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A new class of pyrene based multifunctional chemosensors for differential sensing of metals in different media: Selective recognition of Zn^{2+} in organic and Fe^{3+} in aqueous medium

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ABSTRACT

Pyrene based Bigineilli compounds **1**–**4** were synthesized through one pot, multicomponent organic synthesis and were assessed for their metal binding ability under both organic medium and through forming their ONPs (aqueous medium). Sensors **3** and **4** selectively bind Zn^{2+} in acetonitrile through quenching in fluorescence intensity of excimer peak at 470 nm and amplifying monomer peak (which consist of two shoulder peaks at 380 nm and 395 nm). ONPs of **3** and **4** in aqueous medium displayed AIEE (aggregation induced enhanced emission) phenomenon through enhancement in fluorescence intensity. Furthermore, ONPs of **3** and **4** sense Fe^{3+} by quenching fluorescence intensity of both monomer and excimer emission peak. Sensing event of Fe^{3+} by organic nanoparticles of **3** and **4** was authenticated with CV profile of **3** and **4** with Fe^{3+}.

1. Introduction

Design, synthesis and development of the fluorescent organic nanoparticles (FONs) over simple chemo sensors are highly demanding these days due to their high sensitivity, quick response and easy operation towards different analytes at low concentrations [1,2]. FONs have gained lots of importance in the field of chemical research owing to exclusive optical properties [3,4]. Many types of inorganic fluorescent nano particles like quantum dots, metal nano particles like gold, silver are known. Though, FONs are superior to inorganic nano particles in terms of biomedical applications, excellent suspension in water and less toxicity [5]. These diverse applications of the FONs have motivated the utilization of FONs as chemosensors for the detection of cations, anions and biomolecules. Some of the reported FONs as chemosensors include 1,8-naphthalimide [6], thiourea–thiadiazole-pyridine [7], phenothiazine [8], thiacyanine [9], triazolo-thiadiazole [10], oligofluorene [11], cyanine [12], polydopamine [13], BODIPY [14], conjugate of (BMVC, 3,6-bis-(1-methyl-4-vinylpyridinium)carbazole diiodide) and (porphyrin or metalloporphyrin) [15], carbazole [16] and urea [17]. Based on the structural variations, different sensors detect different analytes under same or different solvent systems. Thus, variation in the structure of sensor and solvent system also play important role in chemical recognition of different analytes. Structural change may lead to the development of multifunctional sensors over single analyte sensor for estimation of two or more analytes [18]. Similarly, variation in the solvent system may lead to the alteration in optical sensing properties, possibly due to change in host–guest interactions or aggregation of sensor molecule in the selected solvent. These modulations are helpful in the detection of more than one analyte as interactions in two solvents can be different with two analytes [19]. Furthermore, use of green solvent such as water is always beneficial since it rapidly change the photophysical properties of the sensors on shifting from organic solvent to aqueous medium, helps in the analysis of biological samples and reduces environment pollution. Keeping in view the various applications of FONs as sensors and role of the solvent in detection of different analytes, it was decided to focus our study to the pyrene based sensor system in organic solvent as well as in aqueous medium (ONPs) and to explore the multifunctional response of chemosensors for cations.

2. Experimental

All the chemicals were purchased from commercial supplier and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol 300 NMR spectrometer, which operated

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at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Fourier transform infrared (FT-IR) spectra of dried compounds were measured on Bruker Tensor 27 spectrophotometer, using KBr pellet technique. The CHN analysis was performed on Perkin Elmer 2400 CHN Elemental Analyser for cation recognition studies, the UV–vis absorption spectra were taken using dilute solutions in quartz cells (1 cm path length). The fluorescence profile of sensor solutions were recorded on Perkin Elmer LS 55 Fluorescence spectrophotometer using 1 cm path length of quartz cells. The slit width for the excitation and emission was set at 10 nm and scan speed was maintained at 200 scans per second throughout the experiments. Scanning electron microscopic studies were conducted by drying the aqueous solutions of materials (10 μM). SEM images were taken with Jeol JSM-6610LV scanning electron microscope which operated at 15 keV. The particle size of ONPs was determined with Dynamic Light Scattering (DLS) using external probe feature of Microtrac Ultra Nanotrac Particle Size Analyser instrument. For analysing 10 μM concentration of solution was used and presented results are the average of 20 scans. Mass spectra were recorded on Waters, Q-TOF micro mass spectrometer.

