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ARTICLE TYPE

Pyrene pyridine-conjugate as Ag selective Fluorescent chemosensor

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A new pyrene pyridine conjugate (**PPC**) has been developed as a selective fluorescent sensor for Ag^+ ion. Probe **PPC** exhibits high selectivity and sensitivity towards Ag^+ as fluorescence 'on–off' behaviour in HEPES-buffered DMSO/H_2O (1:1, (v/v) HEPES = 50 mM, pH=7.4) solution with a detection limit of 0.29 X 10^{-8} M^{-1}. The turn-off fluorescence sensing of Ag^+ ion occurs through dual pathways i.e. changes and alternations in the photophysical properties. Binding of Ag^+ ion prevents excimer formation and also induces intramolecular photoinduced electron transfer (PET) from Pyridine-Ag^+ ion bound receptor to pyrene due to structural rigidification, which respectively quenches excimer and monomer emissions with a butterfly like skeleton.

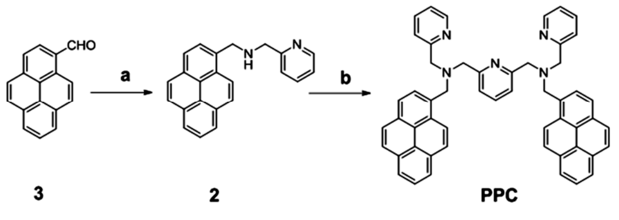
1. Introduction

The development of metal-selective fluorescent chemosensors for sensing heavy and transition metal ions (HTMs) are receiving continually increasing attention by researchers since these metal ions show severe toxicity to living organisms including humans.[1,2] Silver ions have been utilized in killing harmful bacteria[3] and its complexes find extensive applications in electric, photographic, imaging, and pharmaceutical industries. The overuse of medication containing silver salts, though results in accumulation of silver in liver tissues, its adverse effect on patients has caused potential concerns.[4,5] Therefore detecting trace levels of silver is of much importance. Over the years, there are many developmental studies focused on chemical sensors for Ag^+.[6] However, not much report are available for the detection of Ag^+ when compared to that of other heavy metal ions such as mercury and cadmium. Indeed, almost all reported sensors for Ag^+ still suffer from serious drawbacks such as poor water solubility, poor sensitivity, and low selectivity.[7] As a consequence, the design and synthesis of a selective and sensitive fluorescent chemosensor for Ag^+ is still highly desirable.

The traditional analytical methods used for the trace-quantity determination of Ag^+ ion are generally based on different instrumental techniques.[8] Fluorescent probes are prevailing tools for monitoring biologically relevant species in vitro/in vivo, because of their simplicity and high sensitivity.[9] So far, Ag^+-ion reported probes have been classified according to their molecular structures as cyclic N, O, S-donor crown ethers,[10] acyclic N, O, S-donor crown ethers,[11] excimer,[12] Ag^+–π interaction,[13] porphyrin or phthalocyanine[14] and polymers, quantum dots, nanoparticles, DNAs or oligonucleotides.[15] On continuation with our previous work,[16] we herein report a new pyrene pyridine conjugate (**PPC**) bearing two pyrene and three pyridine groups as a selective fluorescent sensor for Ag^+ ion. Probe **PPC** shows fluorescence quenching selectively for Ag^+ ions by the intramolecular photo induced electron transfer mechanism assisted by the excimer-monomer emissions of the pyrenes at a physiological pH of 7.4. A possible mechanism is proposed for the interaction of **PPC** with Ag^+ through fluorescence changes, NMR experiments, mass spectrum and theoretical calculations.

