Multitasking Behaviour of a Small Organic Compound: Solid State Bright White-Light Emission, Mechanochromism and Ratiometric Sensing of Al(III) and Pyrophosphate

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Experimental Section:

Materials. The reactions and workup procedures were performed at ambient condition. 9,10-phenanthrenequinone, ammonium acetate and Glacial acetic acid were purchased from Spectrochem Pvt. Ltd., India; 2-hydroxy-1-naphthaldehyde and 2-methoxy-1-naphthaldehyde were purchased from Alfa Aesar. Perchlorate salt of metals and tert-butylammonium salt of PPi were obtained from Aldrich and were used as received. HPLC-grade solvents and doubly distilled water were used in spectral measurements. NMR solvent DMSO-$d_6$ was purchased from Aldrich.

Methods. $^1$H, $^{13}$C, $^1$H-$^1$H COSY, $^1$H-DEPT-135 HSQC and $^1$H-$^{13}$C HMBC NMR experiments were carried out on FT-NMR Bruker DPX 300/400/500 MHz NMR spectrometer, and the chemical shift values for $^1$H and $^{13}$C NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set. High-resolution mass spectrometry (HRMS) analyses were done by QTOF–Micro YA 263 mass spectrometer in positive ESI mode. Fourier transform infrared (FTIR) spectra were recorded on Shimadzu FTIR-8400S infrared spectrophotometer with KBr pellets. Elemental analysis was performed on PerkinElmer 2500 series II elemental analyzer, Perkin Elmer, USA. The UV-vis absorption spectrum was obtained using Perkin Elmer Lambda 950. The solid-state photoluminescence spectra and corresponding CIE diagrams were obtained using an FLS980 spectrofluorimeter (Edinburgh Instruments) and a 450 W xenon lamp as the light source under ambient conditions. An inbuilt filter was present in the fluorimeter to avoid the appearance of the second order harmonic peak. Time-correlated single photon count measurement to determine the lifetime was measured using a 275 nm picosecond pulsed LED and an MCP detector. Solution phase emission spectra were recorded in a FluoroMax-3 spectrophotometer, from Horiba Jobin Yvon.
Caution! Metal perchlorate salts are explosive in the presence of open flames, heat or sparks. Aluminum perchlorate is a skin irritant. All due precautions should be taken to handle these.

Chart S1. Molecular structure of 1H.

Synthesis of 1-(1H-phenanthro[9,10-d]imidazol-2-yl)naphthalen-2-ol (1H). A solution of 9,10-phenanthrenequinone (0.250 g, 1.2 mmol), 2-hydroxy-1-naphthaldehyde (0.206 g, 1.2 mmol), and ammonium acetate (1.5 g, 19.5 mmol) in glacial acetic acid (8 mL) was stirred at 90 °C for 3 h. The reaction mixture was then poured into ice-cold water. Resulting precipitate was filtered, washed properly with water, and dried in air. The cream-white residue was purified by medium-pressure column chromatography with silica gel of 60-120 mesh size using ethyl acetate/ petroleum ether as the eluent. Pure product was isolated at 15% ethyl acetate concentration as white powder (0.30 g, 70%). Elemental analysis: Calcd (%) for C_{25}H_{16}N_{2}O: C, 83.31; H, 4.47; N, 7.77; O, 4.44. Found: C, 83.39; H, 4.40; N, 7.85. FTIR in KBr disc (ν/cm\(^{-1}\)): 3446, 3049, 2921, 2924, 2850, 2363, 1620, 1466, 1331, 1248, 816, 749. ESI-MS [C_{25}H_{16}N_{2}O][H\(^+\)] calcd: m/z 361.41. Found: m/z 361.09. \(^1\)H NMR (500 MHz, DMSO-d\(_6\), Si(CH\(_3\))\(_4\)): δ 13.36 (bs, 1H, OH), 10.93 (bs, 1H, NH), 8.89 (d, J = 10 Hz, 2H, H\(_{g,g'}\)), 8.53 (d, J =
10 Hz, 2H, H_{d,d'}), 7.98 (d, J = 5 Hz, 2H, H_{s,c}), 7.92 (d, J = 10 Hz, 1H, H_{b}), 7.72 (t, J = 15 Hz, 2H, H_{c,c'}), 7.64 (t, J = 15 Hz, 2H, H_{f,f'}), 7.48 (t, J = 15 Hz, 1H, H_{i}), 7.37 (t, J = 15 Hz, 2H, H_{h,a}). \(^{13}\)C NMR (100 MHz, DMSO-\textit{d}_6, Si(CH\textsubscript{3})\textsubscript{4}): \(\delta\) 154.7 (1C, C\textsubscript{k}), 146.2 (1C, C\textsubscript{m}), 132.9 (1C, C\textsubscript{l}), 131.1 (1C, C\textsubscript{a}), 128.0 (1C, C\textsubscript{b}), 127.8, 127.4, 127.0 (3C, C\textsubscript{i,e,e'}), 125.0 (2C, C\textsubscript{f,f'}), 124.2 (1C, C\textsubscript{c}), 123.8 (2C, C\textsubscript{g,g'}), 123.1 (1C, C\textsubscript{a}), 121.8 (2C, C\textsubscript{d,d'}), 118.3 (1C, C\textsubscript{b}), 110.1 (1C, C\textsubscript{i}).

