

# Finding Value in Wastewaters from the Cork Industry: Carbon Dots Synthesis and Fluorescence for Hemeprotein Detection

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## Supplementary Materials

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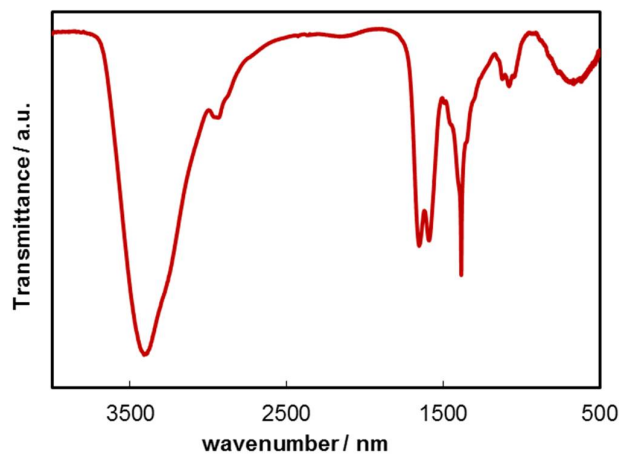


Figure S1. FTIR spectrum of C-dots.

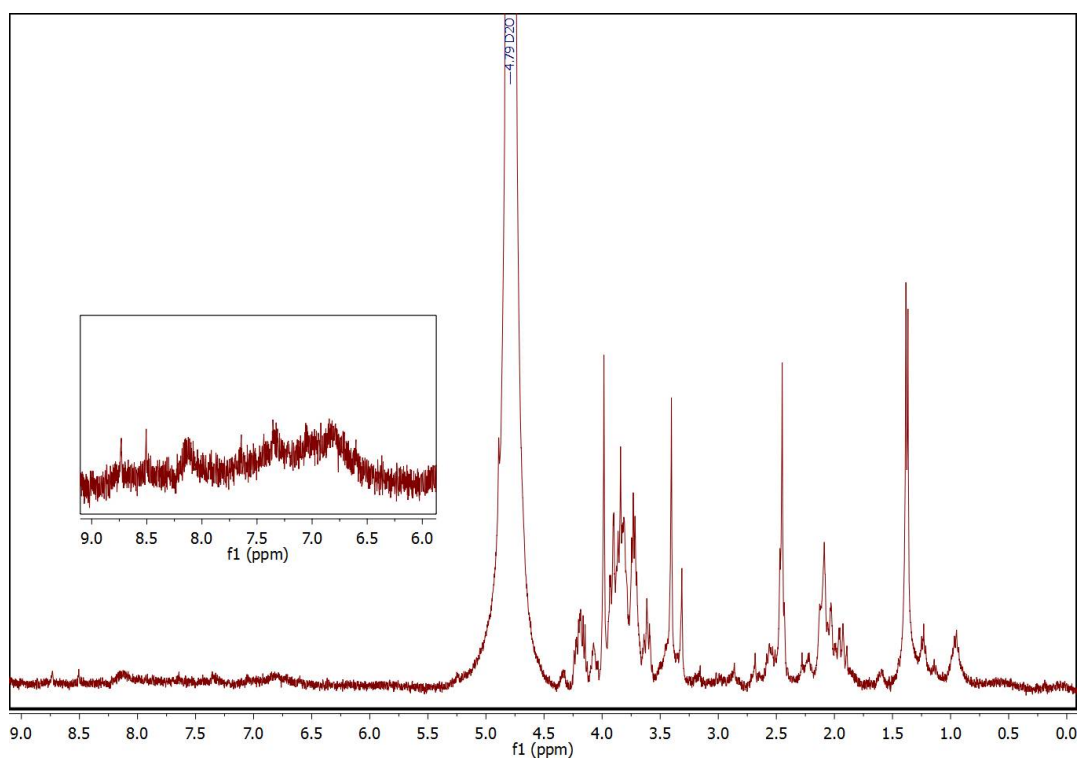


Figure S2. <sup>1</sup>H-NMR spectrum of C-dots (400 MHz, D<sub>2</sub>O, 25 °C).

