluorescence color under the same conditions (Figure 4c). This leads to a selective detection of PA among all of the NACs studied even on Whatman cellulose paper strip.

NAC-Induced Supramolecular Features of $L_1$ in Thin Film by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Since $L_1$ selectively detects PA and not other NACs in the solid state, it is interesting to compare the species formed by $\{L_1 + PA\}$ from the rest of the NACs. As both the $L_1$ and NACs possess aromatic moieties, the aggregation of these is expected to reflect in their morphological features and the same is supported by AFM and SEM. When $L_1$ is treated with PA, the smaller aggregates of $L_1$ (Figure 5a) are transformed into larger ones with size of 200–300 nm in AFM (Figure 5c). However, the same in the presence of other nitroaromatic compounds, e.g., $\{L_1 + 4-NP\}$, did not show any aggregated-like structures (Figure S14 in the Supporting Information). The SEM study (Figure 5d–f) reveals that $L_1$ exhibits spherical vesicular-like structures. However, upon interaction with PA, the spherical particles are joined together to form clustered aggregate-like structures. which were also noted in AFM and is attributable to the complex formed between $L_1$ and PA. However, AFM and SEM studies carried out with PA alone as control exhibited features (Figure 5b,e) which are uniformly distributed with a dimension of 40–60 nm. Thus, the microstructural features observed in AFM and SEM arise from a similar origin, and the features observed for $L_1$ and its complex with PA differ distinctly, supporting that the complex formed between these is reflected in their microstructures.

Computational Modeling of the Complex of PA and $L_1$. To establish the energetics and the structural features of the

Figure 5. AFM and SEM images, respectively, for: (a, d) $L_1$; (b, e) PA; and (c, f) $\{L_1 + PA\}$. All of the three AFM images are for $5 \mu m$ total length in $x$ axis. In each case of scanning electron microscopy, the line corresponds to $1 \mu m$. 

work.
complex formed between L₁ and the nitroaromatic compound (NAC), density functional theory (DFT) calculations were performed for PA, 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), and 4-NP using Gaussian 09. The initial structure for L₁ was prepared by taking the crystallographic coordinates of L₂, followed by replacing the anthracenyl unit by the pyrenyl one and optimizing the resultant structure. The optimization was carried out starting from semiepipirical → PM6 → DFT in a cascade fashion. The structure thus optimized for L₁ was used for building the complex with the corresponding preoptimized NAC. Even the {L₁···NAC} complex was optimized in the cascade fashion starting from semiepipirical and finally taking it to the DFT level. Each of the complex, viz., {L₁···NAC}, was optimized at the M06-2X level of theory using 6-31+G(d,p) basis set, and the resultant structures are shown in Figure 6a–d. In all of the four complexes studied by the computation, the carbohydrate moiety extends H-bond interactions with the NAC, and this is further manifested to have π···π interaction between the aromatic moiety of NAC and that of the pyrene moiety of L₁. The fluorescence quenching is by π···π overlap between the NAC and the receptor molecule. Thus, the H-bonding mainly contributes to additional stabilization for the complex formed between the probe and the NAC and not the fluorescence quenching. Thus, the complexes are doubly stabilized while the H-bonding stabilization energy varies from one complex to the other. The centroid-to-centroid distances between the pyrene and the aromatic moiety of NAC are farther by 3.21, 3.41, 3.25, and 3.32 Å in the {L₁···NAC} complexes of PA, 1,3-DNB, 2,4-DNT, and 4-NP, respectively. The H-bond stabilization energy for {L₁ + PA} is much larger compared to the other three {L₁ + 1,3-DNB/2,4-DNT/4-NP} complexes owing to the presence of two H-bonds in the first case, while it is only one in the case of the others (Table S4).

