

Supplementary Material (ESI) for Analytical Methods

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

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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.

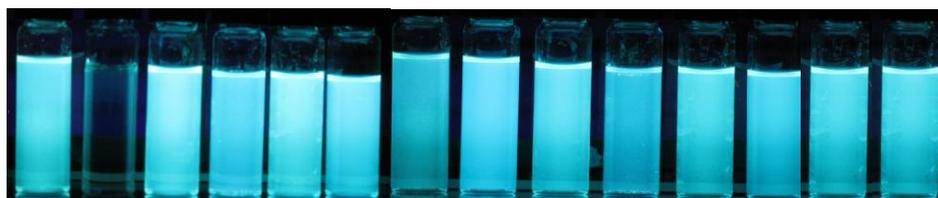


Figure S1. CN-CPE microcrystal suspension in the absence and presence of anions (250 μ M) :
From left to right; no anion, CrO₄²⁻, AsO₄³⁻, NO₂⁻, NO₃⁻, Br⁻, Cl⁻, I⁻, ClO₄⁻, SO₄²⁻, PO₄³⁻,
HCO₃⁻ and CH₃CO⁻, Cr(III).

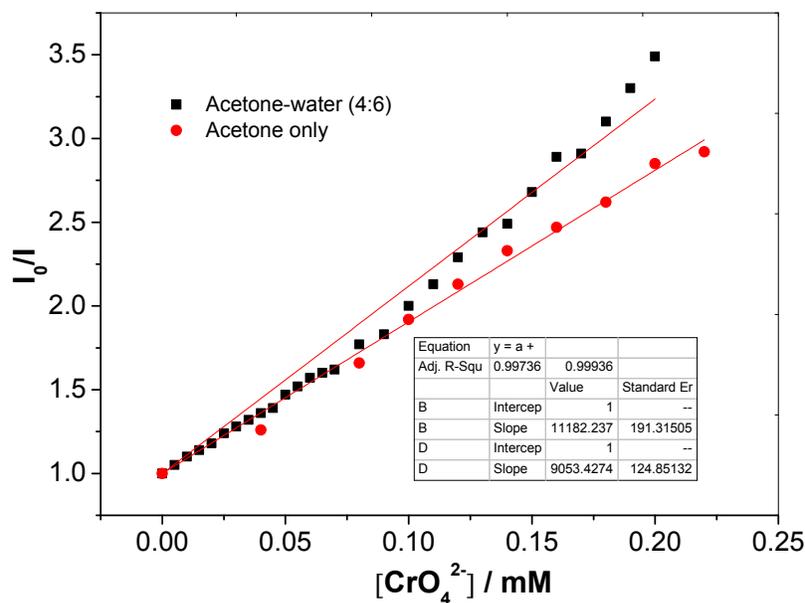


Figure S2. Stern-Volmer plot of fluorescence quenching of CN-CPE acetone-water (4:6) mixture and acetone only solution by chromate (Concentration of CN-CPE = 10 μ M).