2.1. Synthesis of compound **1**

A solution of pyrene-1-carboxaldehyde (230 mg, 1 mmol), methylacetoacetate (129 mL, 1.2 mmol), 2-aminobenzthiazole (225 mg, 1.5 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (2 mol%) in 5 mL of methanol was refluxed for 8 h. A yellow coloured solid product was obtained and the precipitate was filtered, washed with water and recrystallized from an acetone/water solvent mixture to afford the pure product. A yellow solid was obtained in a 78.9%, yield (363 mg). mp. 180–182 °C; IR (KBr): ν_{max}/cm^{-1} 1730, 1334; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, 1H, ArH), 7.93–7.88 (m, 2H, ArHs), 7.80–7.60 (m, 6H, ArHs), 7.21 (dd, 1H, ArH), 7.09 (s, 1H, C4H), 6.88–6.84 (ddd, 1H, ArH), 6.58–6.54 (ddd, 1H, ArH), 6.39 (dd, 1H, ArH), 3.83 (s, 3H, OCH_3), 2.51 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.5, 165.1, 140.9, 136.1, 132.9, 131.2, 130.7, 130.0, 129.0, 127.3, 126.7, 126.5, 126.4, 126.3, 126.2, 125.7, 124.9, 124.8, 124.7, 124.4, 122.9, 52.5, 27.3. Mass (ESI): m/z 461 (M−1); Anal. calcd. for $C_{29}H_{20}N_2O_2S$ C, 75.63; H, 4.38; N, 6.08; Found C, 75.58; H, 4.29; N, 5.96.

2.2. Synthesis of compound **2**

A solution of pyrene-1-carboxaldehyde (230 mg, 1 mmol), ethylacetoacetate (152 mL, 1.2 mmol), 2-aminobenzthiazole (225 mg, 1.5 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (2 mol%) in 5 mL of methanol was refluxed for 8 h. After the completion of reaction (TLC), solvent was evaporated under reduced pressure and product **2** were separated by column chromatography over silica gel (Acme Synthetic Chemicals, Mumbai, India, pH ~7, 60–120 mesh, 30 g, packed in hexane), using 2% chloroform in hexane as eluant. A pale yellow coloured solid product was obtained and the precipitate was filtered, washed with water and recrystallized from an acetone/water solvent mixture to afford the pure product. A pale yellow solid was obtained in a 89% yield (422 mg). mp. 292–294 °C; IR (KBr): ν_{max}/cm^{-1} 1734, 1663, 1330; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (dd, 2H, ArHs), 7.84 (d, 1H, ArH), 7.79–7.72 (m, 3H, ArHs), 7.69 (d, 2H, ArH), 7.62 (t, 1H, ArH), 7.22 (dd, 1H, ArH), 6.98 (s, 1H, C4H), 6.87–6.83 (ddd, 1H, ArH), 6.59–6.55 (m, 1H, ArH), 6.40 (dd, 1H, ArH), 4.23 (q, 2H, OCH_2CH_3), 2.47 (s, 3H, CH_3), 1.31 (t, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.1, 163.5, 138.5, 135.9, 131.5, 131.4, 130.7, 128.9, 128.3, 127.9, 127.4, 126.7, 126.4, 126.2, 126.0, 125.4, 124.9, 124.0, 123.5, 122.6, 122.1, 60.2, 23.8, 14.3; Mass (ESI): m/z 476 (M+1); CHN analysis for $C_{30}H_{22}N_2O_2S$: calcd C, 75.93; H, 4.67; N, 5.90; found C, 75.85; H, 4.53; N, 5.81.

