

Supplementary Material

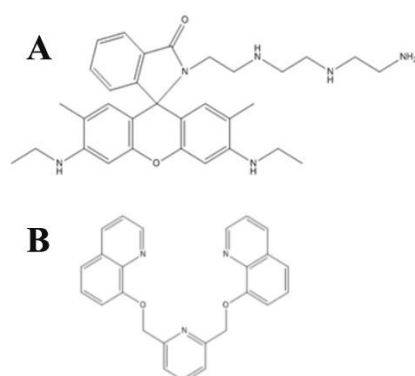


Fig. S1 Structural formula of (A) Cr(III) and (B) Cd(II) fluorescent probes.

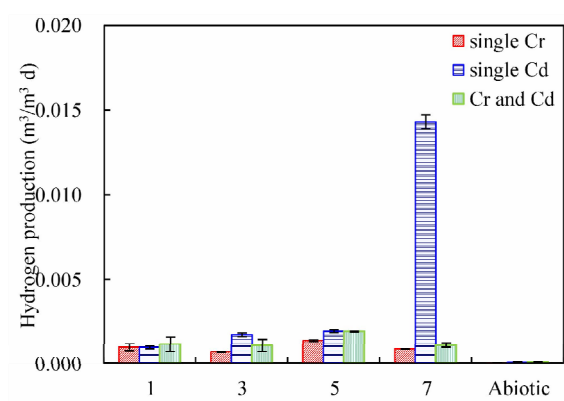


Fig. S2 Comparison of hydrogen production in the presence of both Cd(II) and Cr(VI), single Cd(II) or individual Cr(VI).

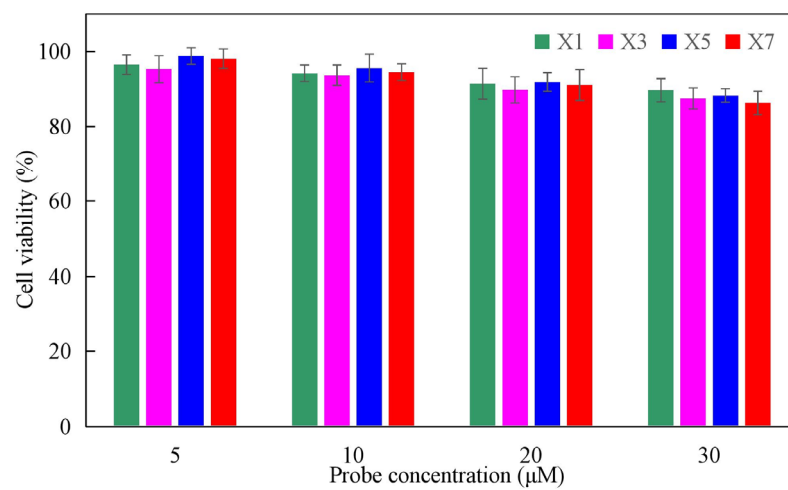


Fig. S3 Toxicity of the equivalent concentrations of Cd(II) and Cr(III) fluorescence probes to the four electrochemically active bacteria.