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

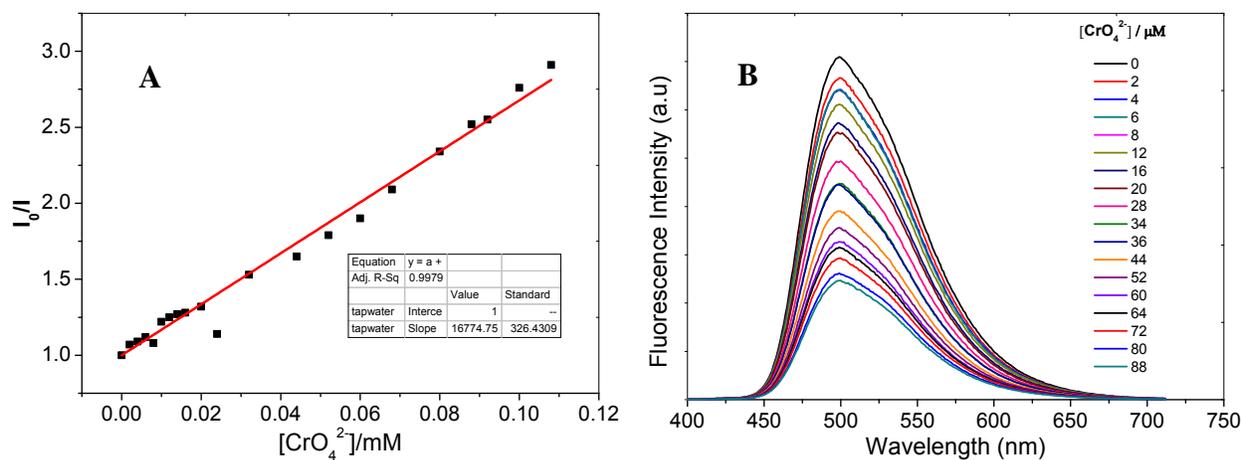


Figure S3. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE acetone-water (4:6) mixture (tap water) by chromate (Concentration of CN-CPE = 10 μ M). (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture (tap water).

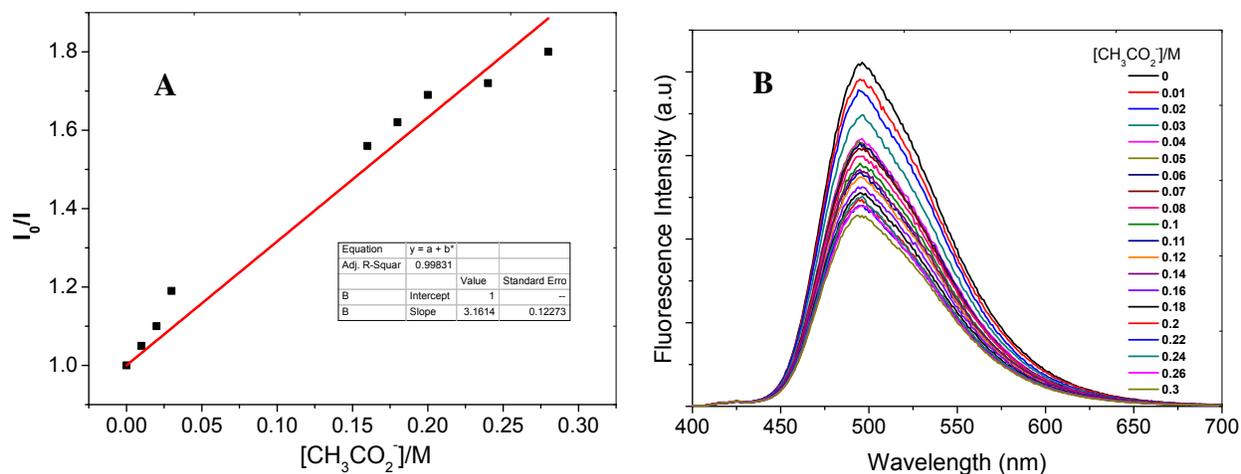


Figure S4. (A). Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by acetate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

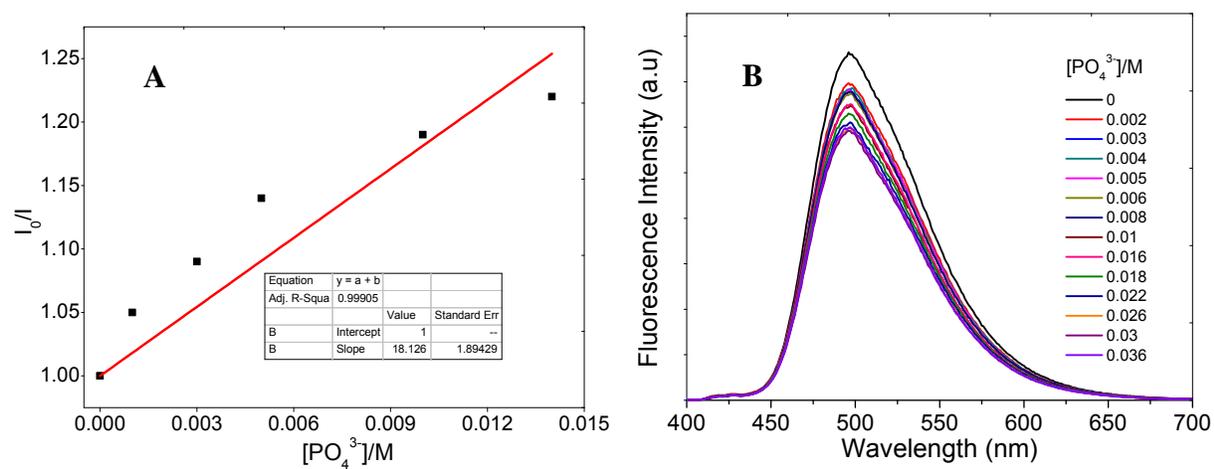


Figure S5. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by phosphate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

