



ChemComm

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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-08-2022-004732.R1
Article Type:	Communication

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# Optical sensing of aqueous nitrate anion by a platinum(II) trimine salt based solid state material

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<sup>†</sup>This work is dedicated to William B. Connick, who passed away in April 2018

Supporting Information Placeholder

**ABSTRACT:** Selective and quantitative measurement of aqueous nitrate ( $\text{NO}_3^-$ ) anion is achieved using solid  $[\text{Pt}(\text{Cl-4-tpy})\text{Cl}]\text{ClO}_4$  salt ( $\text{Cl-4-tpy}$  = 4-chloro-2,2':6'2''-terpyridine) as is, and as the salt supported on controlled porous glass. This detection method relies on the color change of the Pt(II) complex from yellow to red and intense luminescence response upon  $\text{ClO}_4^-$  exchange with  $\text{NO}_3^-$  due to concomitant enhancement of Pt•••Pt interactions. The spectroscopic response is highly selective for  $\text{NO}_3^-$  over a large range of halides and oxoanions.

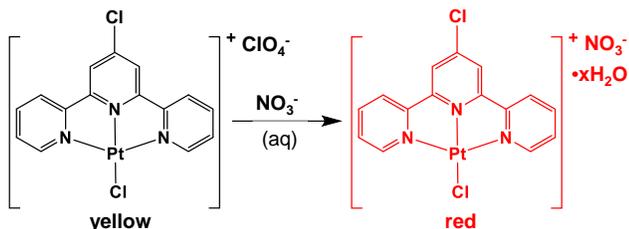
The selective and sensitive detection of specific anions for the monitoring and assessment of water quality remains a global environmental and chemical challenge.<sup>1,2</sup> One such example is the nitrate ( $\text{NO}_3^-$ ) anion; it has widespread use in munitions/explosives manufacturing and chemical fertilizer preparation,<sup>3-5</sup> and an abundance of nitrate found in livestock as well as organic wastes<sup>6</sup> has led to groundwater and food supply contamination and raised public health concerns. Epidemiologic studies have associated continued  $\text{NO}_3^-$  exposure via ingestion to multiple medical issues that include spontaneous abortions in pregnant women,<sup>7</sup> birth defects of the central nervous system and intrauterine growth restriction in children,<sup>8</sup> and cardiovascular effects<sup>9</sup> and gastric cancer in adults.<sup>10</sup> According to recent World Health Organization (WHO) reports,  $\text{NO}_3^-$  concentrations in surface waters have increased significantly over the last 30 – 40 years,<sup>11</sup> emphasizing a growing need for its rapid *in situ* detection and prompting the United States Environmental Protection Agency (US-EPA) to set the ambient water quality limit of  $\text{NO}_3^-$  at 10 ppm.<sup>12</sup>

Current EPA strategies for aqueous  $\text{NO}_3^-$  detection involve ion selective electrode based potentiometry<sup>13</sup> or *in-situ*  $\text{NO}_3^-$  reduction followed by  $\text{NO}_2^-$  colorimetry. Alternate methods proposed for *in-situ*  $\text{NO}_3^-$  detection include UV-spectroscopy,<sup>13</sup> ion chromatography,<sup>14</sup> and capillary electrophoresis.<sup>15</sup> These proposed techniques suffer from limitations including imperfect selectivity, longer processing times, complicated and expensive instrumentation, or need for processing expertise. This impacts rapid testing and impedes water quality assessment particularly in remote corners of the globe where such timely testing can be critical.<sup>16</sup> An

elegant study by Daniel et al. relied on two-step colorimetric sensing of nitrate comprised of (i) an initial enzymatic reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  using nitrate reductase and its cofactors followed by (ii) colorimetric detection of the  $\text{NO}_2^-$  at concentrations  $\geq 22\mu\text{M}$  using two sets of Au nanoparticles (NPs), one functionalized with aniline and the other with naphthalene groups. At  $\text{NO}_2^-$  concentrations  $\geq 22\mu\text{M}$ , they trigger the formation of a diazo bond between the aniline and the naphthalene units, leading to crosslinking of the Au NPs and consequently their precipitation from solution. This is reflected in the color change of the solution from red to colorless. While this technique offers a selective, sensitive, and robust method for rapid *in-situ*  $\text{NO}_2^-/\text{NO}_3^-$ , the need for multiple processing steps makes it less than ideal in terms of operational flexibility for on-site deployment.