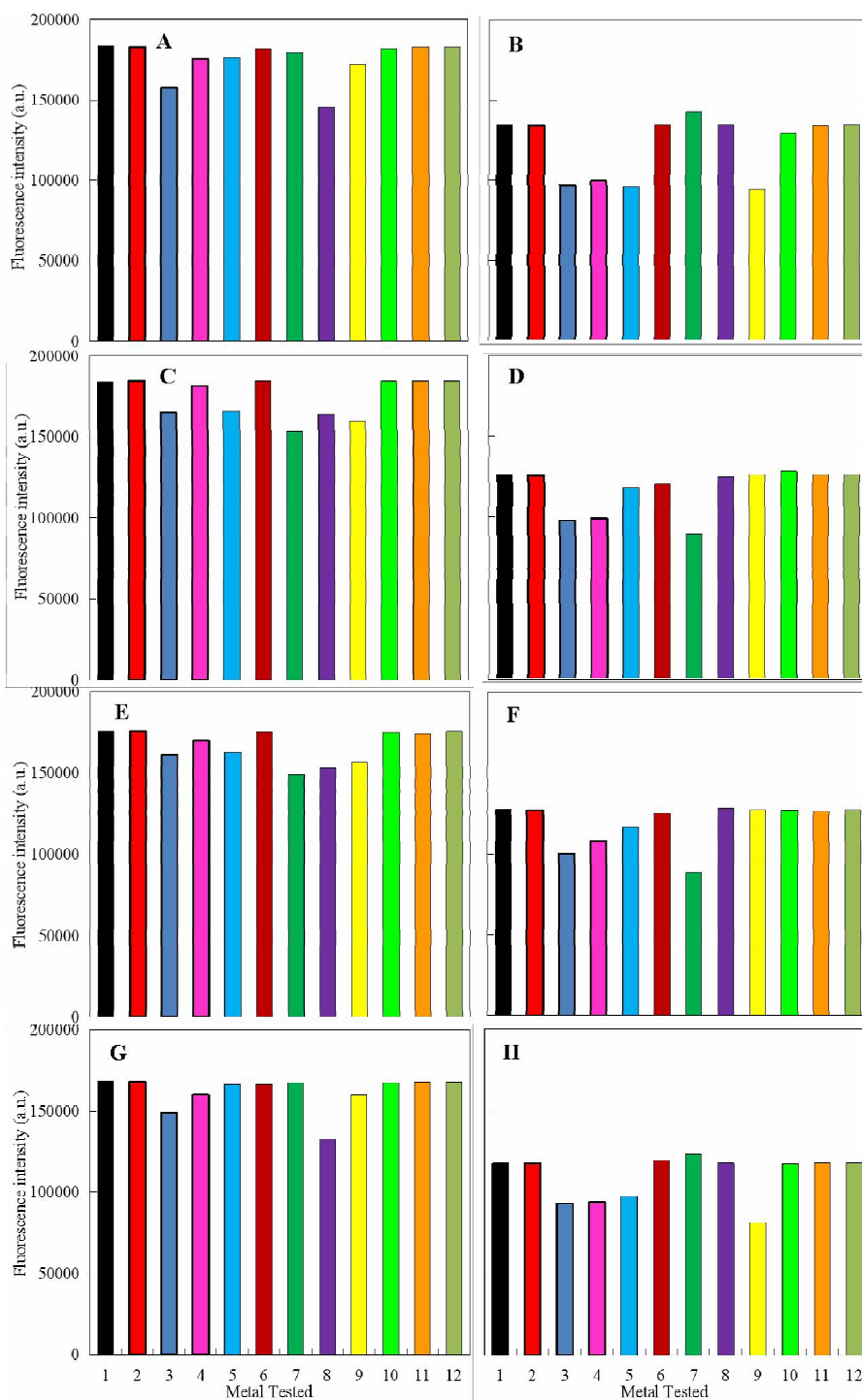


Fig. S4 Emission responses of the Cd(II) probe (10 μ M) in either periplasmic (A, C, E and G) or cytoplasmic (B, D, F and H) solutions of X1 (A and B), X3 (C and D), X5 (E and F), and X7 (G and H) in the presence of equivalent concentrations (20 μ M) of various metal ions.

1: Cd(II); 2: Cr(III)+Cd(II); 3: Cr(III)+Cd(II)+Cu(II); 4: Cr(III)+Cd(II)+Zn(II); 5: Cr(III)+Cd(II)+Fe(III); 6: Cr(III)+Cd(II)+Co(II); 7: Cr(III)+Cd(II)+Mg(II); 8: Cr(III)+Cd(II)+Ni(II); 9: Cr(III)+Cd(II)+Mn(II); 10: Cr(III)+Cd(II)+Ca(II); 11: Cr(III)+Cd(II)+ K(I); 12: Cr(III)+Cd(II)+Na(I).
 $\lambda_{\text{ex}} = 302 \text{ nm}$.