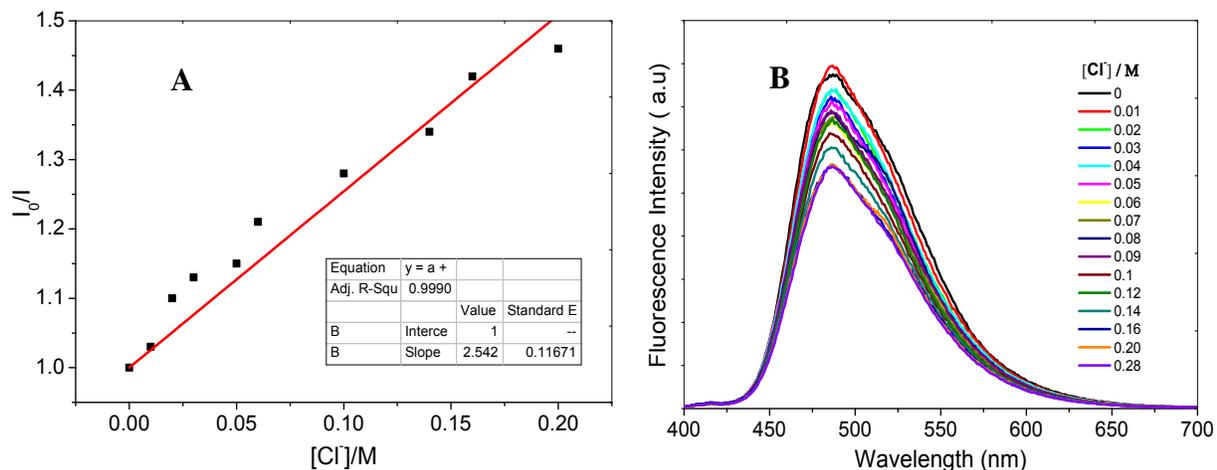


Figure S6. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by chloride. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

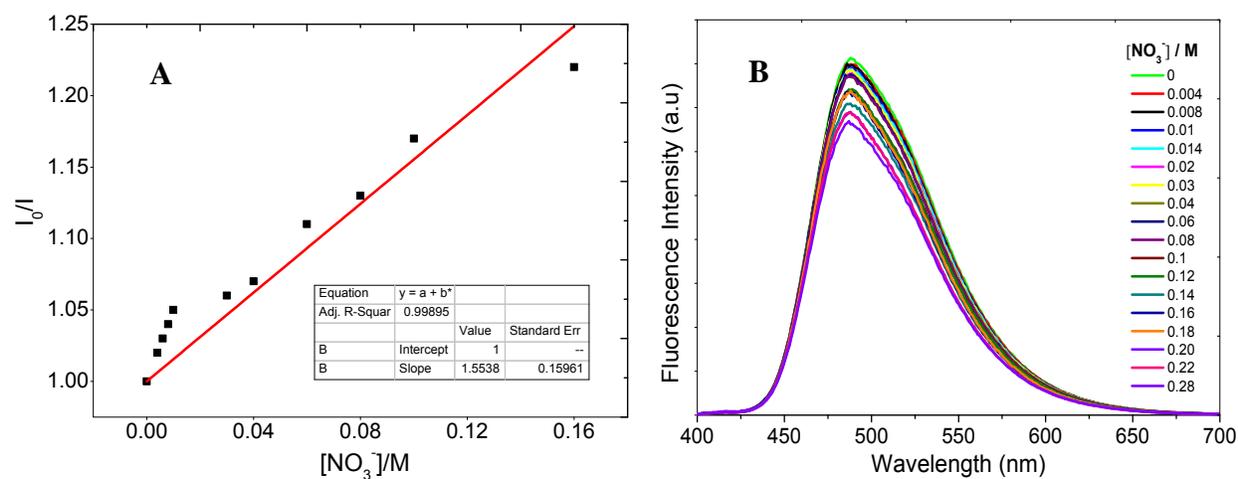


Figure S7. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by nitrate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