2. Results and discussion

The receptor 1,1'-(pyridine-2,6-diyl)bis(N-(pyren-1-ylmethyl)-N-(pyridin-2-ylmethyl)methanamine), **PPC** was conveniently synthesized from pyrene carboxaldehyde through a two-step protocol as shown in Scheme 1. The reaction between pyrene carboxaldehyde (**3**) and pyridine-2-methylamine in a co solvent of ethanol and chloroform, followed by sodium borohydride reduction yielded compound **2.** Subsequently, compound **2** and 2,6-bis(bromomethyl)pyridine were reacted in the presence of potassium carbonate in acetonitrile and silica gel column chromatography afforded the designed receptor **PPC** in a moderate yields. The structure of all the compounds was confirmed by the NMR and mass spectral analysis (Figures S1-S6). **PPC** is designed in such a way that the reporter unit, pyrene is covalently attached to the receptor unit, pyridyl moiety, through saturated, flexible, sp^3 hybridized carbon. This feature enables the controlling of the distance or the intramolecular interaction between the pyrene units by means of the geometrical changes accompanied upon binding of the metal ions with pyridine scaffold.



(a) (i) pyridine-2-methylamine, EtOH/$CHCl_3$, reflux, 3 h, (ii) EtOH, $NaBH_4$, 3 h, rt. (b) 2,6-bis(bromomethyl)pyridine, K_2CO_3, CH_3CN, reflux, 12 h.

Scheme 1. Synthesis of Compound **PPC**

The UV-visible absorption spectrum of **PPC** measured in DMSO-H_2O, 1;1 v/v, HEPES = 50 mM, pH=7.4 (SI, Figure S7) shows features similar to that of pyrene and the spectral features are found to be independent of the concentration used in these studies. The fluorescence spectrum of **PPC** given in Figure 1, displayed both a typical intramolecular excimer emission around 453 nm and monomer emissions around 378 and 396 nm in DMSO/H_2O (1:1, (v/v) HEPES = 50 mM, pH=7.4). The excimer emission band is attributed to the interaction of two intramolecular pyrene units through π-π interaction, which is fixed by the pyridine scaffold.[17] The cation-binding property of **PPC** was then investigated by fluorescence spectroscopy by the addition of metal ions such as Na^+, K^+, Al^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zr^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Ce^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and Ag^+ in aqueous solution. The fluorescence spectra of **PPC** ($4x10^{-6}$ M) in presence of different metal ions, given in Figure 1, reveal that the fluorescence intensity becomes suppressed by smaller to significant extent, characteristic to that of metal ions (100 equiv.) added to the receptor solution. Indeed, significant amount quenching of **PPC** fluorescence by the addition of Ag^+ ions (100 equiv.) suggests that **PPC** can exclusively recognize Ag^+ ion over the other cations including the paramagnetic ones *via* fluorescence turn-off mechanism.

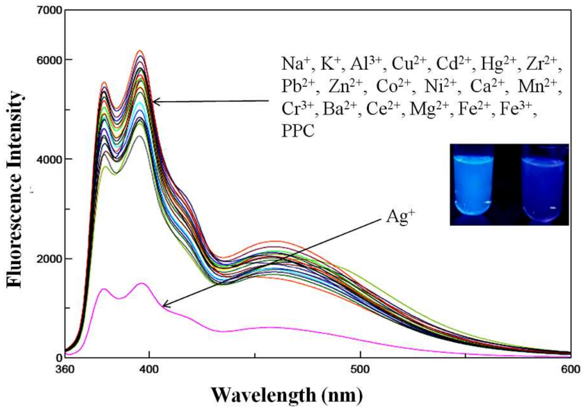


Figure 1. Fluorescence changes of **PPC** (4×10^{-6} M) solution (DMSO/H_2O, 1;1 v/v, HEPES = 50 mM, pH=7.4) in the presence of various metal ions (100 equ. of each, excited at 348 nm).

To understand the sensing behaviour of Ag^+ ion by **PPC** at molecular level, fluorescence titration experiments were performed and the spectra is shown in Figure 2. Upon incremental addition of Ag^+ (0–100 equiv.) to **PPC** solution, the fluorescence emission intensity was quenched gradually and reached the saturation level when 100 equiv. of Ag^+ ions was employed. The stoichiometry for the **PPC** and Ag^+ was found to be 1:1 based on Electrospray Ionization (ESI) mass spectrum (Fig. S6) and the Job's method of continuous variation.[18] A significant peak at m/z 858.3, which pertains to $[\mathbf{PPC}+Ag]^+$ was clearly noticed in the mass spectrum. On the basis of the titration profile, the association constant (Ka)[19] for **PPC**+Ag^+ was determined to be 1.60×10^4 M^{-1} using Benesi-Hildebrand equation.[20] The extrapolation of the plot suggests that the lowest possible detection limit of Ag^+ by **PPC** was determined to be $0.29 X 10^{-8}$ M^{-1}, (Fig. S8) which is much above than the allowed Ag^+ concentration in drinking water 0.05mg/L.