**Scheme S1.** Synthetic scheme for 1H.

**Figure S1.** \(^1\)H-NMR (500 MHz) spectrum of 1H in DMSO-\textit{d}_6.
Figure S2. $^1$H-$^1$H COSY-NMR (500 MHz) spectrum of $^1$H in DMSO-$d_6$.

Figure S3. $^{13}$C-NMR (125 MHz) spectrum of $^1$H in DMSO-$d_6$. 
Figure S4. DEPT-135-NMR (125 MHz) spectrum of 1H in DMSO-$d_6$.

Figure S5. $^1$H-DEPT-135 HSQC-NMR (500 MHz) spectrum of 1H in DMSO-$d_6$. 
Figure S6. $^1$H-$^{13}$C-HMBC NMR (500 MHz) spectrum of 1H in DMSO-$d_6$.

Figure S7. ESI-MS of 1H.
**X-ray Crystallographic Refinement Details for 1H.** The crystals of 1H were obtained from slow evaporation of the compound in DMSO. From there, a diffractable size crystal was collected, dipped in paratone oil, and then was cemented on the tip of a glass fiber using epoxy resin. Intensity data of the crystal were collected using Mo Kα (λ = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer, equipped with a CCD area detector at 293K. Data integration and reduction were processed by SAINT\textsuperscript{1} software. Empirical absorption correction to the collected reflections was done by applying SADABS.\textsuperscript{2} The structure was solved using SHELXTL\textsuperscript{3} and was refined on F\textsuperscript{2} by the full-matrix least-squares technique using the SHELXL-97\textsuperscript{4} program package. PLATON-97\textsuperscript{5} and MERCURY 3.8\textsuperscript{6} were used to generate graphics. CCDC-1857506 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Figure S8.** Single-crystal X-ray structure of 1H (thermal ellipsoids are drawn at 60% probability level) showing the asymmetric unit. Color code: O, red; N, blue; C, gray; H, pink.
### Table S1. Crystallographic parameter details of 1H.