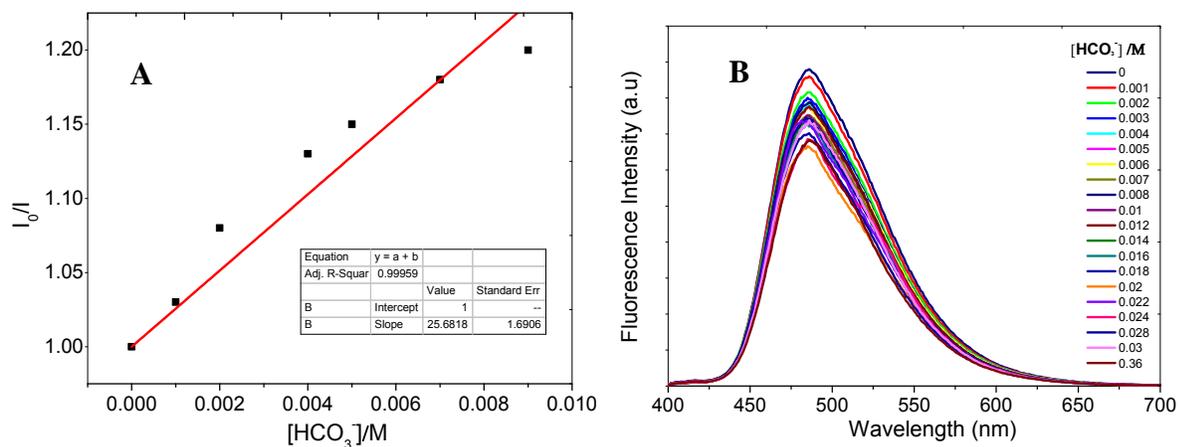


Figure S8. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by bicarbonate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

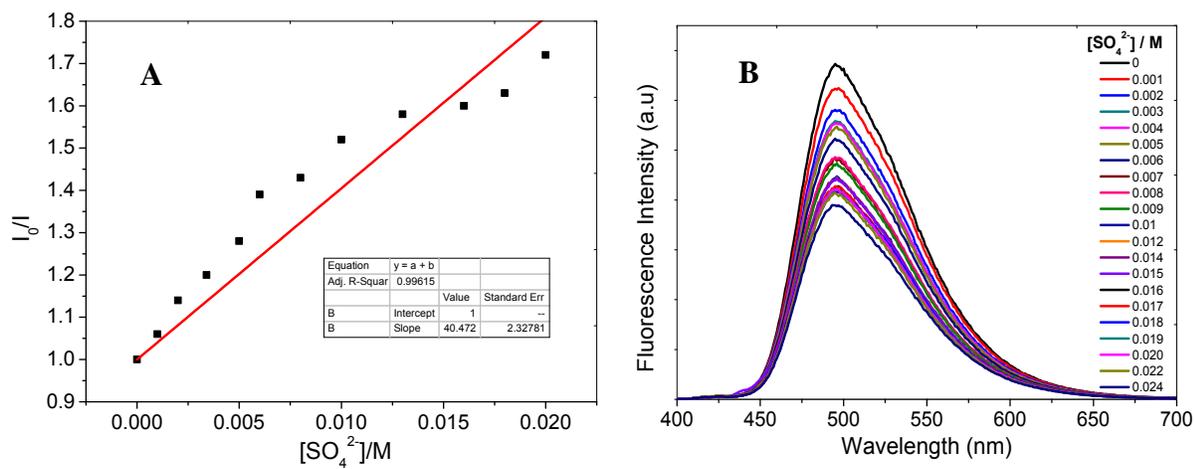


Figure S9. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by sulfate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