Most of the sensors based on two pyrene units covalently linked through the common binding unit, generally shows ratiometric fluorescence response by virtue of changes in the ratio of excimer-monomer emissions caused by the difference in the conformational changes before and after binding. To our surprise, binding of Ag^+ ion through the coordination of three 'N' atoms of the pyridine rings in **PPC** occurred through the quenching of both excimer and monomer emission. The Ag^+ coordination with pyridine scaffold resulted in the rigidification of **PPC** and inhibits the π-π stacking by forcing the pyrene group's move far away from each other thereby preventing the formation of an excimer.[21] To confirm this hypothesis we have optimized the geometries of **PPC** and **PPC**-Ag^+ at B3LYP/6-31G* level of theory using Gaussian 03 software[22] and the figures are given in supporting information. The energy minimized geometry of **PPC** reveals that both pyrene moieties are oriented diagonal to each other, which are in fact held covalently by the flexible pyridine scaffold. The molecular flexibility offers the **PPC** to form an intramolecular excimer upon photoexcitation. However, after Ag^+ ion binding with pyridine scaffold, the **PPC** shows butterfly like skeleton and both pyrene units are kept far away from each other by the rigid pyridine-Ag^+ moiety (Fig. S9-12). Thus, the binding of Ag^+ ions prevents the formation of excimer and thereby causes the quenching of excimer fluorescence when compared to the free **PPC**. On the other hand, monomer emission quenching can be explained by the heavy atom effect of Ag^+, and preferably by intramolecular photoinduced electron transfer mechanism (PET)[23] from the nitrogen atoms of pyridine ring to the pyrene unit.[24] The PET has been possible because of the rigidification of the pyridine scaffold, which aids the electron transfer process. This hypothesis is also confirmed by the theoretical calculations that the electron density is redistributed from pyridine-Ag^+ scaffold to pyrene during transition from highest occupied molecular orbitals (HOMO) to lowest unoccupied molecular orbital (LUMO) (Fig.S12).

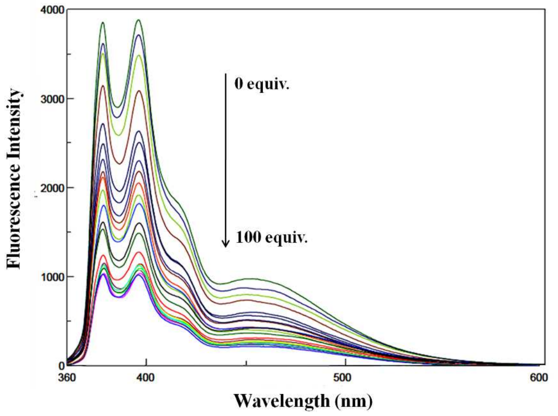


Figure 2. Changes of fluorescence intensity of **PPC** (4×10^{-6} M) solution (DMSO/H_2O, 1:1 v/v, HEPES = 50 mM, pH=7.4) upon addition of different amount of Ag^+ (0-100 equ. of each, excited at 348 nm).

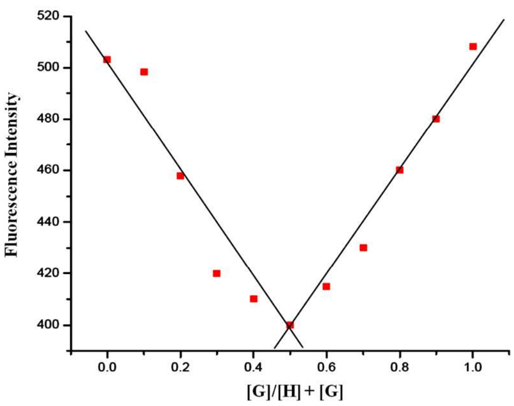


Figure 3. Job's plot for probe **PPC** in (DMSO/H_2O, 1:1 (v/v), HEPES = 50 mM, pH=7.4) ($\lambda_{ex.}$ = 348 nm).

