Electronic Supplementary Material (ESI) for Environmental Science: Nano.


# Supplementary Information

## Ratiometric Detection of Heavy Metal Ions Using Fluorescent Carbon Dots

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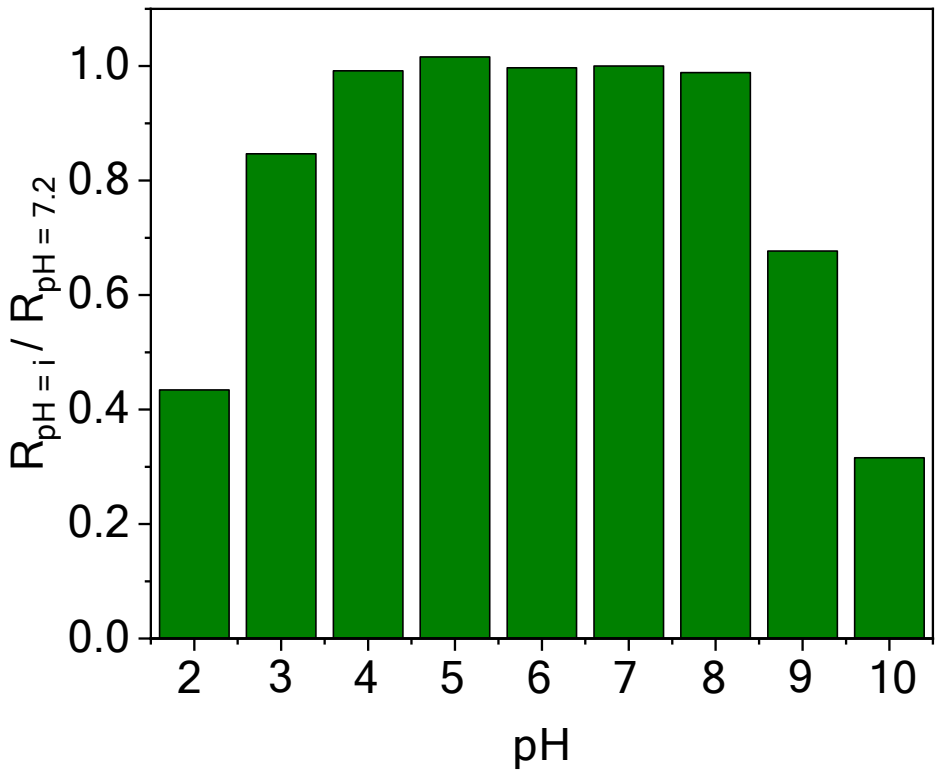


**Figure S1.** Relative red-to-blue fluorescence ratio of CD colloidal dispersions at different pH levels. It is noted that the ratios do not change significantly between pH 4 - 8.

**Table S1**. Quenching assay protocol for all metals used.

| Run | Concentration of metal solution (M) | Volume added to cuvette (µL) | Concentration in cuvette (nM) |
|---|---|---|---|
| **Q1** | 0.000001 | 3.0 | 1 |
| **Q2** | 0.0001 | 2.4 | 81 |
| **Q3** | 0.0001 | 2.4 | 161 |
| **Q4** | 0.0001 | 2.4 | 241 |
| **Q5** | 0.0001 | 2.4 | 321 |
| **Q6** | 0.0001 | 2.4 | 401 |
| **Q7** | 0.0001 | 2.4 | 481 |
| **Q8** | 0.0001 | 2.4 | 561 |
| **Q9** | 0.0001 | 2.4 | 641 |
| **Q10** | 0.0001 | 2.4 | 721 |
| **Q11** | 0.0001 | 2.4 | 801 |
| **Q12** | 0.0001 | 2.4 | 881 |
| **Q13** | 0.0001 | 2.4 | 961 |
| **Q14** | 0.1 | 60 | 2000000 |