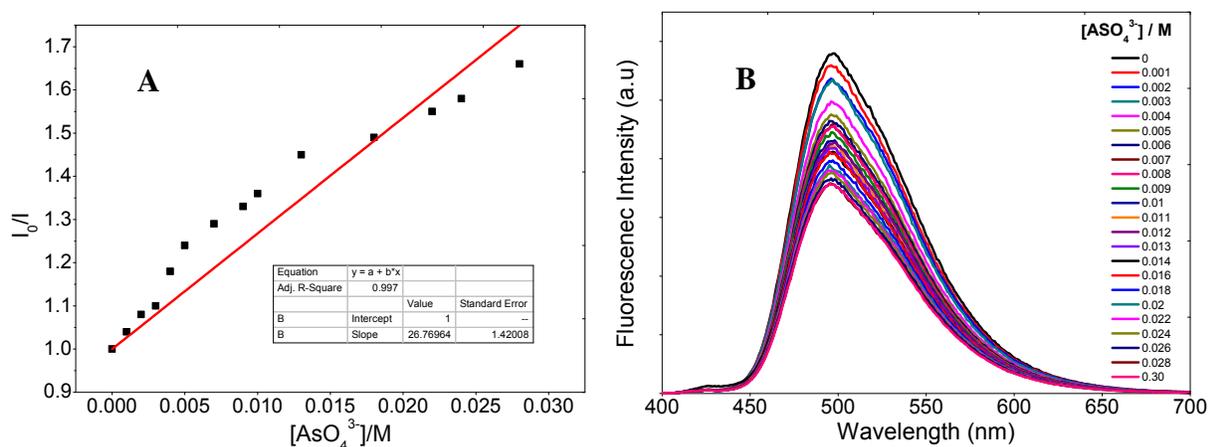


Figure S10. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by arsenate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

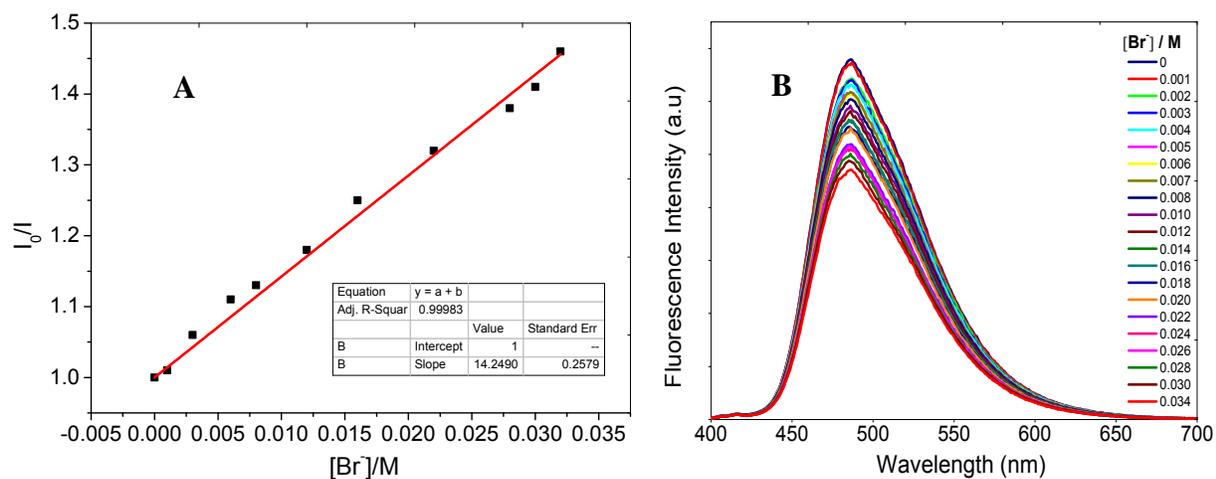


Figure S11. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by bromide. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