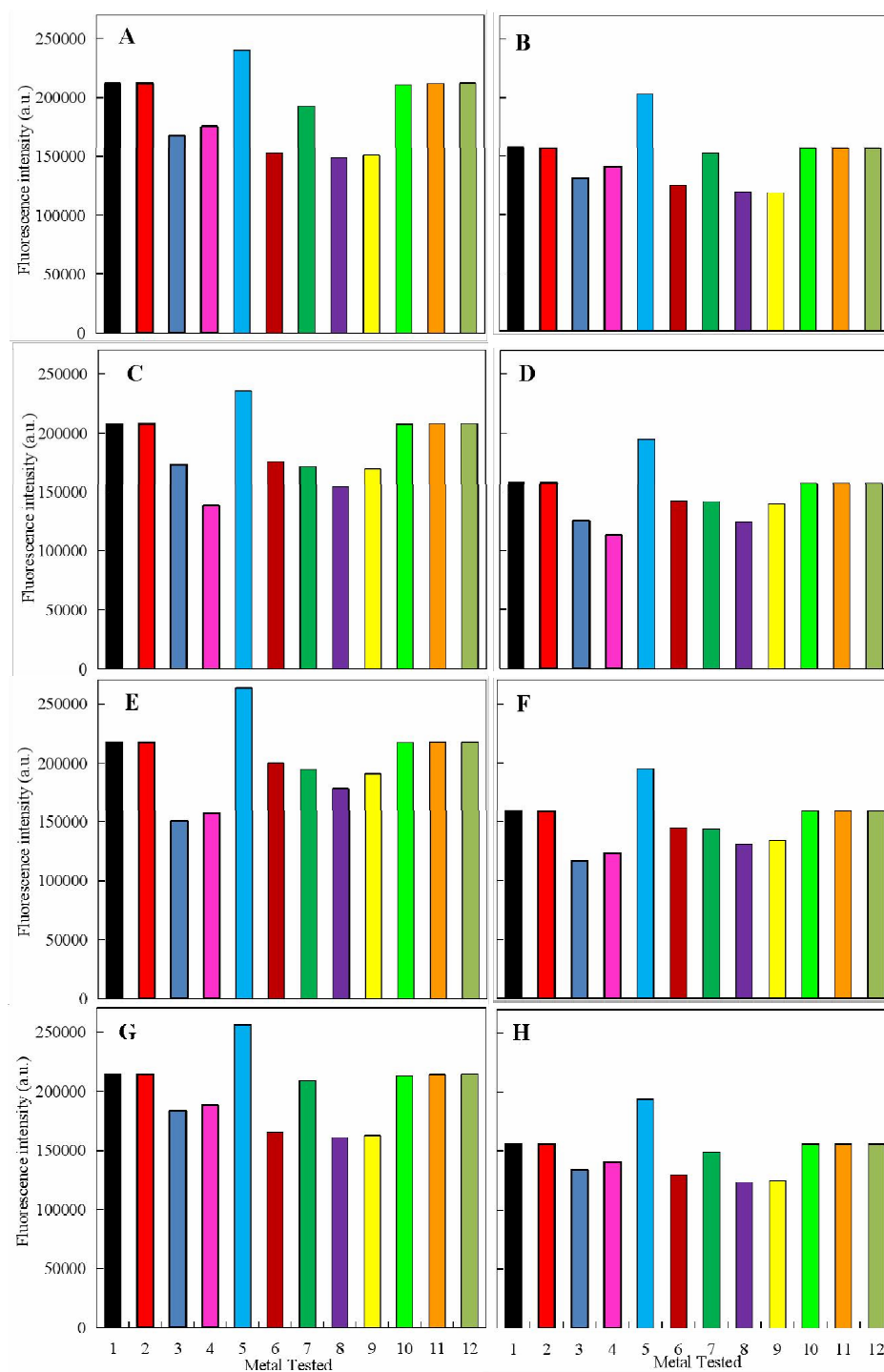


Fig. S5 Emission responses of the Cr(III) probe (10 μM) in either periplasmic (A, C, E and G) or cytoplasmic (B, D, F and H) solutions of X1 (A and B), X3 (C and D), X5 (E and F), and X7 (G and H) in the presence of equivalent concentrations (100 μM) of various metal ions.
 1: Cr(III); 2: Cr(III)+Cd(II); 3: Cr(III)+Cd(II)+Cu(II); 4: Cr(III)+Cd(II)+Zn(II); 5: Cr(III)+Cd(II)+Fe(III); 6: Cr(III)+Cd(II)+Co(II); 7: Cr(III)+Cd(II)+Mg(II); 8: Cr(III)+Cd(II)+Ni(II); 9: Cr(III)+Cd(II)+Mn(II); 10: Cr(III)+Cd(II)+Ca(II); 11: Cr(III)+Cd(II)+ K(I); 12: Cr(III)+Cd(II)+Na(I).
 $\lambda_{\text{ex}} = 500 \text{ nm}$.