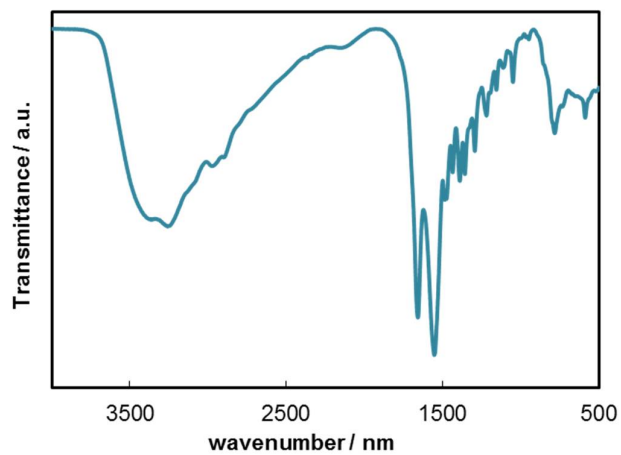


Figure S3. FTIR spectrum of C-dots/CA.

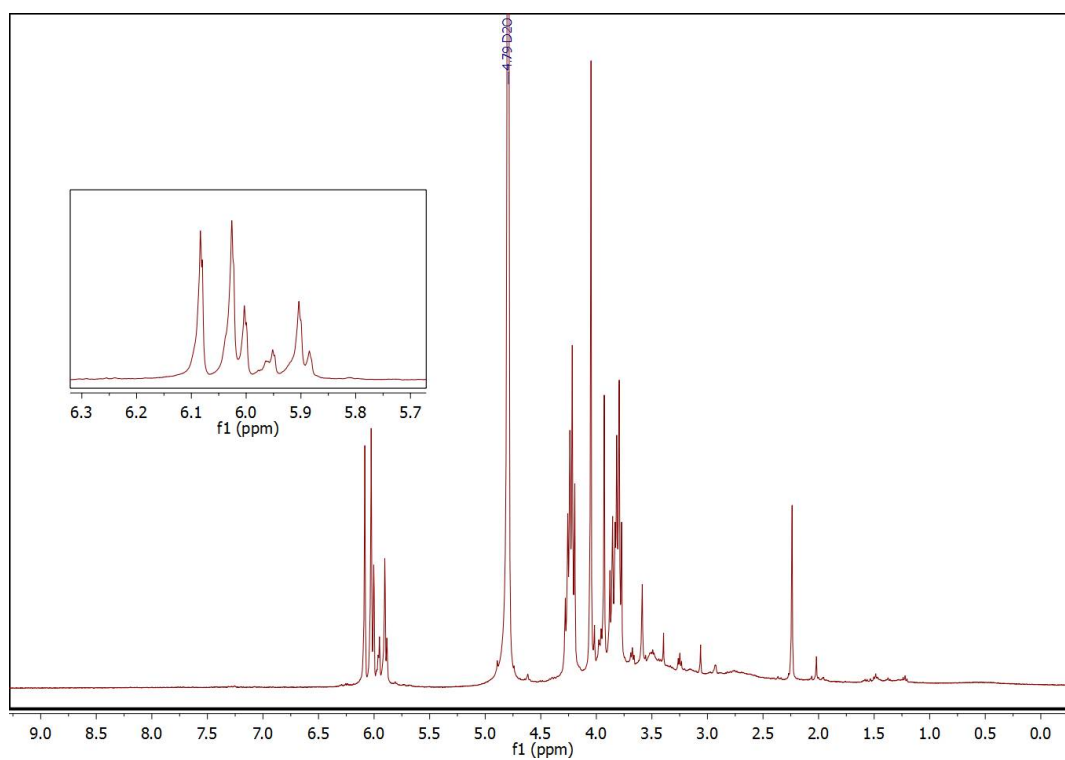
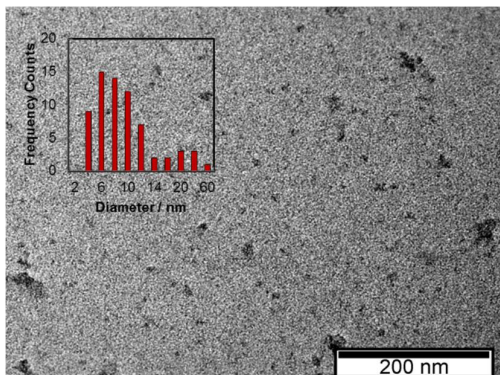
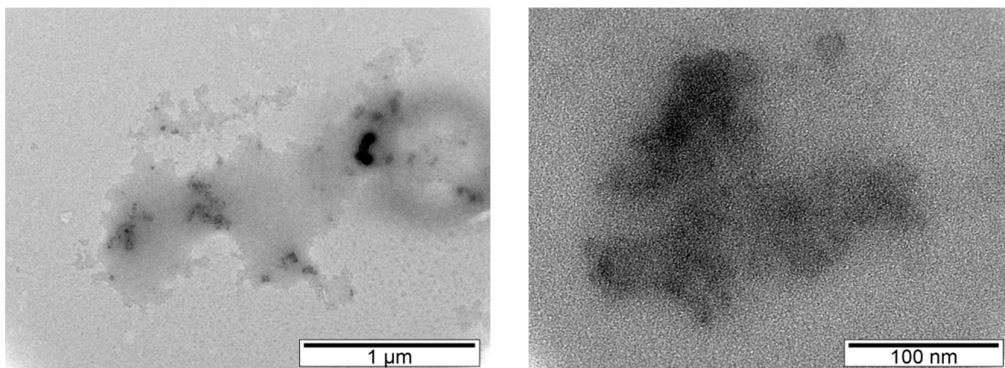