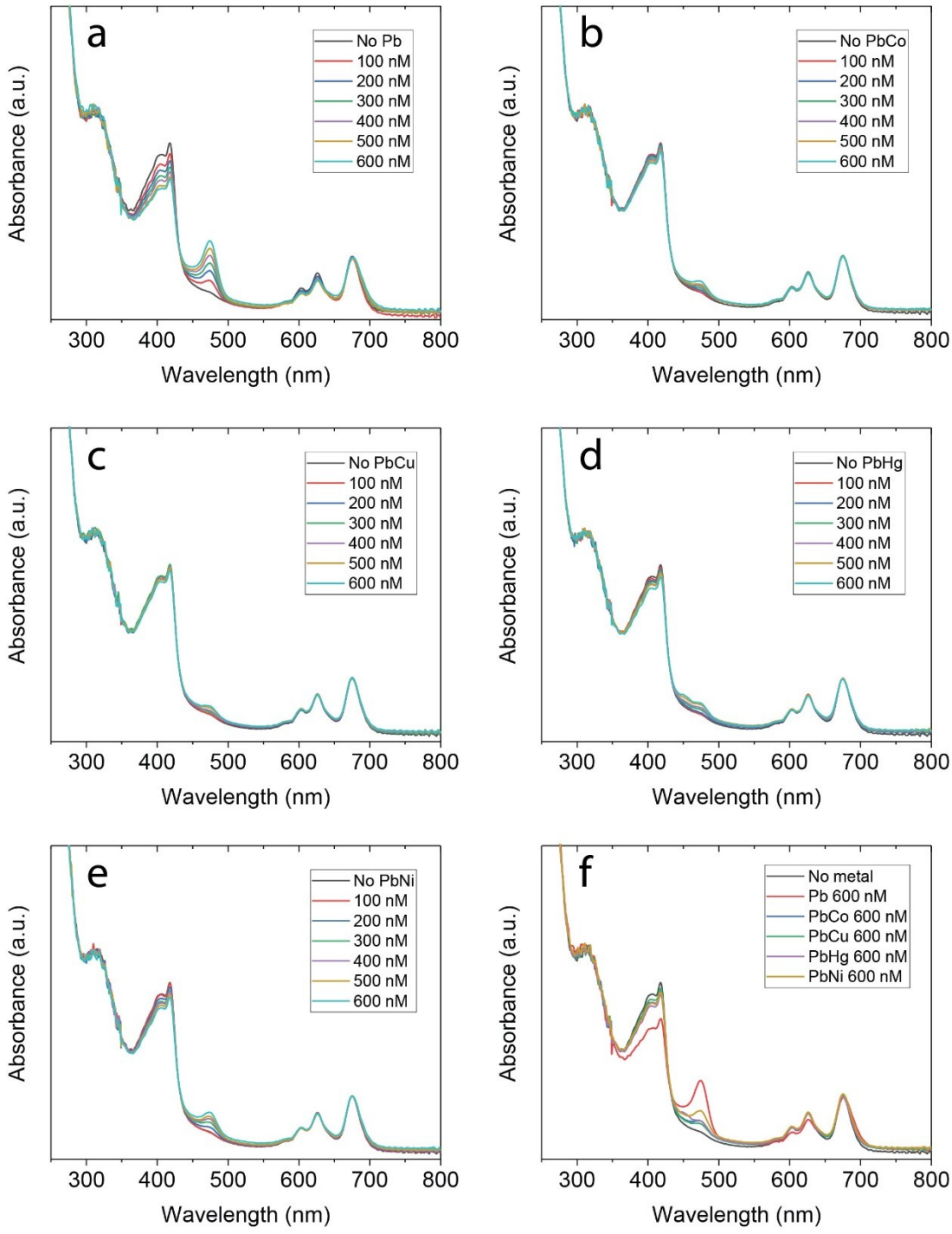


**Figure S2**. Heavy metal monitoring with a 50 µg/mL dispersion of CD through absorbance spectroscopy in the range 100-600 nM (a) Quantitation of $Pb^{2+}$ (b) Assay of a mixture of $Pb^{2+}$ and $Co^{2+}$ (c) Assay of a mixture of $Pb^{2+}$ and $Cu^{2+}$ (d) Assay of a mixture of $Pb^{2+}$ and $Hg^{2+}$ (e) Assay of a mixture of $Pb^{2+}$ and $Ni^{2+}$ (f) Overlaid spectra of the different mixture of ions at 600 nM.