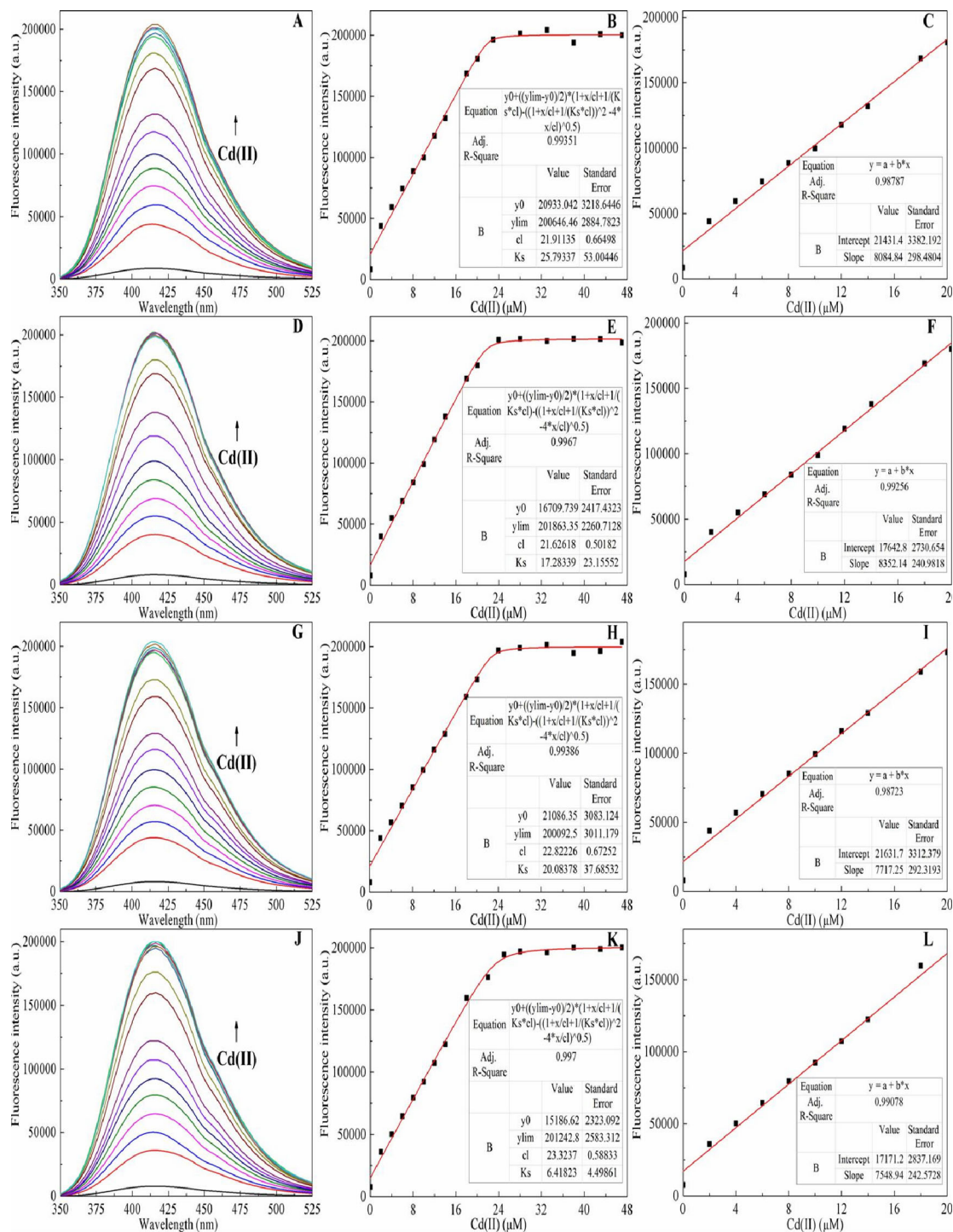


Fig. S6 (A, D, G and J) Fluorescence spectra of the Cd(II) probe (10 μM) upon the addition of equal amount of Cr(III) and Cd(II) ions (each 1 – 30 μM), and (B, C, E, F, H, I, K and L) curve of fluorescence intensity at 417 nm of the Cd(II) probe (10 μM) versus increasing concentrations of Cd(II) ions in related with periplasmic components of X1 (A, B and C), X3 (D, E and F), X5 (G, H and I) and X7 (J, K and L). $\lambda_{\text{ex}} = 302 \text{ nm}$.