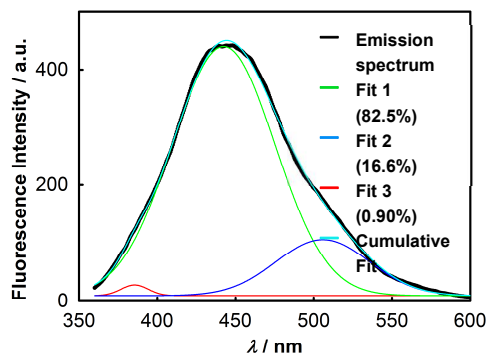
Figure S4. <sup>1</sup>H-NMR spectrum of C-dots/CA (400 MHz, D<sub>2</sub>O, 25 °C).



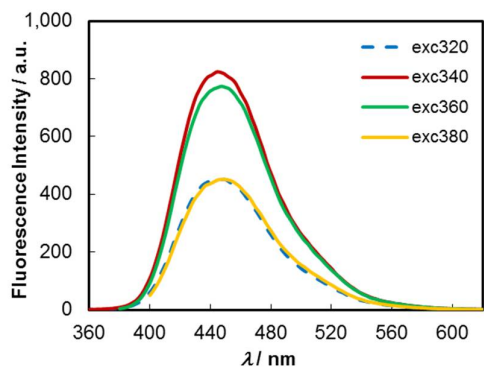
**Figure S5.** TEM images of C-dots prepared from CIWW at 200 °C during 8 h.



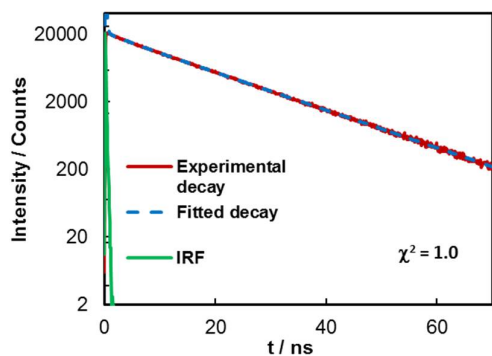
**Figure S6.** TEM images of C-dots/CA prepared from CA and ED at 175 °C for 4 h.