<table>
<thead>
<tr>
<th>Compound reference</th>
<th>1H</th>
<th>Space group</th>
<th>P2(1)/n</th>
</tr>
</thead>
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<tr>
<td>Chemical formula</td>
<td>C$<em>{27}$H$</em>{22}$N$_2$O$_2$S</td>
<td>No. of formula units per unit cell, Z</td>
<td>4</td>
</tr>
<tr>
<td>Formula Mass</td>
<td>438.53</td>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Absorption coefficient, μ/mm-1</td>
<td>0.160</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.8651(5)</td>
<td>No. of reflections measured</td>
<td>22865</td>
</tr>
<tr>
<td>b/Å</td>
<td>19.3795(13)</td>
<td>No. of independent reflections</td>
<td>4228</td>
</tr>
<tr>
<td>c/Å</td>
<td>18.3270(13)</td>
<td>R$_{int}$</td>
<td>0.0615</td>
</tr>
<tr>
<td>α/°</td>
<td>90.00</td>
<td>Final R1 values (I &gt; 2σ(I))</td>
<td>0.0669</td>
</tr>
<tr>
<td>β/°</td>
<td>99.218(2)</td>
<td>Final wR(F2) values (all data)</td>
<td>0.1858</td>
</tr>
<tr>
<td>γ/°</td>
<td>90.00</td>
<td>Goodness of fit on F2</td>
<td>1.219</td>
</tr>
<tr>
<td>Unit cell volume/Å$^3$</td>
<td>2406.8(3)</td>
<td>CCDC</td>
<td>1857506</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure S9. Three-dimensional crystal packing of 1H illustrating the layered array of molecules connected via intermolecular interactions; Color code: O, red; N, blue; C, gray; H, white.
Figure S10. A slice of three-dimensional (3-D) crystal packing of 1H along the crystallographic $a$ axis showing intermolecular stacking (thermal ellipsoids are drawn at 60% probability level). Color code: O, red; N, blue; C, gray (H atoms are omitted for clarity).

Figure S11. A slice of three-dimensional (3-D) crystal packing of 1H along the crystallographic $b$ axis (thermal ellipsoids are drawn at 60% probability level). Color code: O, red; N, blue; C, gray (H atoms are omitted for clarity).
Figure S12. (a) Thermo-gravimetric and (b) differential scanning calorimetric analysis of 1H.

Figure S13. Solid state excitation spectrum of 1H (a) before ($\lambda_{em} = 580$ nm) and (b) after grinding ($\lambda_{ex} = 475$ nm).

Quantum yield calculation. The PL quantum yield ($\Phi_f$) was calculated using an analytical approach following the equation given below.$^7$

$$
\Phi_f = \frac{\int_{\lambda_{em}}^{\lambda_{em,2}} \left[ I_X(\lambda_{em}) - I_B(\lambda_{em}) \right] \lambda_{em} d\lambda_{em}}{\int_{\lambda_{ex} - \Delta\lambda}^{\lambda_{ex} + \Delta\lambda} \left[ I_B(\lambda_{ex}) - I_X(\lambda_{ex}) \right] \lambda_{ex} d\lambda_{ex}} = \frac{N_{em}}{N_{abs}}
$$
where, the total number of emitted photons \( (N_{em}) \) is obtained upon integration of the blank-corrected \( (I_b(\lambda_{em})) \) and spectrally corrected \( (I_x(\lambda_{em})) \) emission spectrum of the sample. The number of absorbed photons \( (N_{abs}) \) follows from the integrated difference between the excitation light resulting from measurements with the blank \( (I_b(\lambda_{ex})) \) and the sample \( (I_x(\lambda_{ex})) \). \( s(\lambda_{em}) \) and \( s(\lambda_{ex}) \) are spectral responsivity of the emission and excitation channel respectively.

**Figure S14.** Fluorescence decay profiles of 1H monitored at 470 and 580 nm (a) before and (b) after grinding.

**Figure S15.** Change in emission color of 1H during application of mechanical pressure and its regeneration by heating.
Figure S16. (a) Thermo-gravimetric and (b) differential scanning calorimetric analysis of 1H after grinding.