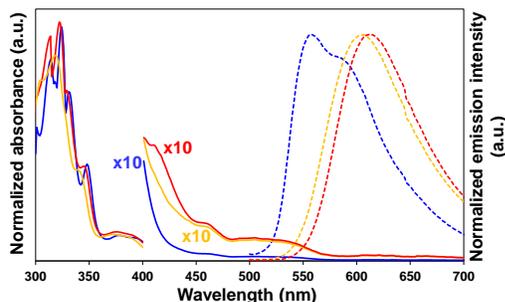
We have recently demonstrated a new method of colorimetric aqueous  $\text{NO}_3^-$  detection, complemented by a second and more sensitive luminescent mode.<sup>17</sup> This method utilizes solid-state hybrid materials based on square-planar platinum(II) salts supported on mesoporous silica.<sup>18</sup> The strategy relies on selective recognition of the aqueous  $\text{NO}_3^-$  anion by a square-planar Pt(II) salt, which results in changes in the extended solid-state lattice structure, (i.e., altering the Pt•••Pt interactions) upon anion exchange. Square-planar, coordinately-unsaturated Pt(II) complexes with sterically permitting ligands demonstrate rich spectroscopic properties that are modulated by changing the Pt•••Pt interactions.<sup>1,19-21</sup> Incorporation of an anion guest into the crystal lattice that can significantly alter the Pt•••Pt interactions in a desired way, triggers correlated changes in the electronic structure of the Pt(II) compound. This is reflected in vivid changes in their optical spectroscopies.<sup>1,2,17</sup> Our previous aqueous  $\text{NO}_3^-$  detection method required adjusting the pH of the material to  $<0$ , which could negatively impact or render the technique useless for a wider selection of environmental samples. Herein, we present a new Pt(II) salt,  $[\text{Pt}(\text{Cl-4-tpy})\text{Cl}]\text{ClO}_4$  (**1**• $\text{ClO}_4$ ), which shows a unique optical response to aqueous  $\text{NO}_3^-$  anion without the need for pH adjustment. This simplifies the detection process for on-site applications and expands the applicability of the new Pt(II) salt to broader matrices.

$\mathbf{1}\bullet\text{ClO}_4$  is a sparingly water-soluble salt that crystallizes as yellow needles. To assess the colorimetric response, yellow microcrystalline powder ( $\sim 10$  mg) or an aqueous suspension ( $\sim 10$  mg/mL) of  $\mathbf{1}\bullet\text{ClO}_4$  were exposed to aqueous  $\text{NO}_3^-$  (1 mL 1 M solution, Scheme 1). Exposure of either the solid or the suspension resulted in a distinct color change from yellow to red within 2-5 minutes.



**Scheme 1.** Conversion of yellow  $[\text{Pt}(\text{Cl-4-tpy})\text{Cl}]\text{ClO}_4$  ( $\mathbf{1}\bullet\text{ClO}_4$ ) to red  $[\text{Pt}(\text{Cl-4-tpy})\text{Cl}]\text{NO}_3 \cdot x\text{H}_2\text{O}$  ( $\mathbf{1}\bullet\text{NO}_3 \cdot x\text{H}_2\text{O}$ ) upon exposure to aqueous  $\text{NO}_3^-$ .