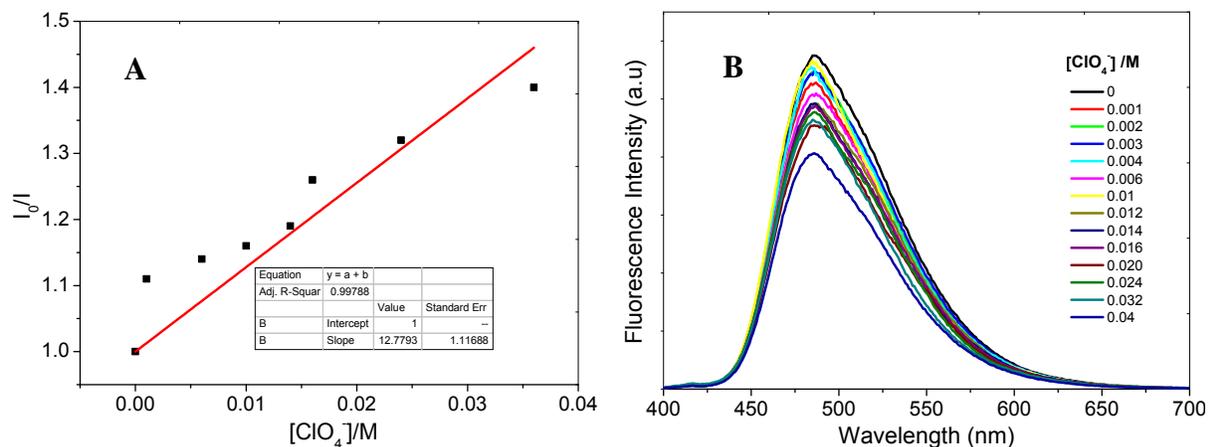


Figure S12. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by perchlorate. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

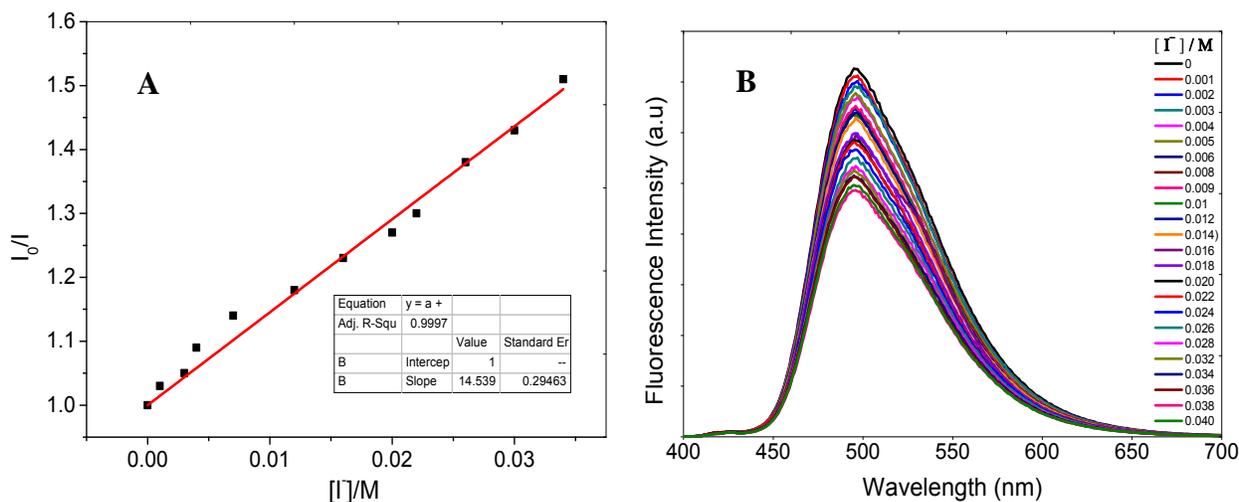


Figure S13. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by iodide. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