Figure S17. (a) Change in PXRD pattern of 1H during application of mechanical pressure and its regeneration by heating; (b) change in PXRD pattern of 1H during its regeneration from the grinded form by applying heat; (c) change in I580/I475 value of 1H with repetitive cycles of grinding and heating at 65°C for 4h.
Synthesis of 2-(2-Methoxyphenyl)-1H-phenanthro[9,10-d]-imidazole (1Me). A solution of 9,10-phenanthrenequinone (0.250 g, 1.2 mmol), 2-methoxybenzaldehyde (0.223 g, 1.2 mmol), and ammonium acetate (1.5 g, 19.5 mmol) in glacial acetic acid (8 mL) was stirred at 90 °C for 4 h. The reaction mixture was poured into ice-cold water. Resulting precipitate was filtered, washed properly with water, and dried. Pure product was obtained as brownish white powder (0.382 g, 85%). Elemental analysis: Calcd (%) for C\textsubscript{22}H\textsubscript{16}N\textsubscript{2}O: C, 81.46; H, 4.97; N, 8.64; O, 4.93. Found: C, 81.22; H, 5.13; N, 8.31; O, 4.65. ESI-MS \([\text{C}_{26}\text{H}_{18}\text{N}_{2}\text{O}]^{+}\) calcd: m/z 375.43. Found: m/z 375.00. \(^1\text{H}\) NMR (500 MHz, DMSO-\(d_6\), Si(CH\textsubscript{3})\(_4\)): 13.47 (s, 1H), 8.92-8.87 (m, 2H), 8.55 (d, J = 8 Hz, 1H), 8.40 (d, J = 8 Hz, 1H), 8.19 (d, J = 8 Hz, 1H), 8.00 (d, J = 8 Hz, 1H), 7.74-7.70 (t, J = 16 Hz, 3H), 7.69-7.65 (t, J = 16 Hz, 3H), 7.46-7.42 (m, 2H), 3.93 (s, 3H).

**Scheme S2.** Synthetic scheme for 1Me.
Figure S19. $^1$H-NMR (400 MHz) spectrum of 1Me in DMSO-$d_6$.

Figure S20. ESI-MS of 1Me.
Figure S21. Absorption and emission spectral behavior of 1Me.

Figure S22. Emission spectra of 1H and 1Me in solvents of different polarity ($\lambda_{ex} = 360$ nm).

Solvent polarity dependent photoluminescence studies of 1H does not show any well shifted emission bands for enol and keto forms, even in aprotic nonpolar solvents like hexane, toluene etc., which is commonly observed in case of ESIPT based systems. Both 1H and 1Me display shift in the wavelength of higher energy emission band, while, the position of the lower energy emission band does not change significantly (Fig. S22, ESI†). The results suggest that the higher
energy emission band (~ 460 nm) might be originated from the locally excited state (LE), while, the lower energy emission (~ 420 nm) could arise from the excited state intramolecular charge transfer (ESICT) process which is occurring in both the systems. The extent of ESICT is less in 1Me. However, the steric repulsion between the imidazole NH group and the nearby naphthyl CH part might cause difficulty for 1H to adopt planar geometry which is needed for ESIPT to happen and that is why the molecule does not show ESIPT process even in solution.

36. ESIPT is a fast (picosecond) intramolecular proton-transfer process, occurs in excited state of suitable molecules containing -OH/-NH and C=N/C=O, etc. functionalities, which results large Stokes shift.

Figure S23. Solid state emission spectral change of 1Me upon grinding, with corresponding CIE diagrams (λex = 362 nm) (inset are the solid state colors of 1Me before and after grinding).

Microscopic studies: 1H, when dissolved in THF shows bright cyan coloured fluorescence, atomic force microscopic (AFM) study with which (1 x 10^{-3} M) displays formation of mutually interconnected ring like structures of 800 nm dimension in average (Fig. S20, ESI†). Dynamic light scattering (DLS) study also suggests the same size distribution (Fig. S21, ESI†). Addition of up to 50% water in this increases the fluorescence intensity slightly (Fig. S22, ESI†), which could be due to the formation of fluorescent aggregates. Such aggregation is confirmed by the AFM analysis and DLS study. However, in acetonitrile, 1H forms rectangular shaped microscopic crystal, which can easily be visible even under microscope, besides the AFM evidence.
Figure S24. AFM image of 1H in THF, THF-water and acetonitrile showing interconnected ring-like structure formation in THF, aggregate formation in THF-water and rectangular crystal formation in acetonitrile; last one is the normal microscopic image.

Figure S25. DLS study of 1H in THF and 50% THF-water.
Figure S26. Change in PL intensity of THF solution of 1H (1 x 10^{-5} M) in presence of increasing concentration of water; given are the % of THF.

Figure S27. Absorption titration spectra of 1H (10 μM) with Al^{3+}.

Figure S28. PL titration spectra of 1H (10 μM) with (a) Al^{3+} and (b) PPi.
Figure S29. Equivalent plot from PL titration data for 1H with (a) Al$^{3+}$ and (b) PPi.

