Supplementary Material (ESI) for Analytical Methods

Selective Detection of Cr(VI) in Aqueous Media by Carbazole-Based Fluorescent Organic Microcrystals

Karasinghe A. N. Upamali, Leandro A. Estrada and Douglas C. Neckers

Center for Photochemical Sciences, Bowling Green State University,
132 Overman Hall, Bowling Green, Ohio, 43403, USA.

Table of Contents

Page

A. Experimental Section .................................................................................................................. 1

A.1. General Information ............................................................................................................. 1

A.2. Electrochemistry ................................................................................................................... 2

B. Supporting Figures .................................................................................................................. 2

B.1. Selectivity towards detection of Cr(VI) in water ............................................................... 2-3

B.2. Selectivity towards detection of Cr(VI) in Bowling Green tap water .............................. 3-9

B.3. Detection of Cr(VI) in pH-7 and ground water ................................................................. 10

B.4. Cyclic voltammetry of CN-CPE in 0.1M TBAP/DCM solution ........................................ 11

C. References .............................................................................................................................. 11

A. Experimental Section.

A.1. General Information. CN-CPE was synthesized and fully characterized previously.¹

Microcrystal suspension of CN-CPE was prepared via reprecipitation. UV-Vis absorption
spectra were recorded using a double beam spectrophotometer accurate to ±0.1 nm. Fluorescence
spectra were recorded using a conventional spectrofluorimeter, where emission lifetimes were measured using a pulsed nano-LED operating at 370 nm. Fluorescence decays were monitored at the corresponding wavelength of the emission maximum of the solution. In-built software allowed the fitting of the decay spectra ($\chi^2 = 1.0-1.5$) which yielded the fluorescence lifetime. The pH of the water samples were measured by a conventional electronic pH-meter.

**A.2. Electrochemistry.** Cyclic voltammograms were performed in dichloromethane using 0.1M tetrabutyl-ammonium perchlorate (TBAP) as a supporting electrolyte. Freshly distilled HPLC grade dichloromethane was used for electrochemistry measurement. TBAP was previously recrystallized from methanol, and dried under vacuum. A conventional 3-electrode system was used: platinum working electrode (1.6 mm diameter), platinum wire auxiliary electrode, and non-aqueous Ag/Ag$^+$ reference electrode ([Ag$^+$]=0.01M). Concentration of CN-CPE was 1.0mM.

**B. Supporting Figures**

**B.1. Selectivity towards detection of Cr(VI) in water.**

![Figure S1. CN-CPE microcrystal suspension in the absence and presence of anions (250µM):](image)

From left to right; no anion, CrO$_4^{2-}$, AsO$_4^{3-}$, NO$_2^-$, NO$_3^-$, Br$^-$, Cl$^-$, Br$^-$, ClO$_4^-$, SO$_4^{2-}$, PO$_4^{3-}$, HCO$_3^-$ and CH$_3$CO$^-$, Cr(III).
Figure S2. Stern-Volmer plot of fluorescence quenching of CN-CPE acetone-water (4:6) mixture and acetone only solution by chromate (Concentration of CN-CPE = 10µM).

B.2. Selectivity towards detection of Cr(VI) in Bowling Green tap water.

Figure S3. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE acetone-water (4:6) mixture (tap water) by chromate (Concentration of CN-CPE = 10µM). (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture (tap water).
Figure S4. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by acetate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

Figure S5. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by phosphate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.
**Figure S6.** (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by chloride. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

**Figure S7.** (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by nitrate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.
Figure S8. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by bicarbonate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

Figure S9. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by sulfate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.
Figure S10. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by arsenate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

Figure S11. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by bromide. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.
Figure S12. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by perchlorate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

Figure S13. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by iodide. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.
Figure S14. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by nitrite. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

Figure S15. (A) Stern-Volmer plots of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by Cr(III). (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.
B.3. Detection of Cr(VI) in pH-7 and ground water.

**Figure S16.** (A) Stern-Volmer plot of fluorescence quenching of CN-CPE acetone-water (4:6) mixture (pH 7 buffer) by chromate (Concentration of CN-CPE = 10µM). (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture (pH 7 buffer).

**Figure S17.** Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (ground water) by chromate.
B.4. Cyclic voltammetry of CN-CPE in 0.1M TBAP/DCM solution.

![Cyclic voltammograms of CN-CPE with 0.1M TBAP in dichloromethane.](image)

**Figure S18.** Cyclic voltammograms of CN-CPE with 0.1M TBAP in dichloromethane.

C. References