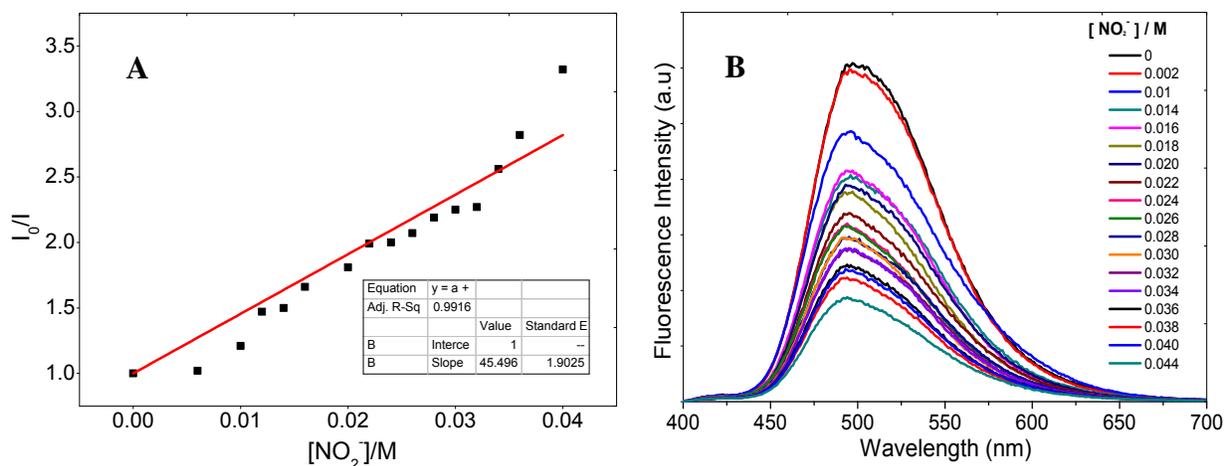


Figure S14. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by nitrite. (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

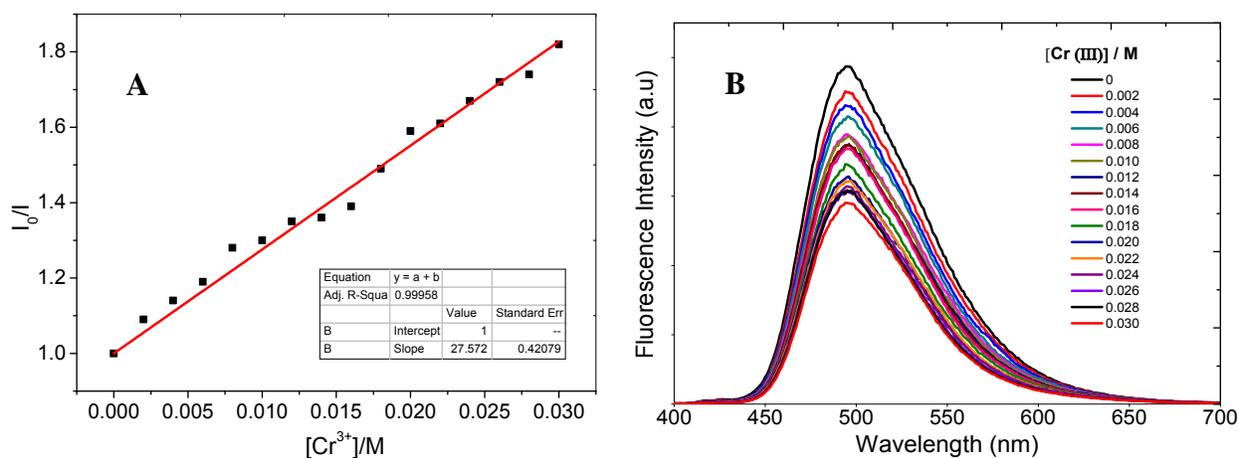


Figure S15. (A) Stern-Volmer plots of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (tap water) by Cr(III). (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture.