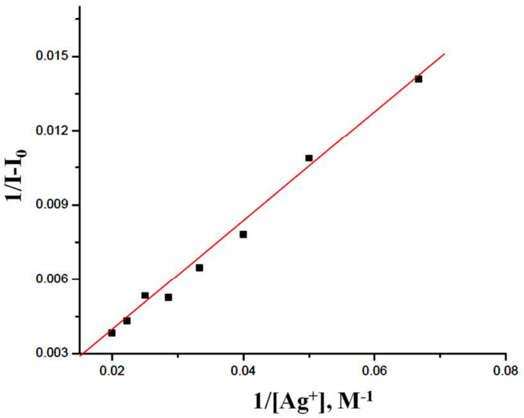


Figure 4. Benesi–Hildebrand plot of **PPC**, assuming 1:1 stoichiometry for association between **PPC** and Ag^+.

To better investigate the practical applicability of **PPC** as Ag^+ ion selective fluorescent sensor, competitive experiments were carried out in the presence of Ag^+ ion (100 equiv.) mixed with Na^+, K^+, Al^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zr^{2+},Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Ce^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} at 100 equiv. as shown in Figure. 5. No significant interference in the detection of Ag^+ with the sensor **PPC** was observed in the presence of other most competitive metal ions, for which interference with the detection signal abolished the quenching effect on binding of Ag^+ ion. Accordingly, these observations suggested that sensor **PPC** can be used as selective fluorescent sensors for Ag^+ ion in the presence of most competitive metal ions.

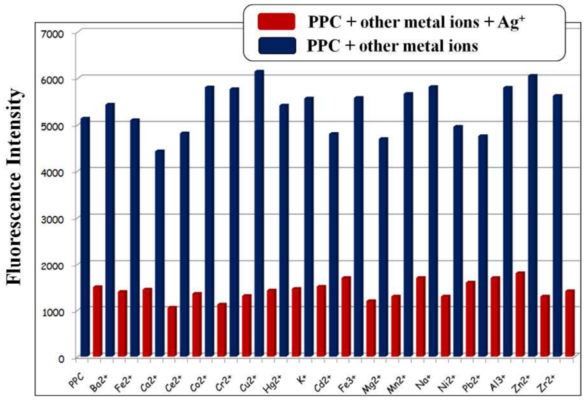


Figure 5. Metal ions competition analysis of **PPC** (4×10^{-6} M) in DMSO/H_2O, 1:1 v/v, HEPES = 50 mM, pH = 7.4. The blue bars represent the fluorescence emission of **PPC** and 100 equiv. of other metal ions. The red bars represent the fluorescence changes that occur upon addition of 100 equiv. of other metal ions to the solution containing **PPC** and Ag^+ (100 equiv.).

Furthermore, the ^1H NMR titration experiment was performed to understand the nature of interactions between the **PPC** and Ag^+ ion interactions and the selected spectra are given in Figure. 6. The comparison of ^1H NMR spectra of **PPC** and **PPC** mixed with 10 equiv. of Ag^+ ion suggest that the addition of Ag^+ into the solution of **PPC** led to an upfield shift of the aromatic protons on pyridine rings. In these NMR-titration spectrum, pyridine H_a, H_b, H_c, H_d -protons shifted from δ 8.25-8.27 to 8.20-8.22 ppm, 7.12-7.15 to 7.06-7.10 ppm, 7.58-7.62 to 6.44-6.47 ppm, 7.53-7.55 to 7.49-7.51 ppm and pyridine methylene protons shifted from δ 4.29 to 4.12 ppm. In the addition of Ag^+ to **PPC**, the pyridine groups come closer together during the coordination and hence there exists notable wide ranges of upfield chemical shifts, which was also confirmed by theoretical calculations.[16]