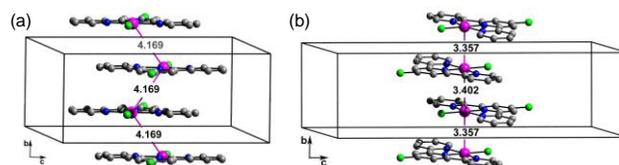
Optical spectroscopy was used to corroborate the visual color changes of  $\mathbf{1}\bullet\text{ClO}_4$  from yellow to red (Figure 1). Absorption spectra of microcrystalline powders of  $\mathbf{1}\bullet\text{ClO}_4$  dispersed on a glass slide exhibit spin-allowed intra-ligand ( $\pi\text{-}\pi^*$ ) transitions at wavelengths below 365 nm. In addition, a broad low-energy absorption band at wavelengths between 365 and 450 nm is assigned to the  $d\pi(\text{Pt})\text{-}\pi(\text{Cl-4-tpy})$  metal-to-ligand charge transfer (MLCT) transition of the  $[\text{Pt}(\text{Cl-4-tpy})\text{Cl}]^+$  chromophore *vide-infra*.<sup>22</sup> Immersion of the glass slide with dispersed  $\mathbf{1}\bullet\text{ClO}_4$  microcrystals into a 1.0 mM aqueous  $\text{NO}_3^-$  solution results in the appearance of a new band at longer wavelengths. This new band is nearly identical to that observed for an independently synthesized  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$  sample. Based on comparison with similar Pt(II) salts, this low-energy band is attributed to a metal-metal-to-ligand charge-transfer MMLCT transition [ $d\sigma^*(\text{Pt})\text{-}\pi^*(\text{Cl-4-tpy})$ ] where the  $d\sigma^*$  arises from the interaction of the  $d_z^2(\text{Pt})$  orbitals of adjacent complexes, which in turn is suggestive of extended  $\text{Pt}\cdots\text{Pt}$  interactions.<sup>2,20,22-24</sup>



**Figure 1.** Optical spectroscopy of  $\mathbf{1}\bullet\text{ClO}_4$  and  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$ : (blue lines) spectra of  $\mathbf{1}\bullet\text{ClO}_4$ , (red lines) spectra of  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$ , (yellow lines) spectra of  $\mathbf{1}\bullet\text{ClO}_4$  post exposure to aqueous  $\text{NO}_3^-$ ; solid lines represent absorption and dashed lines represent emission ( $\lambda_{\text{ex}} = 436$  nm).

On the other hand, the emission spectrum ( $\lambda_{\text{ex}} = 436$  nm) shows a characteristic asymmetric emission band maximizing near 557 nm (dashed blue line in Figure 1) with a shoulder at 590 nm. The emission for  $\mathbf{1}\bullet\text{NO}_3$  is red-shifted showing a new emission maximum at 617 nm (dashed red line in Figure 1). When  $\mathbf{1}\bullet\text{ClO}_4$  was exposed to 1.0 mM aqueous  $\text{NO}_3^-$  solution, a similar new band was observed at 608 nm (dashed yellow line in Figure 1). As in the case

of the absorption spectra, the new band at lower energy is attributed to a metal-metal-to-ligand charge-transfer MMLCT [ $d\sigma^*(\text{Pt})\text{-}\pi^*(\text{Cl-4-tpy})$ ] transition, further supporting extended  $\text{Pt}\cdots\text{Pt}$  interactions in both  $\mathbf{1}\bullet\text{NO}_3$  and  $\mathbf{1}\bullet\text{ClO}_4$  post aqueous  $\text{NO}_3^-$  exposure. We have previously shown that nano-structured platforms with high surface area (e.g. controlled porous glass (CPG) beads of pore sizes 383 Å) respond more rapidly.<sup>17,18</sup> Aqueous  $\text{NO}_3^-$  exposure of  $\mathbf{1}\bullet\text{ClO}_4$  encapsulated in the CPGs ( $\mathbf{1}\bullet\text{ClO}_4$ @CPG-383) produced similar optical changes, albeit with the expected faster response times, which is attributed to the surface area of the sample in the nano-structured environment.