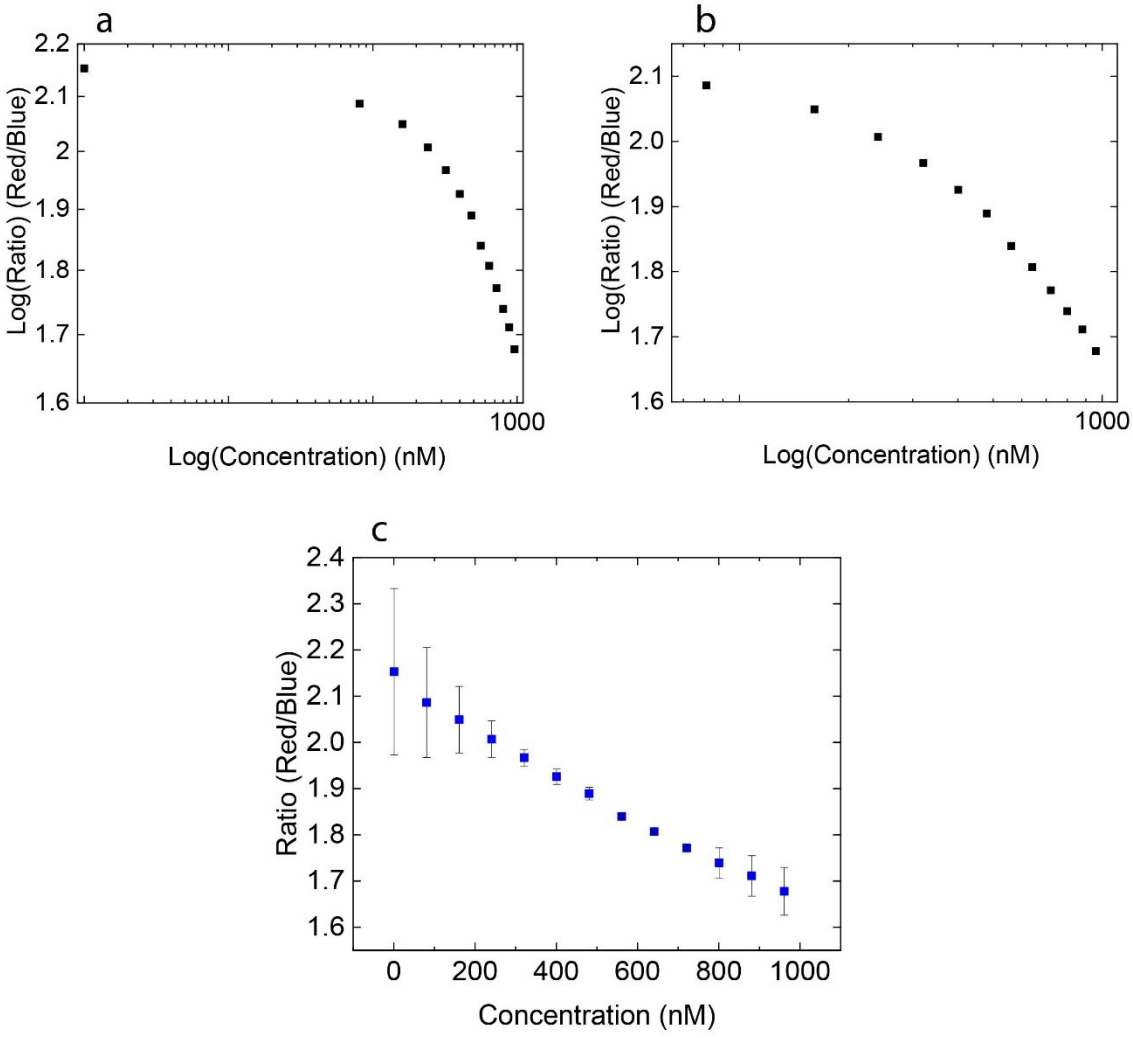


**Figure S3**. (a) Log-log plot for the $Pb^{2+}$ calibration curve; (b) Log-log plot for the $Pb^{2+}$ calibration curve excluding the first measurement; (c) Calibration curve for the quenching assays for $Pb^{2+}$ (in triplicates), which shows the relative standard deviation at each point of the calibration. It is noted that there is a deviation from linearity at the first concentration point (1 nM) (Fig S3a) for the calibration curve over the entire concentration range. When excluding the first point of the calibration curve (as shown in Fig. S3b), a more linear trend is observed. Therefore, since the measurements of this system diverge from an ideal behavior at low concentrations, a study on how the ratio of each of the points varied from assay to assay was carried out (Fig S3c). This figure depicts the fluctuation of the ratio from the calibration curves of the standard measurements at each concentration. At very low concentrations there is an 8% variation in measurements. Likewise, above the LOD of 37.1 nM, a variation of 1 to 3% is expected.