The complexation energies of {L₁···NAC} were computed using the formula ΔE = [E_{comp} − (E_{L₁} + E_{NAC})], and the corresponding interaction energies are given in Table S5 and the coordinate in Tables S6–S14. Based on the complexation energies obtained, it is evident that the {L₁···PA} complex exhibits greater interaction energy and the complexation energies (in kcal/mol) follow a trend, viz., [L₁ + PA] (−24.20) > [L₁ + DNT] (−22.11) > [L₁ + DNB] (−19.02) > [L₁ + 4-NP] (−17.35), and the difference among these arises from the H-bonding interactions present between the glycomoiety and the NAC. Thus, among all of the NACs, the PA binds strongly to the probe L₁.

The fluorescence was quenched when NAC is added to L₁, and this is attributed to the electron transfer from the donor L₁ to the acceptor NAC. However, the extent to which such electron transfer occurs is dependent on the positioning of its lowest unoccupied molecular orbital (LUMO) with respect to the donor, and the same is given for [L₁···PA] complex in Figure S15 in the Supporting Information. The highest occupied molecular orbital (HOMO) and LUMO data support that the electron transfer is maximum in the case of PA and, as a result, it exhibits maximum fluorescence quenching. The LUMO of the [L₁ + PA] complex has contribution mainly from PA with significant reduction of its energy compared to L₁. The energy of the HOMO, which is mainly located on the pyrene moiety of L₁, does not change much. The energy difference between the HOMO and LUMO is considerably reduced upon forming a complex with PA.

### CONCLUSIONS AND COMPARISONS

A water-soluble fluorescent probe (L₁) for sensing PA has been designed and synthesized by integrating the pyrene group into the glucopyranosyl moiety via Knoevenagel condensation. Among the three control conjugates synthesized using anthracenyl (L₂), naphthyl (L₃), and phenyl (L₄), the structure of L₂ was established by single-crystal XRD. The conjugate L₁ is a selective probe for PA by switch off fluorescence to an extent of ~96% among 11 other NACs studied in solution. The L₁ exhibited a minimum detection limit of 12 ± 1 ppb {(0.5 ± 0.1) × 10⁻⁷ M} for PA in water. Even in the solid state, the PA is selectively sensed by L₁ with a fluorescence quench of ~95% and exhibited a minimum detection limit of 4.5 ± 1.0 μM. Even as a thin film on Whatman cellulose filter paper, L₁ provides a selective detection for PA with a fluorescence quench of ~90% and a minimum detection limit of 145 ± 1 ppb (6 ± 1 μM). Thus, L₁ is a rare molecule among the probes that are sensitive to PA in the solution, in the solid state, and on the cellulose paper, although the sensitivity is about an order of magnitude greater in solution. Thus, L₁ is a molecular probe sensitive to micromolar levels in the solid state and on cellulose paper, and is sensitive to submicromolar levels in aqueous solution. This is well within the range to detect the permissible levels of nitroaromatics in drinking water. Thus, the demonstration of selective detection of PA by L₁ in solution, solid state, and a thin layer on Whatman cellulose paper provides a real-time application of this probe molecule to detect an industrially important NAC, i.e., PA.

The only other probe having pyrene moiety that is reported in the literature in sensing the picric acid has been the one that is attached to choline moiety to bring water solubility. Although this pyrene-derivatized choline sensor shows the lowest detection limit of 23.2 nM for picric acid in solution, the current probe is twice as sensitive on cellulose paper. On the other hand, the present receptor has been additionally shown to sense picric acid in the solid state as well on the cellulose paper. As reported in this paper, this work addresses the changes occurred in the supramolecular aggregation in the

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**Figure 6.** Optimized structures of the complexes of L₁ with (a) PA, (b) DNB, (c) DNT, and (d) 4-NP at the M06-2X/6-31G(d,p) level.
Scheme 3. Schematic Representation of Different Features Noted in Sensing PA by L1