**Figure 2.** Extended packing arrangements for (a)  $\mathbf{1}\bullet\text{ClO}_4$  and (b)  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$  ( $\text{ClO}_4^-$  and  $\text{NO}_3^- \cdot 2\text{H}_2\text{O}$  units omitted for clarity).  $\text{Pt}\cdots\text{Pt}$  stacking distances are shown in Å.

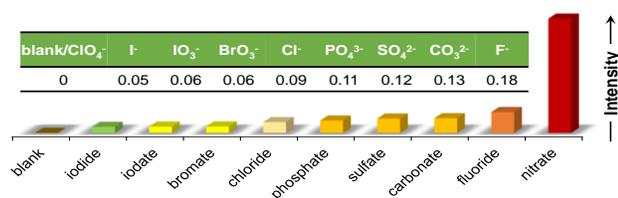
The cumulative observations of the colorimetric and luminescent changes in  $\mathbf{1}\bullet\text{ClO}_4$  upon exposure to aqueous  $\text{NO}_3^-$  suggests an alteration of the nearest neighbor  $\text{Pt}\cdots\text{Pt}$  interactions. One explanation for the observed changes is the incorporation of  $\text{NO}_3^-$  ions within the lattice as  $\text{ClO}_4^-$  is displaced. This anion replacement presumably perturbs stacking in the square planar Pt(II) units, and consequently alters the lowest lying MMLCT [ $d\sigma^*(\text{Pt})\text{-}\pi^*(\text{Cl-4-tpy})$ ] energy; this is expressed in the color and luminescence changes in the material.<sup>20,25,26</sup> Structural studies were undertaken to test this hypothesis and gain insight into the  $\text{Pt}\cdots\text{Pt}$  interactions.

Single crystal X-ray structures were determined for independently synthesized  $\mathbf{1}\bullet\text{ClO}_4$  and  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$  salts (Figure S1, Tables S2-S4). Yellow crystals of  $\mathbf{1}\bullet\text{ClO}_4$ , grown from a 1:1 water:acetone solution, show a lattice devoid of solvent and consisting of equally-spaced  $[\text{Pt}(\text{Cl-4-tpy})\text{Cl}]^+$  cations with long  $\text{Pt}\cdots\text{Pt}$  interaction distances, 4.169(3)Å, and highly-bent  $\text{Pt}\cdots\text{Pt}\cdots\text{Pt}$  angles, 106.28(1)° (Figure 2).<sup>27</sup> In contrast, orange-red crystals of  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$ , grown from acetone- $\text{HNO}_3$  solution, show incorporation of 2 molecules of water in the lattice. The nearest neighbor  $\text{Pt}\cdots\text{Pt}$  distances are shortened and alternate between 3.357(4)Å and 3.4018(4)Å and the  $\text{Pt}\cdots\text{Pt}\cdots\text{Pt}$  angle is essentially linear, 172.66(1)° (Figure 2).<sup>28</sup>

Powder X-ray diffraction (PXRD) measurements corroborate identification of the species generated during exposure of  $\mathbf{1}\bullet\text{ClO}_4$  to aqueous  $\text{NO}_3^-$  for a specified length of time, and therefore provides mechanistic insight. The diffractogram of powdered  $\mathbf{1}\bullet\text{ClO}_4$  measured post exposure to aqueous  $\text{NO}_3^-$  for 1 hour shows peaks of the starting  $\mathbf{1}\bullet\text{ClO}_4$  complex in addition to a set of new broad peaks. While retention of the parent peaks indicates incomplete conversion, the new peaks match the simulated diffraction pattern from  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$  single crystals (Figure S2). Thus, it can be concluded that exposure of  $\mathbf{1}\bullet\text{ClO}_4$  to aqueous  $\text{NO}_3^-$  anions leads to the substitution of the  $\text{ClO}_4^-$  with  $\text{NO}_3^-$  within the lattice structure.