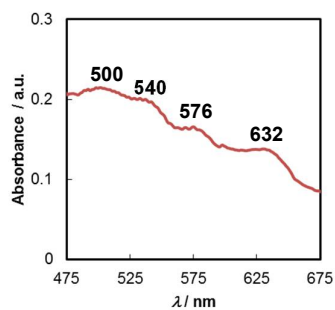
**Figure S7.** Spectral deconvolution of emission spectrum of C-dots ( $\lambda_{exc} = 340$  nm).



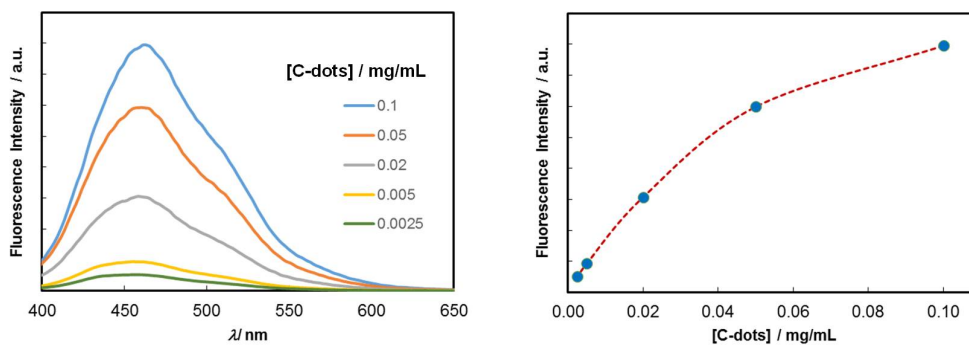
**Figure S8.** Dependence of fluorescence emission of aqueous solutions of C-dots/CA (0.005 mg/mL) on illumination at different excitation wavelengths.



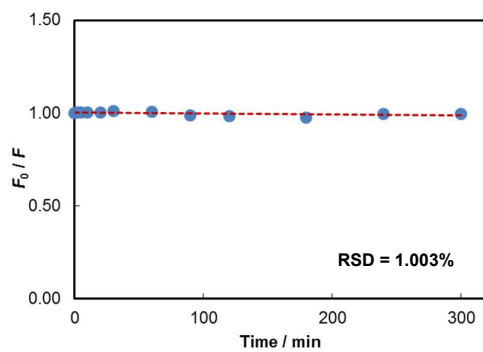
**Figure S9.** Time-resolved intensity decay of a buffered solution (pH = 7.2) of C-dots/CA obtained by the single-photon timing method under excitation at 340 nm.



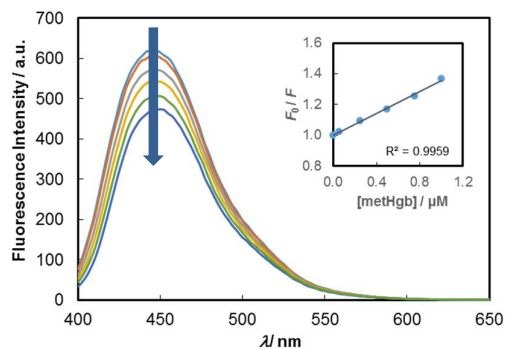
**Figure S10.** Q bands of methHgb (6.6  $\mu\text{M}$ ) in phosphate buffer solution (pH = 7.2) at 25  $^{\circ}\text{C}$ .



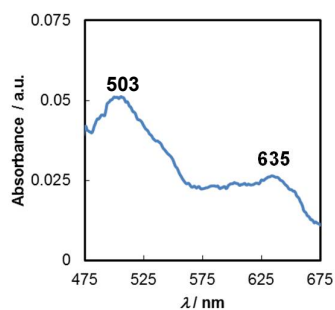
**Figure S11.** Concentration effects on the fluorescence intensity of aqueous solutions of C-dots ( $\lambda_{\text{exc}} = 380 \text{ nm}$ ).