Knoevenagel condensation product of 2,4-pentanedione with and the negative demonstrated based on ITC, where the binding is exothermic formation between PA and at 400 and 500 MHz. All of the 13C NMR spectra reported in spectra were measured on Bruker NMR spectrometers working and phenyl (L4), and the sensitivity of the detection of PA follows a similar trend, viz., pyrenyl (L3) > anthracenyl (L2) > naphthyl (L1) > and phenyl (L4), to that reflected in their minimum detection limits. Thus, a strong fluorescent probe (L1) is the Knoevenagel condensation product of 2,4-pentanediol with D-glucose reported in this paper, is a highly promising molecular probe for real-time optical applications mainly because of its specific and selective interaction with PA in solution, in the solid state, and on the cellulose paper.

![Diagram](Image)

EXPERIMENTAL SECTION

General Information and Materials. 1H and 13C NMR spectra were measured on Bruker NMR spectrometers working at 400 and 500 MHz. All of the 13C NMR spectra reported in this paper are proton-decoupled ones as 13C(1H) spectra. The mass spectra were recorded on maXis impact (Bruker) using electrospray ionization method. Steady-state fluorescence spectra were measured on PerkinElmer LSS5, and steady-state absorption spectra were measured on Varian Cary 100 Bio. All of the NACs, given in Figure 2a, viz., picric acid (PA), 2,4,6-trinitrotoluene, 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 4-nitrophenol (4-NP), 3-nitrophenol, 3-nitrotoluene, nitrobenzene (NB), 4-nitrobenzoic acid, benzoic acid, and methyl benzene or toluene, were procured from either Sigma-Aldrich or local sources.

Synthesis and Characterization of L1. L1 was obtained by the aldol condensation of β-D-glucopyranosyl-propane-2-one (P1) with 1-pyrenecarboxaldehyde. To a solution of β-D-glycosic ketone (P1) (220 mg, 1 mmol) in dry CH3Cl2 (5 mL), pyridoline (30% mol) and 1-pyrenecarboxaldehyde (250 mg, 1.2 mmol) were added. After stirring at room temperature for 3 h, the reaction mixture was evaporated under the reduced pressure and the resultant solid was purified by column chromatography with methanol and dichloromethane (1:9 vol/vol), which afforded the desired product as a yellow solid (0.286 g, 66% yield). Melting point 195–198 °C. 1H NMR (400 MHz, CD3OD, δ ppm): 3.1–3.2 (m, 2H), 3.23–3.32 (m, 2H), 3.51 (dd, 1H), 3.72 (t, 1H), 3.84 (t, 1H), 7.15 (d, J = 12.3 Hz, 1H), 7.58–7.98 (m, 3H), 8.01–8.1 (m, 2H), 8.14 (d, 1H), 8.67 (d, J = 8.64 Hz, 1H), 8.25 (d, J = 7.52 Hz, 1H), 8.36 (d, J = 7.42 Hz, 1H), 8.65 (d, J = 12.46 Hz, 1H) ppm. 13C NMR (100 MHz, CD3OD, δ ppm, 13C(1H)): 30.7, 43.6, 61.1, 70.3, 73.6, 76.1, 78.2, 80.8, 122.6, 123.7, 124.5, 124.6, 125.3, 125.9, 126.1, 126.6, 127.3, 128.3, 128.5, 128.6, 129.3, 129.4, 130.2, 130.3, 132.2, 138.1, 198.2. High-resolution mass spectrometry (HRMS) (ESI-time-of-flight (TOF)) m/z: [M + Na]+ calcld C26H24NaO6 455.1465, found 455.1464.