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

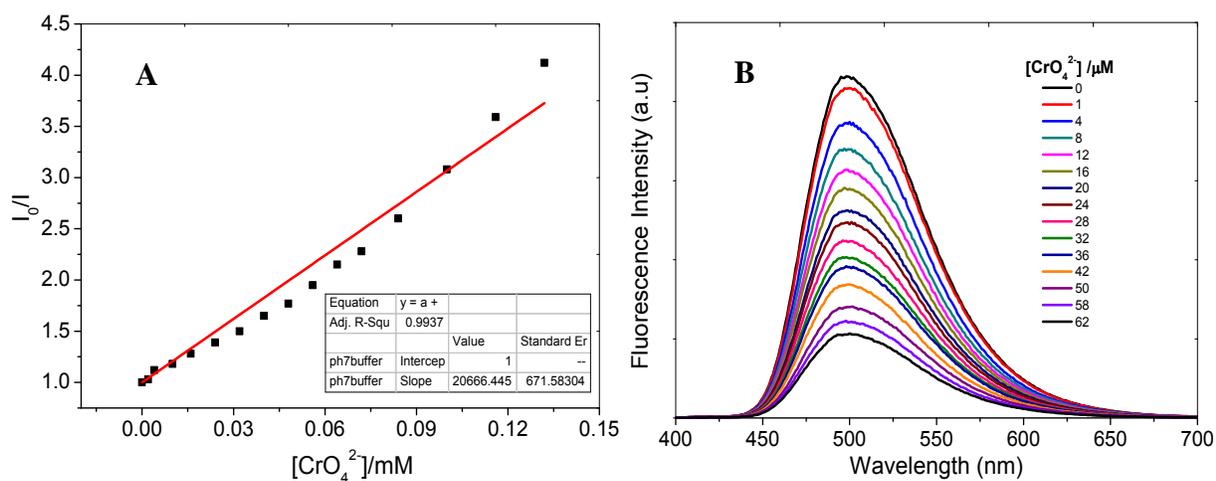


Figure S16. (A) Stern-Volmer plot of fluorescence quenching of CN-CPE acetone-water (4:6) mixture (pH 7 buffer) by chromate (Concentration of CN-CPE = 10 μM). (B) Corresponding fluorescence quenching spectra of CN-CPE in acetone-water mixture (pH 7 buffer).

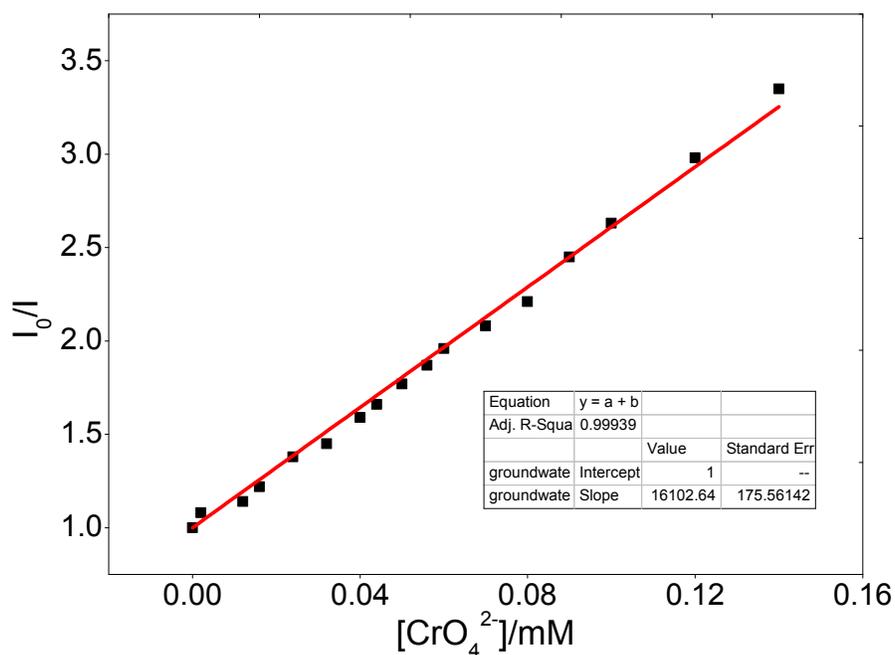


Figure S17. Stern-Volmer plot of fluorescence quenching of CN-CPE in acetone-water (4:6) mixture (ground water) by chromate.

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

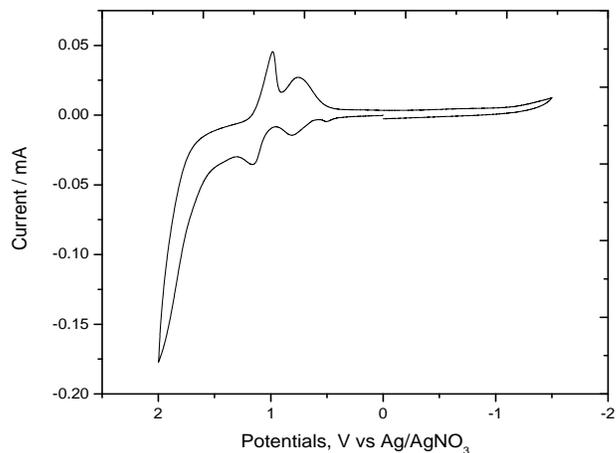


Figure S18. Cyclic voltammograms of CN-CPE with 0.1M TBAP in dichloromethane.

C. References

- ¹ K. A. N. Upamali, L. A. Estrada, P. K. De, X. Cai, J. A. Krause, D. C. Neckers, *Langmuir*, **2011**, *27*, 1573.