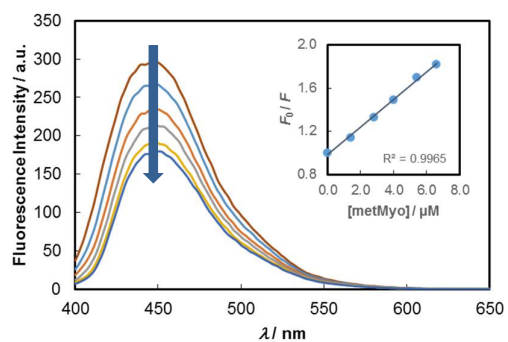
**Figure S12.** Change of fluorescence emission of C-dots (0.1 mg/mL) upon continuous irradiation at 380 nm for 5 h.



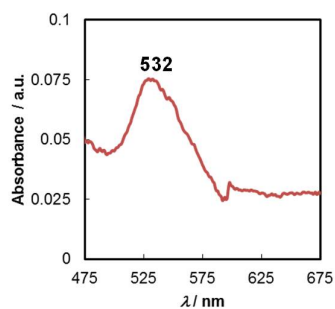
**Figure S13.** Emission spectra of C-dots/CA (0.005 mg/mL) upon addition of metHgb (0, 0.05, 0.25, 0.5, 0.75, 1.0  $\mu\text{M}$ ) in phosphate buffer solution at 25  $^{\circ}\text{C}$  (pH = 7.2). Inset: Stern-Volmer plot obtained from steady-state fluorescence data ( $\lambda_{\text{exc}} = 380 \text{ nm}$ ).



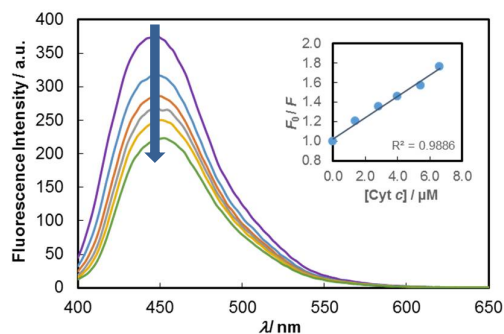
**Figure S14.** Q bands of metMyo (6.6  $\mu\text{M}$ ) in phosphate buffer solution (pH = 7.2) at 25  $^{\circ}\text{C}$ .



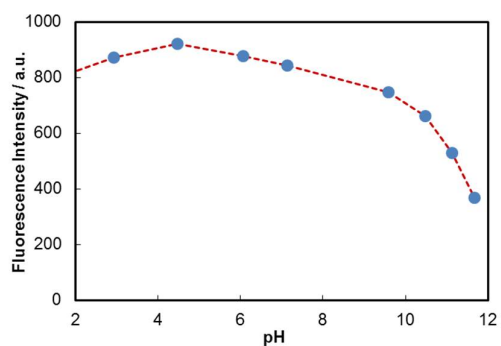
**Figure S15.** Emission spectra of C-dots/CA (0.005 mg/mL) upon addition of metMyo (0, 1.4, 2.8, 4.0, 5.4, 6.6  $\mu\text{M}$ ) in phosphate buffer solution at 25  $^{\circ}\text{C}$  (pH = 7.2). Inset: Stern-Volmer plot obtained from steady-state fluorescence data ( $\lambda_{\text{exc}} = 380 \text{ nm}$ ).



**Figure S16.** Q bands of Cyt *c* (6.6  $\mu\text{M}$ ) in phosphate buffer solution (pH = 7.2) at 25  $^{\circ}\text{C}$ .