To determine the structural fate of the complexes upon incorporation within the CPG, diffractograms were recorded on both  $\mathbf{1}\bullet\text{ClO}_4$ @CPG-383 and  $\mathbf{1}\bullet\text{NO}_3 \cdot 2\text{H}_2\text{O}$ @CPG-383 samples (Figure

**S2).** Both species are characterized by broad, amorphous silica peaks at  $2\theta = 21^\circ$ , along with several additional features. For the  $1\bullet\text{ClO}_4\text{@CPG-383}$  composite, the additional features match diffraction peaks in the pristine  $1\bullet\text{ClO}_4$  sample. Similarly, the additional features observed for  $1\bullet\text{NO}_3\bullet 2\text{H}_2\text{O@CPG-383}$  also match the pristine  $1\bullet\text{NO}_3\bullet 2\text{H}_2\text{O}$  peaks. This indicates that for both composites, the structural integrity of the starting Pt(II) salts remains preserved even after incorporation into the CPGs. Exposure of  $1\bullet\text{ClO}_4\text{@CPG-383}$  to aqueous  $\text{NO}_3^-$  results in  $\text{ClO}_4^- \rightarrow \text{NO}_3^-$  anion exchange as demonstrated by the PXRD profile showing peaks from both the starting complex as well as the freshly generated  $1\bullet\text{NO}_3\bullet 2\text{H}_2\text{O@CPG-383}$  species. Scanning electron micrographs on  $1\bullet\text{ClO}_4\text{@CPG-383}$  show microcrystalline deposits rich in Pt covering the CPG surface (Figure S4). This is similar to our observations in previous studies.<sup>18</sup> Magnified transmission electron micrographs demonstrate the microcrystals to comprise of hexagonal elongated rods with a seeming tendency to aggregate upon contact with aqueous  $\text{NO}_3^-$  (Figure S5). However, more detailed analysis of this phenomenon is required and is presently underway.

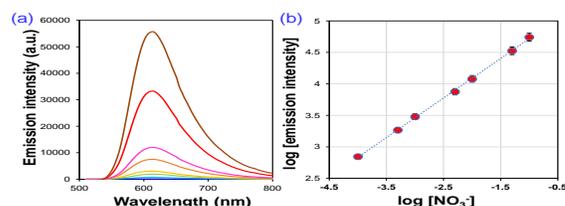


**Figure 3.** A bar chart comparing the maximum emission intensity of  $1\bullet\text{ClO}_4\text{@CPG-383}$  post exposure to 1.0 M aqueous solutions of different anions for 1 hour compared to 1.0 mM aqueous  $\text{NO}_3^-$  ( $\lambda_{\text{ex}} = 532$  nm). The inset table lists the selectivity factors calculated as the ratio of the maximum emission intensity measured in the presence of interfering anions to that observed in the presence of  $\text{NO}_3^-$ .