Synthesis and Characterization of L2. The procedure used for the synthesis of L1 was also used for the synthesis of L2, but by using 9-antracenecarboxaldehyde (206 mg, 1 mmol) in place of 1-pyrenecarboxaldehyde to obtain the product and resultant that was purified by column chromatography with methanol and dichloromethane (1:9 vol/vol), which afforded the desired product as a yellow solid (0.253 g, 62% yield). Melting point 174–176 °C. 1H NMR (400 MHz, CD3OD, δ ppm): 2.98–3.04 (m, 2H), 3.1–3.2 (m, 2H), 3.68–3.72 (m, 1H), 4.28 (t, J = 8.4 Hz, 1H), 4.4 (t, J = 7.86 Hz, 1H), 4.78–4.82 (dd, J = 3.8 Hz, 1H) 4.84–4.9 (m, 2H), 4.94 (d, J = 5.4 Hz, 1H), 5.14 (d, J = 5.62 Hz, 1H), 6.71 (d, J = 7.64 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 7.5–7.6 (m, 2H), 7.48–7.55 (m, 3.29-3.35 ppm).
2H1), 7.56−7.64 (m, 2H), 7.68 (d, J = 7.42 Hz, 1H), 8.01 (d, J = 8.64 Hz, 1H), 8.1−8.16 (dd, J = 5.2, 5.0 Hz, 1H), 8.36 (d, J = 7.28 Hz, 1H), 8.65 (d, J = 12.46 Hz, 1H) ppm. 13C NMR (100 MHz, DMSO, δ ppm; 13C{1H}): 34.5, 61.2, 70.3, 73.7, 76.4, 78.2, 80.9, 125.1, 125.6, 126.6, 128.0, 128.7, 129.5, 130.8, 135.9, 138.7, 198.0. HRMS (ESI-TOF) m/z: [M + Na]+ calc C20H22NaO6 381.1306, found 381.1309.

Synthesis and Characterization of L3. The procedure used for the synthesis of L1 was also used for the synthesis of L3, but by using 1-naphthaldehyde (156 mg, 1 mmol) in place of 1-pyrenecarboxaldehyde to obtain the product and resultant that was purified by column chromatography with methanol and dichloromethane (2:8 vol/vol), which afforded the desired product as a brown solid (0.215 g, 60% yield). Melting point 162−164 °C; 1H NMR (D2O ppm): 3.07 (m, 1H), 3.56 (m, 1H), 3.70 (m, 2H), 3.74 (m, 2H), 3.82 (m, 2H), 4.08 (d, 1H, J = 5.4 Hz), 4.32 (d, 1H, J = 5.6 Hz), 6.62 (d, 1H, J = 7.2 Hz), 6.96 (d, 1H, J = 7.6 Hz), 7.04−7.15 (m, 2H), 7.35 (t, 1H, J = 12.6 Hz), 7.4−7.5 (m, 3H), 8.23 (d, 1H, J = 8.2 Hz). 13C NMR (100 MHz, D2O, δ ppm; 13C{1H}): 44.8, 60.3, 61.6, 68.7, 72.3, 75.7, 78.6, 87.2, 115.7, 118.7, 122.8, 123.7, 128.6, 129.8, 130.2, 133.5, 143.2, 150.5, 173.6. HRMS (ESI-TOF) m/z: [M + Na]+ calc C24H24NaO6 431.1465, found 431.1467.

Synthesis and Characterization of L4. The procedure used for the synthesis of L1 was also used for the synthesis of L4, but by using benzaldehyde (106 mg, 1 mmol) in place of 1-pyrenecarboxaldehyde to obtain the product and resultant that was purified by column chromatography with methanol and dichloromethane (2:8 vol/vol), which afforded by grinding it along with 1, 2, 3, 5, 10, and 25 mg of PA to have the desired product in the form of white amorphous solid (0.170 g, 55% yield). Melting point 152−154 °C; 1H NMR (CD3OD, ppm): 2.95 (t, J = 8.5 Hz, 1H), 3.22−3.31 (m, 1H), 3.52−3.53 (m, 2H), 3.56−3.58 (m, 1H), 3.70−3.74 (m, 2H), 3.82−3.87 (m, 1H), 3.87 (s, 1H) 5.12 (d, J = 4.3 Hz, 1H), 5.23 (d, J = 4.5 Hz, 1H), 6.78−6.81 (m, 1H), 7.21−7.25 (m, 2H), 8.36 (d, J = 9.5 Hz, 1H). 13C NMR (100 MHz, D2O, δ ppm; 13C{1H}): 48.9, 48.2, 48.9, 49.8, 60.4, 68.9, 72.3, 75.8, 78.8, 87.5, 99.2, 104.3, 121.7, 124.1, 137.2, 142.3, 144.2 144.5, 145.8. HRMS (ESI-TOF) m/z: [M + Na]+ calc C20H22NaO6 381.1306, found 381.1307.