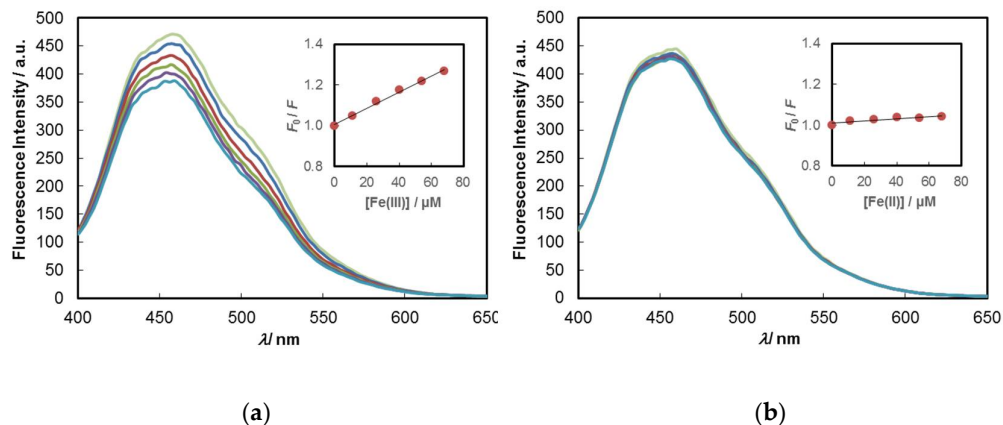


**Figure S17.** Emission spectra of C-dots/CA (0.005 mg/mL) upon addition of Cyt *c* (0, 1.4, 2.8, 4.0, 5.4, 6.6  $\mu\text{M}$ ) in phosphate buffer solution at 25  $^{\circ}\text{C}$  (pH = 7.2). Inset: Stern-Volmer plot obtained from steady-state fluorescence data ( $\lambda_{\text{exc}} = 380 \text{ nm}$ ).

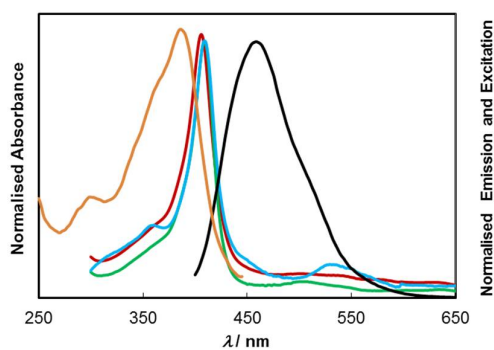


**Figure S18.** Photoluminescence of aqueous solutions of C-dots (0.1 mg/mL) at various pH;  $\lambda_{\text{exc}} = 380 \text{ nm}$ .





**Figure S19.** Emission spectra of C-dots (0.005 mg/mL) upon varying the amount of added Fe(III) (a) and Fe(II) (b) in aqueous solution at 25 °C. Insets: Stern-Volmer plots obtained from steady-state fluorescence data ( $\lambda_{exc} = 380$  nm).



**Figure S20.** Emission (black line;  $\lambda_{exc} = 380$  nm) and excitation (orange line; monitored at 460 nm) spectra of C-dots overlaid with the absorption spectra of methHgb (red line), metMyo (green line) and Cyt c (cyan line).

**Table S1.** Decay data of C-dots in the presence of metHgb.

[metHgb]/ $\mu M$	$\tau_1/ns$ (%)	$\tau_2/ns$ (%)	$\tau_3/ns$ (%)	$\tau_{ave}/ns$	$\chi^2$	$\tau_0/\tau$
0	9.38 (48.6)	3.12 (43.1)	0.60 (8.3)	6.0	1.2	1.00
0.5	9.18 (50.8)	2.96 (41.8)	0.55 (7.4)	5.9	1.2	1.00
1.5	9.53 (47.5)	3.22 (43.2)	0.75 (9.3)	6.0	1.2	0.99
3	9.43 (47.7)	3.19 (42.8)	0.72 (9.5)	5.9	1.2	1.01
6	9.56 (45.6)	3.32 (43.9)	0.7 (10.5)	5.9	1.1	1.01