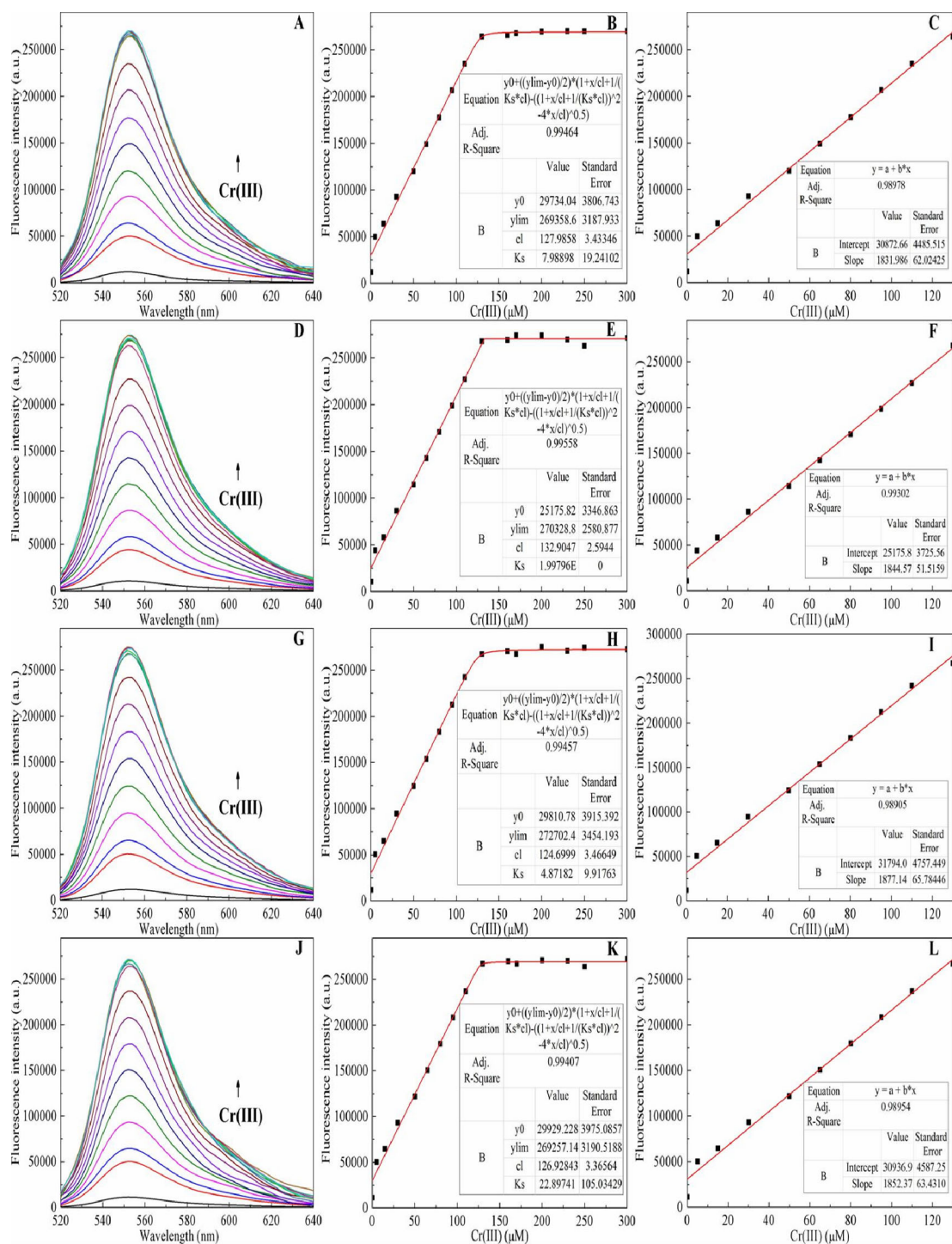


Fig. S7 (A, D, G and J) Fluorescence spectra of the Cr(III) probe (10 μ M) upon the addition of equal amount of Cr(III) and Cd(II) ions (each 1 – 30 μ M), and (B, C, E, F, H, I, K and L) curve of fluorescence intensity at 552 nm of the Cr(III) probe (10 μ M) versus increasing concentrations of Cr(III) ions in related with periplasmic components of X1 (A, B and C), X3 (D, E and F), X5 (G, H and I) and X7 (J, K and L). λ_{ex} = 500 nm.