To qualitatively determine the selectivity for the  $\text{NO}_3^-$  anion over other anionic species, powdered  $1\bullet\text{ClO}_4$  was loaded onto CPG-383 beads (0.2 g, 2 wt%  $1\bullet\text{ClO}_4\text{@CPG-383}$ ) and separately exposed to a range of 1.0 M aqueous solutions of  $\text{I}^-$ ,  $\text{IO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{F}^-$  for 1 h. These anions were chosen as they are key anions present in environmental water matrices. The emission intensities ( $\lambda_{\text{ex}} = 532$  nm) of the exposed CPGs were compared with CPGs exposed to  $10^{-3}$  M  $\text{NO}_3^-$  for the same time period. Because practical matrices are expected to contain an overwhelming excess of interfering species compared to the target species, the concentrations of the interfering anions were deliberately chosen to be four orders of magnitude greater than aqueous  $\text{NO}_3^-$  concentrations with the objective of demonstrating the uniqueness of the targeted response of  $1\bullet\text{ClO}_4\text{@CPG}$  to the  $\text{NO}_3^-$  anion. The emission intensity responses of the  $1\bullet\text{ClO}_4\text{@CPG-383}$  composite post exposure to various anions is shown in Figure 3. As can be seen, there is an overwhelming response of the composite towards aqueous  $\text{NO}_3^-$ . The selectivity factor for the interfering anions (calculated as the ratio of the maximum emission intensities observed in the presence of interfering anions to that observed in the presence of  $\text{NO}_3^-$ ) range from 0.05 for  $\text{I}^-$  to 0.18 for  $\text{F}^-$ , confirming the high selectivity of  $1\bullet\text{ClO}_4$  for  $\text{NO}_3^-$  anion (Figure 3, inset, Figure S4).

As demonstrated in our previous works on anion quantification, luminescence spectroscopy was used for  $\text{NO}_3^-$  quantification.<sup>1,21</sup> In the test, equal amounts of  $1\bullet\text{ClO}_4\text{@CPG-383}$  were exposed to

aqueous solutions with different  $\text{NO}_3^-$  concentrations (1 mL of  $10^{-4}$  to 1 M). Three independent measurements were conducted for each concentration. Upon excitation at 532 nm,  $1\bullet\text{ClO}_4\text{@CPG-383}$  showed a weak asymmetric emission ( $\lambda_{\text{max}} = 566$  nm) with a shoulder at 604 nm, prior to  $\text{NO}_3^-$  exposure. Upon exposure to  $10^{-4}$  M aqueous  $\text{NO}_3^-$  for 15 mins, a broader asymmetric band centered at  $\sim 610$  nm was observed with a  $\sim 7$ -fold increase in emission intensity (Figure 4a). Further addition of aqueous  $\text{NO}_3^-$  (in 0.1 mL aliquots until 0.1 M) resulted in an increase in intensity (Figure 4a), and an emission maximum shifted to higher wavelength until a maximum was reached at 620 nm. The emission band also narrows at higher  $\text{NO}_3^-$  concentrations suggestive of an equilibrium shift to a single platinum species. The logarithm of luminescence intensity of the respective emission maxima was observed to increase linearly with the logarithm of nitrate concentration (Figure 4b).



**Figure 4.** (a) Luminescence spectra of  $1\bullet\text{ClO}_4\text{@CPG-383}$  upon exposure to varying concentrations of aqueous  $\text{NO}_3^-$  for 1 hour: (—) 0 M, (—)  $10^{-4}$  M, (—)  $5\times 10^{-4}$  M, (—)  $10^{-3}$  M, (—)  $5\times 10^{-3}$  M, (—)  $10^{-2}$  M, (—)  $5\times 10^{-2}$  M, (—)  $10^{-1}$  M ( $\lambda_{\text{ex}} = 532$  nm), (b) logarithmic plot of the maximum emission intensity ( $\lambda_{\text{max}} = 605$  nm) of  $1\bullet\text{ClO}_4\text{@CPG-383}$  versus the concentration of solution  $\text{NO}_3^-$  in solution. The error bars are obtained from standard deviations based on three independent measurements.

The limit of detection (LOD) was calculated from the log-log plot based on the IUPAC recommended Equation 1 reported by Long et al.<sup>29</sup>

$$DL = \frac{k \cdot S_b}{m} \quad [1]$$

Here, DL is the detection limit, k is a numerical constant, m is the slope of the linear region of the plot, and  $S_b$  is the standard error for the blank measurements. Per IUPAC recommendations, a k value of 3 was applied, which corresponds to a 99.87% confidence level. Based on this, a detection limit of  $0.046 \pm 0.005$  mM ( $2.85 \pm 0.31$  ppm) is obtained, significantly lower than the ambient water quality limit of 0.16 mM (10 ppm) set by US-EPA.