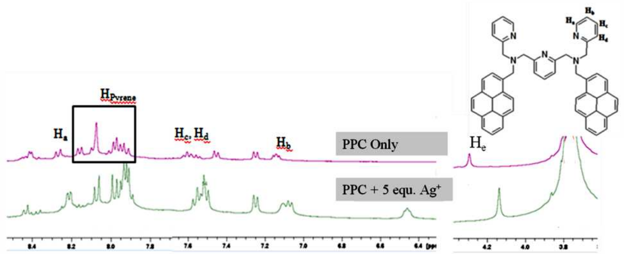


Figure 6. Partial ^1H-NMR Spectrum of **PPC** and **PPC** + Ag^+

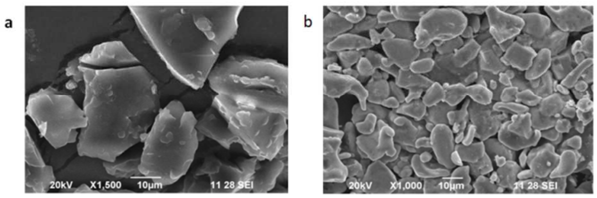
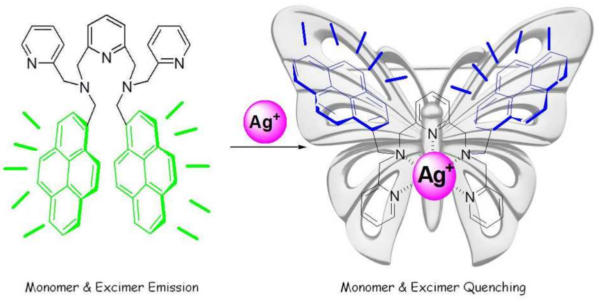


Figure 7. SEM images of a) Ligand (**PPC**) only and b) Ligand **PPC** + $AgNO_3$

In addition, the SEM images of **PPC** and **PPC**+Ag^+ are displayed in Fig. 7. The morphological change after silver insertion was confirmed by using SEM analysis. Receptor **PPC** shows large molecular size in free state. However, on the addition of Ag^+, the size of the complex molecule compared with **PPC** becomes smaller and agglomerated because of the formation of the **PPC**+Ag^+ coordination complex, which further confirms the probe **PPC** selectivity towards Ag^+ ions.

On the basis of NMR and theoretical studies, the plausible binding mechanism of **PPC** in the present system is schematically depicted in Scheme 2. 'N' of the three pyridine rings, and pyridine methyl amine of the two 'N' are engaged in complexation with Ag^+-ion.



Scheme 2. Proposed binding mode of **PPC** with Ag^+

The sensing system with real application is important to monitor the Ag^+ concentration in practical samples. In addition to prove the viability of Ag^+ sensing system by using **PPC,** we tested the Ag^+ in Karunya nagar tap and waste water samples with a variety of interferences. The insoluble substances were removed from tap and waste water samples by membrane filtration. Tap water were spiked with target Ag^+ at two different concentration levels of 4 and 8 ppm and without spiking of Ag^+ in waste water samples concentration were 9 and 13 ppm. The sensing and recoveries of Ag^+ from four water samples were from 97 % to 100 % as shown in table 1. The above results show that the **PPC** can be used for the detection of Ag^+ in practical samples.

Determination of Ag^+ in Tap and Waster water samples

Sample	Amount of Ag^+ present in Blank ppm (AAS)	Ag^+ -ion spiked (ppm)	Ag^+-ion found (ppm) (Fluorescence) (Mean ± S.D.)	Recovery (%)
Tap water 1	0.12	4	4.03 ± 0.03	97
Tap water 2	0.28	8	8.20 ± 0.08	99
Waste water 1	9.17	0	9.22 ± 0.15	100
Waster water 2	13.84	0	13.87 ± 0.02	100