**Calculation of detection limit.** Detection limits (DL) were calculated using the following equation:

$$DL = \frac{3 \times SD}{\text{slope}}$$

where, SD corresponds to the standard deviation of the blank sample, measured using 15 consecutive scans of the blank sample. The slope is obtained from the linear fit plot of PL intensity changes versus the concentration of guest added. The SD value of ligand 1H was 702.24.

Figure S30. Calibration curve for (a) Al$^{3+}$ and (b) PPi derived from corresponding PL titration data with 1H (10 μM) in acetonitrile at room temperature.
Figure S31. (a) Non-linear 1:1 fitting of PL titration data to calculate association constant of 1H with Al³⁺ in acetonitrile at room temperature; (b) selectivity graph of 1H with Al³⁺ in presence of other metal ions in acetonitrile (λem= 435 nm for Al³⁺, Cr³⁺; 460 nm for other metal ions) as their perchlorate salt. Magenta bars represent the PL intensities of 1H in presence of all metal ions (10 equiv) and blue bars correspond to the same in presence of all metal ions and Al³⁺. Codes used: (1) Only 1H (2) Mg²⁺ (3) Fe³⁺ (4) Mn²⁺ (5) Cd²⁺ (6) Pb²⁺ (7) Zn²⁺ (8) Co²⁺ (9) Cu⁺ (10) Ni²⁺ (11) Ag⁺ (12) Hg²⁺ (13) Cr³⁺ (14) Al³⁺.

Table S2. Comparison of Al³⁺ sensing by 1H with some of the previously reported sensors.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>λex (nm)</th>
<th>λem (nm)</th>
<th>Log K_a</th>
<th>LOD</th>
<th>Host-guest stoichiometry</th>
<th>Mode</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS Sens., 2016, 1, 144</td>
<td>468</td>
<td>601</td>
<td>10.30</td>
<td>3.1 nM</td>
<td>1:2</td>
<td>Turn On</td>
<td>10 μM in 0.1% DMSO/HEPES</td>
</tr>
<tr>
<td>RSC Adv., 2014, 4, 5845</td>
<td>317</td>
<td>441</td>
<td>--</td>
<td>0.5 nM</td>
<td>2:1</td>
<td>Turn On</td>
<td>Water</td>
</tr>
<tr>
<td>J. Lumin., 2016, 172, 124</td>
<td>280</td>
<td>455</td>
<td>4.11</td>
<td>80 nM</td>
<td>1:1</td>
<td>Turn On</td>
<td>5% DMSO-Water v/v, pH7</td>
</tr>
<tr>
<td>Spectrochimica Acta Part A: Mol. Biomol. Spec., 2015, 139, 119</td>
<td>450</td>
<td>506</td>
<td>4.10</td>
<td>0.99 μM</td>
<td>1:1</td>
<td>Turn On</td>
<td>CH₃CN–H₂O solution (1:1 v/v, HEPES 50 mM, pH = 7.0)</td>
</tr>
<tr>
<td>J. Phys. Chem. A, 2016, 120, 210</td>
<td>364</td>
<td>426</td>
<td>--</td>
<td>8.64 nM</td>
<td>1:1</td>
<td>Turn On</td>
<td>CH₃CN/H₂O, 95:5, v/v</td>
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<tr>
<td>Tetrahedron Letters, 2011, 52, 5581</td>
<td>435</td>
<td>510</td>
<td>8.70</td>
<td>1.00 μM</td>
<td>1:1</td>
<td>Turn On</td>
<td>MeOH/aqueous HEPES buffer (1 mM, pH 7.4, 3:2 v/v)</td>
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<td>Inorg. Chem., 2016, 55, 9212</td>
<td>355</td>
<td>445</td>
<td>5.53</td>
<td>0.5 nM</td>
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<td>Ratiometric</td>
<td>CH₃CN</td>
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<tr>
<td></td>
<td>366</td>
<td>463</td>
<td>4.90</td>
<td>12 nM</td>
<td>1:1</td>
<td>Ratiometric</td>
<td>9:1 Water/CH₃CN, v/v</td>
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<td>Present work</td>
<td>365</td>
<td>435</td>
<td>4.54</td>
<td>7.62 nM</td>
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<td>Ratiometric</td>
<td>CH₃CN</td>
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Table S3. Comparison of PPi sensing by 1H with some of the previously reported sensors.