UV−Vis Absorption and Fluorescence Studies. The fluorescence titration studies were performed in water using 50 μL of bulk solution of L1 prepared at 6 × 10−4 M using 12 different NACs in a 1 cm quartz cell by maintaining a total volume of 3 mL in each measurement using requisite volume of water. All of this results in a final [L1] of 10 μM in the cuvette, and requisite volumes of NACs were added to L1 to get the mole ratio of [NAC]/[L1] in 0−10 range. The fluorescence spectra were recorded in the wavelength range of 355−700 nm by using λex = 345 nm. The same solutions were used for absorption titration studies.

Isothermal Titration Calorimetry. The calorimetric titration was performed at 25 °C with a MicroCal ITC200 isothermal titration calorimeter (MicroCal) using the solutions that were predegassed for 30 min using N2. The titration was carried out by adding 2 μL of 0.5 mM solution of PA at each time to 200 μL of 0.05 mM L1 taken in the ITC cell, and the addition was continued for 20 successive injections by maintaining 200 s time gap between each addition. The ITC data were fitted with the origin software package provided with the instrument by using the curve fitting model for one set of sites. Three independent titrations were carried out to check the consistency of the data. Each time, a control experiment is being carried out without L1 and the corresponding data were subtracted from the main titration data and the resultant one was subjected to the curve fitting.

Solid-State Fluorescence Microscopy Measurements. Solid samples were prepared by taking 1 mg of L1 and then grinding it along with 1, 2, 3, 5, 10, and 25 mg of PA to have different mole ratios, such as 1:2, 1:4, 1:6, 1:10, 1:20, and 1:50, of L1/PA. All of the samples including the control one, i.e., pure L1 (without the addition of any PA), were studied on a fluorescence microscope (Nikon Eclipse Ti-S) using green and red filters. The fluorescence intensities were measured by using the NIS-Elements BR analysis software, which was provided along with the microscope.

Preparation of Samples on Whatman Cellulose Paper Strips. Whatman cellulose paper was cut into small units of 3 × 1 cm2. The solution of the probe compound (10 μL) was drop-cast on the central portion of these paper strips, and the solvent was dried by leaving these at room temperature. The L1-coated strips were used for fluorescence measurements upon addition of requisite volume of NAC solution. The spots were examined under 365 nm UV illumination. In the case of PA, the fluorescence intensity of the strips was measured. To get error bars in the intensity, the experiment was repeated three times.

Scanning Electron Microscopy (SEM) Studies. The SEM samples of L1 and [L1 + PA] were prepared using 6 × 10−4 M L1. An additional control was carried out with simple PA. The solutions were sonicated for 10 min, after which 20−30 μL of aliquot was taken and spread over an aluminum sheet by the drop-casting method. The samples were then dried under an IR lamp and analyzed by field emission gun SEM.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03352.

Synthesis and characterization of control molecular systems; spectral data; fluorescence and absorption data; X-ray diffraction coordinates for ligand (L2), and Cartesian coordinates for optimized L4 and {[L1]xNAC} complex at the M06-2X/6-31+G(d,p) level of theory (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: cprao@iitb.ac.in.

ORCID

Chebrolu Pulla Rao: 0000-0002-1004-0028

Notes

The authors declare no competing financial interest.

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DEDICATION

We dedicate this paper to Professor C.N.R. Rao, F.R.S. on his 85th birthday.

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