Table 1

3. Experimental Methods

Synthesis of Compound 2

Pyrene carboxaldehyde (1 g, 4.4 mmol) and pyridine-2-methylamine (0.52 g, 4.8 mmol) were dissolved in a mixer of solvents of absolute ethanol (20 mL) and chloroform (10 mL). The mixture was heated under reflux for 3 h and being cooled to room temperature; the precipitate was separated and washed with ethanol to afford the crude Schiff base. The Schiff base was combined with $NaBH_4$ (0.17 g, 4.4 mmol) and ethanol (20 mL). The resulting reaction mixture was stirred at room temperature for 3 h. The solvent was then removed, and methylene chloride (30 mL) and HCl (0.2 N, 30 mL) were added. After being stirred for 1 h, the organic layer was separated and washed with brine, and dried over Na_2SO_4. The crude product was purified by short silica gel column, and eluted with ethylacetate/methanol (10:1) to afford the desired oily product **2.**[16] Yield: 1.15 g (82%). ^1H NMR ($CDCl_3$, 250 MHz): δ (ppm): 8.61 (d, 1H), 8.35 (d, 1H), 8.18-7.98 (m, 8H), 7.59 (t, 1H), 7.31 (d, 1H), 7.15 (t, 1H), 4.52 (s, 2H), 4.09 (s, 2H), 2.46 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 51.33, 54.62, 55.05, 55.45, 76.68, 77.19, 77.39, 77.69, 121.98, 122.42, 123.32, 124.69, 124.98, 125.01, 125.04, 125.84, 127.05, 127.09, 127.47, 127.55, 129.17, 130.68, 130.86, 131.32, 133.68, 136.43, 148.86, 149.30, 149.73, 159.86.

Synthesis of PPC

Compound 2 (0.5 g, 1.66 mmol), K_2CO_3 (0.3 g, 2.22 mmol), and dry CH_3CN (10 mL) were placed in a round-bottom flask at room temperature. To this mixture, a CH_3CN solution (40 mL) of 2,6-bis(bromomethyl)pyridine (0.2 g, 0.75 mmol) was added dropwise over 30 min. The reaction mixture was then heated to reflux for 12 h. After being cooled to room temperature, the insoluble materials were removed by filtration, and washed with chloroform several times until the washing solvent became colorless. The combined filtrate was concentrated, and the resulting residue was purified by silica gel column chromatography by using ethyl acetate/hexanes (1:1) as an eluent to give the final sensor **PPC**. Yield: 60%, Mp: 152^0C. ^1H NMR ($CDCl_3$, 250 MHz): δ (ppm): 8.52-8.54 (d, 2H), 8.34-8.38 (d, 2H), 7.91-8.13 (m, 18H), 7.53 (s, 4H), 7.06-7.35 (m, 3H), 6.75-6.77 (s, 2H), 4.42 (s, 4H). ^{13}C NMR (DMSO, 125 MHz): δ (ppm): 57.22, 60.47, 60.64, 121.51, 121.96, 123.32, 124.07, 124.42, 124.67, 124.88, 124.90, 125.75, 126.96, 127.01, 127.21, 127.35, 128.24, 129.82, 130.69, 130.77, 131.22, 132.50, 136.58, 148.77, 158.62, 159.60. LC-MS m/z: Calcd. for $[M^+]$ 751; Found $[M+H]^+$ 752.

Conclusions

In conclusion, we have developed a new fluorescent chemosensor, bis-pyrene tethered pyridine scaffold for sensing Ag^+ ion. The sensor exclusively senses Ag^+ ion by quenching the fluorescence signals through two ways, where the excimer emission is quenched by avoiding the interaction between the two intramolecular pyrene units and the monomer emission was quenched because of photoinduced electron transfer (PET) from the free tertiary amino nitrogen of Pyridine-Ag^+ ion bound receptor to pyrene. The fluorescent chemosensor was selective and sensitive for Ag^+, capable of detecting the metal ion down to 0.29 X 10^{-8} M^{-1}. The complex formation, stoichiometry, and binding mode have been established by fluorescence spectroscopy, ^1H NMR studies, mass spectroscopy and theoretical calculation and found to be 1:1. The design strategy of the sensor and photophysical properties would be assisting to extend the development of several fluorescent chemosensors for heavy and transition metal ions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: General experimental methods; copies of ^{1}H NMR, ^{13}C NMR, and other optical spectra. See DOI: 10.1039/b000000x/

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Pyrene pyridine- conjugate as Ag selective Fluorescent chemosensor

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