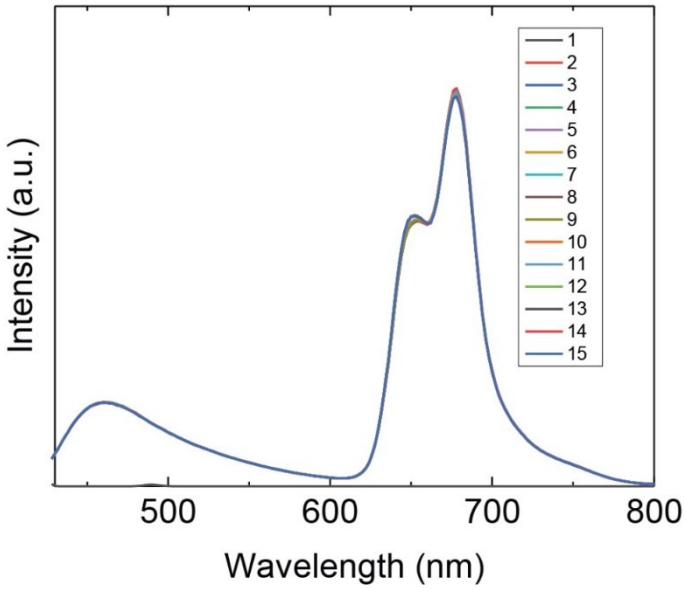


**Figure S4.** Control sample containing a 50 μg/mL dispersion of CDs, which experienced the same light irradiation as the one containing the metal ions: fifteen fluorescence measurements of 30 seconds each at $\lambda_{ex}$= 420 nm, absorbance measurement and three lifetime measurements at 368 nm. No significant photobleaching can be observed for the timescales of our measurements.