<table>
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<tr>
<th>Ref.</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt; (nm)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)</th>
<th>Log K&lt;sub&gt;a&lt;/sub&gt;</th>
<th>LOD</th>
<th>Host-guest stoichiometry</th>
<th>Mode</th>
<th>Solvent</th>
</tr>
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<tr>
<td>Org. Lett., 2008, 10, 473-476</td>
<td>315</td>
<td>376</td>
<td>5.67</td>
<td>--</td>
<td>2:1</td>
<td>Turn Off</td>
<td>tris-HCl (0.01 M) solution (MeOH/H&lt;sub&gt;2&lt;/sub&gt;O) 1:9, v/v, pH 7.22</td>
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<tr>
<td>Org. Lett., 2011, 13, 1362-1365</td>
<td>430</td>
<td>512</td>
<td>4.10</td>
<td>2.18 µM</td>
<td>2:1</td>
<td>Turn On</td>
<td>HEPES buffer</td>
</tr>
<tr>
<td>Tetrahedron Letters, 2016, 57, 5022-5025</td>
<td>352</td>
<td>453</td>
<td>5.61</td>
<td>--</td>
<td>1:1</td>
<td>Turn Off</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN-HEPES buffer (0.02 M, pH 7.2) (v/v = 5:5)</td>
</tr>
<tr>
<td>Anal. Chem. 2013, 85, 8369-8375</td>
<td>350</td>
<td>480</td>
<td>4.24</td>
<td>2 ppb</td>
<td>1:1</td>
<td>Turn Off</td>
<td>MeOH/aqueous HEPES buffer (1 mM, pH 7.4; 3:2 v/v)</td>
</tr>
<tr>
<td>J. Am. Chem. Soc. 1999, 121, 9463-9464.</td>
<td>312</td>
<td>476</td>
<td>8.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>--</td>
<td>2:1</td>
<td>Turn On</td>
<td>MeOH</td>
</tr>
<tr>
<td>Inorg. Chem., 2009, 48, 2993-2999</td>
<td>352</td>
<td>453</td>
<td>4.52</td>
<td>--</td>
<td>1:1</td>
<td>Turn On</td>
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<td>600</td>
<td>14.96</td>
<td>0.02 µM</td>
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<td>Turn On</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
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<tr>
<td>J. Am. Chem. Soc., 2014, 136, 5543-5546</td>
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<td>591</td>
<td>--</td>
<td>0.8 nM</td>
<td>3:1</td>
<td>Turn On</td>
<td>10 mM HEPES buffer (pH 7.4)</td>
</tr>
<tr>
<td>Dalton. Trans., 2018, 47, 6819 (a: K&lt;sub&gt;a1&lt;/sub&gt;; b: K&lt;sub&gt;a2&lt;/sub&gt;)</td>
<td>315</td>
<td>385</td>
<td>5.70&lt;sup&gt;a&lt;/sup&gt;, 5.26&lt;sup&gt;b&lt;/sup&gt;</td>
<td>45.37 nM</td>
<td>1:2</td>
<td>Turn Off</td>
<td>70% aqueous buffer (10 mM HEPES, pH 7.4) / acetonitrile</td>
</tr>
<tr>
<td>Present work</td>
<td>365</td>
<td>478</td>
<td>--</td>
<td>5.67 nM</td>
<td>2:1</td>
<td>Ratiometric</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
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</tbody>
</table>
Figure S32. ESI-MS spectra of the Al$^{3+}$ adduct of 1H and the isotopic distribution pattern of [Al(1)O]$_2$K$^+$ with its corresponding simulated pattern.

Figure S33. Isotopic distribution pattern of [(1H)$_2$ + H$_2$P$_2$O$_7^{2-}$ + 3Na$^+$]$^+$ with the corresponding simulated pattern.
Figure S34. Emission spectral change of 1Me in presence of Al$^{3+}$.

References:
2. SADABS, Empirical Absorption Correction Program; University of Göttingen: Germany, 1997.