2.3. Synthesis of compound **3**

A solution of pyrene-1-carboxaldehyde (230 mg, 1 mmol), methylacetoacetate (129 mL, 1.2 mmol), 2-aminobenzimidazole (199 mg, 1.5 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (2 mol%) in 5 mL of methanol was refluxed for 8 h. A greenish yellow coloured solid product was obtained and the precipitate was filtered, washed with water and recrystallized from an acetone/water solvent mixture to afford the pure product. A greenish yellow solid was obtained in 82% yield (363 mg). mp. 245–250 °C; IR (KBr): ν_{max}/cm^{-1} 1739, 1666; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.19 (s, 1H, NH), 7.91 (d, 2H, ArHs), 7.76–7.73 (m, 3H, ArHs), 7.70 (dd, 2H, ArH), 7.66 (d, 1H, ArHs), 7.61 (t, 1H, ArH), 7.35 (dd, 1H, ArH), 7.08–6.94 (m, 3H, ArHs), 6.57 (s, 1H, C4H), 3.71 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.5, 154.3, 150.1, 143.2, 136.6, 135.7, 132.2, 128.4, 127.3, 125.8, 123.7, 121.8, 120.3, 119.3, 117.8, 116.4, 115.5, 112.0, 109.0, 104.6, 101.0, 53.5, 18.8; Mass (ESI): m/z 441(M+2); CHN analysis for $C_{29}H_{21}N_3O_2$; calcd C, 78.54; H, 4.77; N, 9.47; found C, 78.42; H, 4.61; N, 9.35.

2.4. Synthesis of compound **4**

A solution of pyrene-1-carboxaldehyde (230 mg, 1 mmol), ethylacetoacetate (152 mL, 1.2 mmol), 2-aminobenzimidazole (199 mg, 1.5 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (2 mol%) in 5 mL of methanol was refluxed for 12 h. A greenish yellow coloured solid product was obtained and the precipitate was filtered, washed with water and recrystallized from an acetone/water solvent mixture to afford the pure product. A greenish yellow was obtained in a 80% yield (366 mg). mp. 252–255 °C; IR (KBr): ν_{max}/cm^{-1} 1736, 1671; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.26 (s, 1H, NH), 7.89 (dd, 2H, ArH), 7.82 (d, 1H, ArH), 7.77–7.69 (m, 3H, ArHs), 7.67–7.59 (m, 3H, ArHs), 7.35 (dd, 1H, ArH), 7.08 (dd, 1H, ArH), 7.04–6.94 (m, 3H, ArHs & C4H), 4.22 (q, 2H, OCH_2CH_3), 2.00 (s, 3H, CH_3), 1.36(t, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.3, 152.1, 141.1, 138.3, 136.4, 134.7, 134.3, 133.0, 130.4, 127.4, 127.0, 125.4, 125.0, 124.1, 122.3, 120.4, 117.5, 114.5, 110.0, 107.5, 105.0, 59.4, 25.0, 16.8. Mass (ESI): m/z 457(M); CHN analysis for $C_{30}H_{23}N_3O_2$: calcd C, 78.75; H, 5.07; N, 9.18; found C, 78.65; H, 4.99; N, 9.02.

2.5. Metal recognition properties of **1**–**4**

All the recognition studies were performed at 25 ± 1 °C and before recording any spectrum sufficient time was given with shaking to ensure the uniformity of the solution. The cation binding ability of **1**–**4** was determined by mixing standard solutions of host (10 μM) along with fixed amounts of particular metal nitrate salt (500 μM) in CH_3CN. The fluorescence spectra of **1**–**4** were recorded with excitation wavelengths shown in respective figures. The cation recognition behaviour of **1**–**4** was evaluated from the changes in fluorescence spectrum of sensor upon addition of a particular metal salt. The titration was performed by taking standard solution of sensor **3** and **4** (5 μM) along with successive addition of Zinc nitrate (0–500 μM) in CH_3CN. The binding constant of sensor **3** and **4** with Zn^{2+} was calculated using literature method. To evaluate any possible interference due to different cations for the estimation of Zn^{2+}, solutions were prepared containing **3** and **4** (10 μM) and Zn^{2+} (500 μM) along both with and without other interfering metal ions (500 μM) in AcN.

3. Results and discussion

Pyrene based Biginelli compounds **1**–**4** were synthesized through one pot multicomponent reaction between pyrene-1-carboxaldehyde, 2-aminobenzimidazole/2-aminobenzothiazole