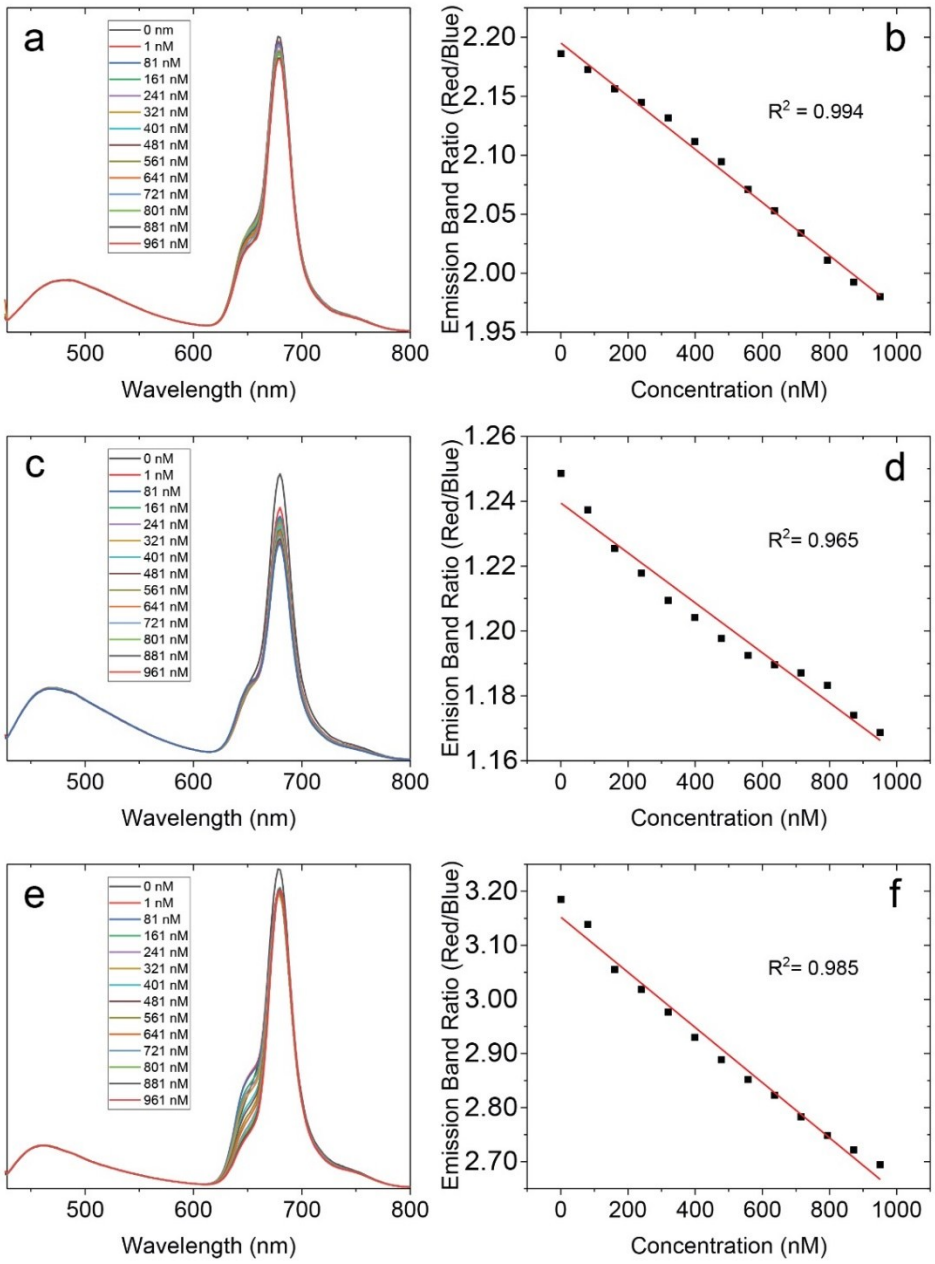


**Figure S5**. Fluorescence monitoring of heavy metal ions: Quantitation of (a,b) $Hg^{2+}$, (c,d) $Co^{2+}$, and (e,f) $Fe^{3+}$ in the range 1-961 nM using the CDs via ratiometric measurements of blue and red fluorescence.

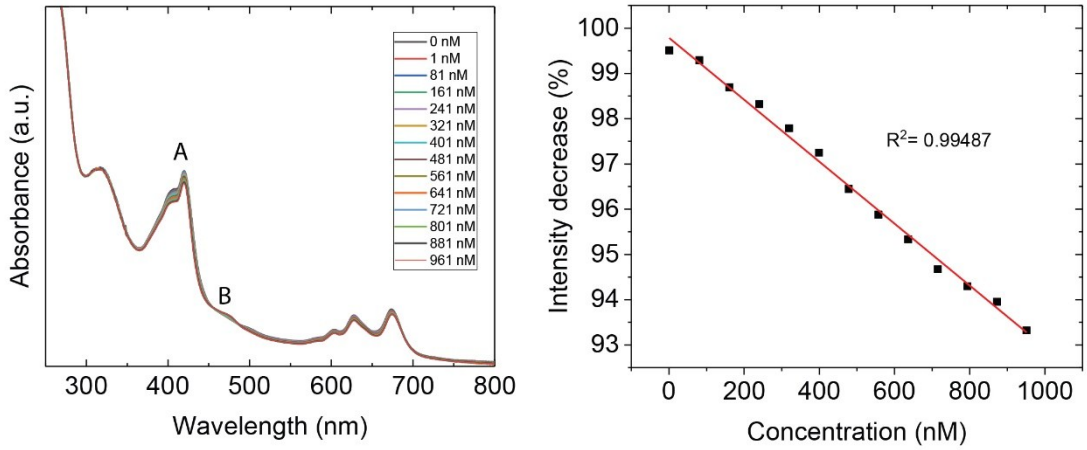


**Figure S6**. (a) Quantitation of $Hg^{2+}$ in the 1-961 nM range through absorbance spectroscopy via decreasing of peak A and increasing peak B.