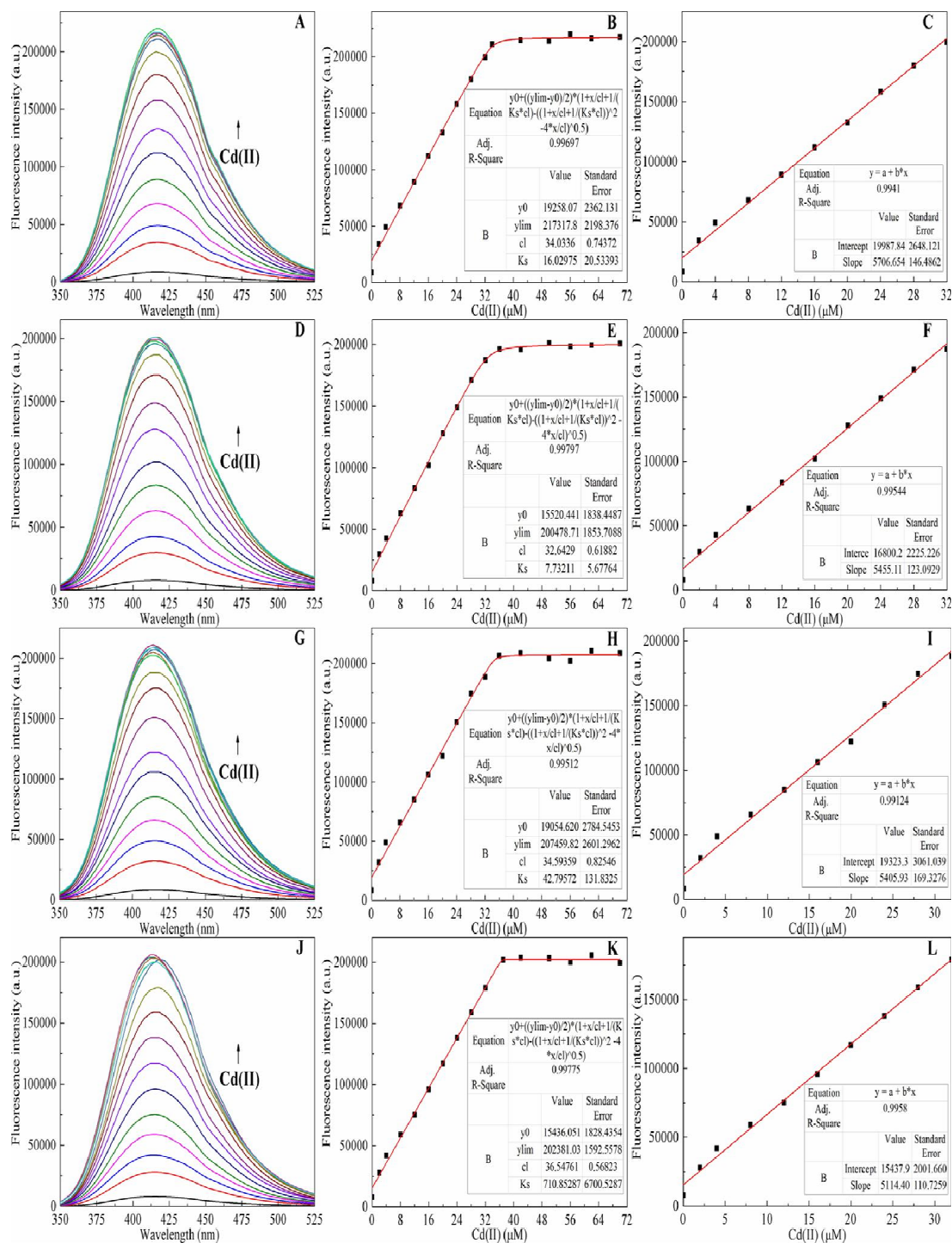


Fig. S8 (A, D, G and J) Fluorescence spectra of the Cd(II) probe (10 μ M) upon the addition of equal amount of Cr(III) and Cd(II) ions (each 1 – 30 μ M), and (B, C, E, F, H, I, K and L) curve of fluorescence intensity at 417 nm of the Cd(II) probe (10 μ M) versus increasing concentrations of Cd(II) ions in related with cytoplasmic components of X1 (A, B and C), X3 (D, E and F), X5 (G, H and I) and X7 (J, K and L). λ_{ex} = 302 nm.