The ability of the  $1\bullet\text{ClO}_4\text{@CPG-383}$  composite to detect aqueous  $\text{NO}_3^-$  from a complex multicomponent matrix was tested using groundwater samples spiked with varying concentrations of  $\text{NO}_3^-$  via standard additions such that the cumulative  $\text{NO}_3^-$  concentrations ranged from  $5\times 10^{-3}$  to  $7.5\times 10^{-2}$  M, as determined by independent ion chromatography (IC) measurements. Although the emission profile is observed to be broader as compared to DI water, a proportional rise in emission intensity with increase in  $\text{NO}_3^-$  concentrations was observed (Figure S5, left panel). The logarithm of luminescence intensity of the respective emission maxima showed a linear increase with the logarithm of total nitrate concentration (Figure S5, right panel), similar to DI water. The slope of the response in the groundwater differs from that of DI water, presumably the groundwater matrix perturbs the electronic structure of the  $1\bullet\text{ClO}_4$  salt differently. Despite the differences, it is

possible to determine the  $\text{NO}_3^-$  concentration from the log-log plot. The  $\text{NO}_3^-$  concentration in groundwater was determined to be  $4.4 \pm 0.3$  mM, consistent with a value of 5.1 mM as determined from independent IC measurements.

Leaching studies performed on both the yellow  $\mathbf{1} \cdot \text{ClO}_4$  and the red  $\mathbf{1} \cdot \text{NO}_3 \cdot 2\text{H}_2\text{O}$  salts @CPG upon prolonged contact with DI water, showed a 4–7% mass loss of the materials over 2 days indicated by optical spectroscopy. While the rate of loss is not significant in the context of rapid sensing applications, efforts are underway to understand and improve the salt retention into the CPG matrix.

This investigation demonstrates the use of a solid-state material for the unambiguous rapid and selective detection of  $\text{NO}_3^-$  in aqueous solution without the requirement of additives, and offers the potential for a new sensor compatible with field deployment. The accumulated evidence establishes that the colorimetric and luminescence response of  $\mathbf{1} \cdot \text{ClO}_4$  to aqueous  $\text{NO}_3^-$  is a consequence of a contraction of the intermolecular Pt...Pt distances exhibiting stronger interactions that results from  $\text{ClO}_4^-/\text{NO}_3^-$  anion exchange. It is presumable that the energy requirements for the molecular rearrangement in going from  $\mathbf{1} \cdot \text{ClO}_4$  to  $\mathbf{1} \cdot \text{NO}_3 \cdot 2\text{H}_2\text{O}$  is compensated by the non-covalent interactions in  $\mathbf{1} \cdot \text{NO}_3 \cdot 2\text{H}_2\text{O}$ . This is presumably due to the steric and electronic complementarity of  $\mathbf{1} \cdot \text{ClO}_4$  towards aqueous  $\text{NO}_3^-$  anions makes this salt suitable for  $\text{NO}_3^-$  sensing. Therefore, it is worth acknowledging that in the vast literature on luminescent Pt(II) complexes, there might be additional salts with similar attributes that are also optimally suitable for  $\text{NO}_3^-$  sensing.

This research was supported by (1) the National Science Foundation (CHE-1152853), (2) a US EPA STAR, FP-91765901 to A.E.N., and (3) the Laboratory Directed Research and Development Program at the Pacific Northwest National Laboratory (PNNL) (S.C.). PNNL is operated by Battelle for the U.S. DOE under Contract DE-AC05-76RL01830. Single crystal data was collected through SCrALS, Beamline 11.3.1, Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. ALS is supported by the U.S. DOE, Office of Energy Sciences Materials Sciences Division, under Contract DE-AC02-05CH11231. We thank Dr. Garry Hanon for helping with resources.

### Conflicts of interest

There are no conflicts to declare.

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