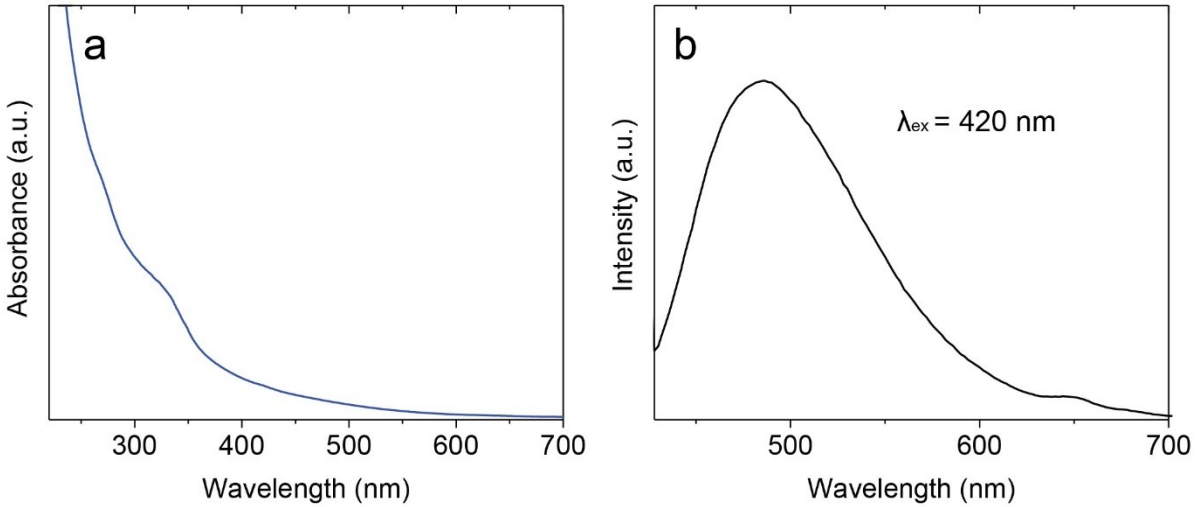


**Figure S7**. Optical characterization of a 50 µg/mL dispersion of bCDs in water; (a) Absorbance spectrum with maximum absorbance at 330 nm; (b) Fluorescence spectrum with maximum intensity centered at 485 nm

**Table S2.** Lifetime measurements for the different metal ions throughout the concentration range 1-961 nM.

*No filter $Hg^{2+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.76 (39%) | 4.49 (46%) | 4.81 (47%) |
| **2** | 0.20 (61%) | 0.19 (54%) | 0.24(53%) |

*Bandpass filter $Hg^{2+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.65 | 4.71 | 4.70 |

*No filter $Fe^{3+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.44 | 4.31 | 4.53 |
| **2** | 0.63 | 0.71 | 0.69 |

*Bandtpass filter $Fe^{3+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.56 | 4.41 | 4.65 |

*No filter $Co^{2+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.93 | 4.73 | 4.99 |
| **2** | 0.62 | 0.58 | 0.60 |

*Bandpass filter $Co^{2+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.97 | 4.73 | 4.96 |

*No filter $Pb^{2+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.65 | 4.61 | 4.62 |
| **2** | 0.42 | 0.40 | 0.41 |

*Bandpass filter $Pb^{2+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 481 nM (ns) | Lifetime at 961 nM (ns) |
|---|---|---|---|
| **1** | 4.70 | 4.71 | 4.70 |

**Table S3.** Lifetime measurements for bCDs upon the addition of $Pb^{2+}$ throughout the concentration range 100-3000 μM.

*No filter bCD $Pb^{2+}$*

| Lifetime number | Lifetime at 0 nM (ns) | Lifetime at 100 μM (ns) | Lifetime at 200 μM (ns) | Lifetime at 600 μM (ns) | Lifetime at 1 mM (ns) | Lifetime at 2 mM (ns) | Lifetime at 3 mM (ns) |
|---|---|---|---|---|---|---|---|
| **1** | 3.95 | 3.74 | 3.46 | 3.60 | 3.36 | 3.28 | 3.00 |