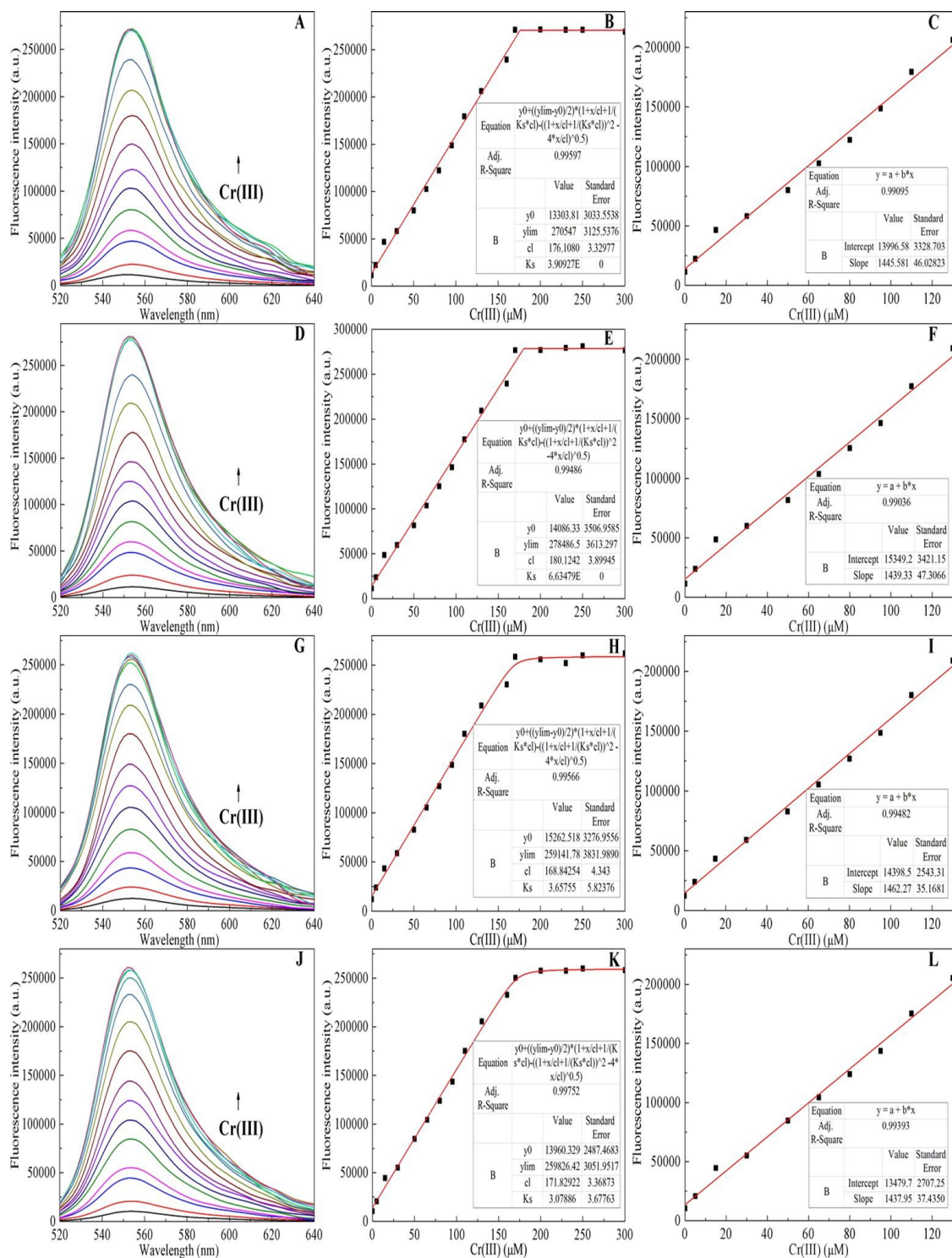


Fig. S9 (A, D, G and J) Fluorescence spectra of the Cr(III) probe (10 μ M) upon the addition of equal amount of Cr(III) and Cd(II) ions (each 1 – 30 μ M), and (B, C, E, F, H, I, K and L) curve of fluorescence intensity at 552 nm of the Cr(III) probe (10 μ M) versus increasing concentrations of Cr(III) ions in related with cytoplasmic components of X1 (A, B and C), X3 (D, E and F), X5 (G, H and I) and X7 (J, K and L). λ_{ex} = 500 nm.

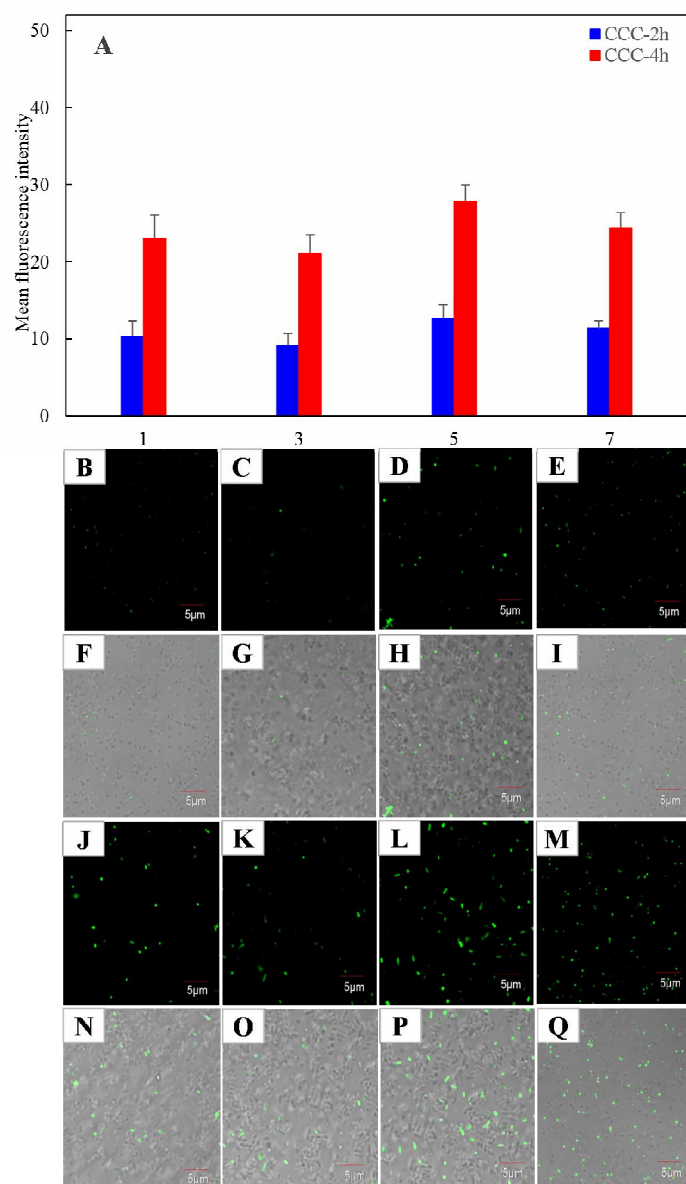


Fig. S10 (A) Mean fluorescence intensity of the electrochemically active bacteria (EAB) in catholyte with Cr(VI) only at an operation time of 2 h or 4 h. Error bars indicate standard error of means for at least 60 cells. Fluorescence images of EAB of X1 (B, F, J and N), X3 (C, G, K and O), X5 (D, H, L and P), and X7 (E, I, M and Q) in MECs with Cr(VI) only at an operation time of either 2 h (B – I) or 4 h (J – Q), after incubation with the Cr(III) and Cd(II) probes (probe concentrations: 10 μ M, touch time: 30 min). Overlay of bright field and fluorescence images for X1 (F and N), X3 (G and O), X5 (H and P), and X7 (I and Q) at an operation time of either 2 h (F – I) or 4 h (N – Q).

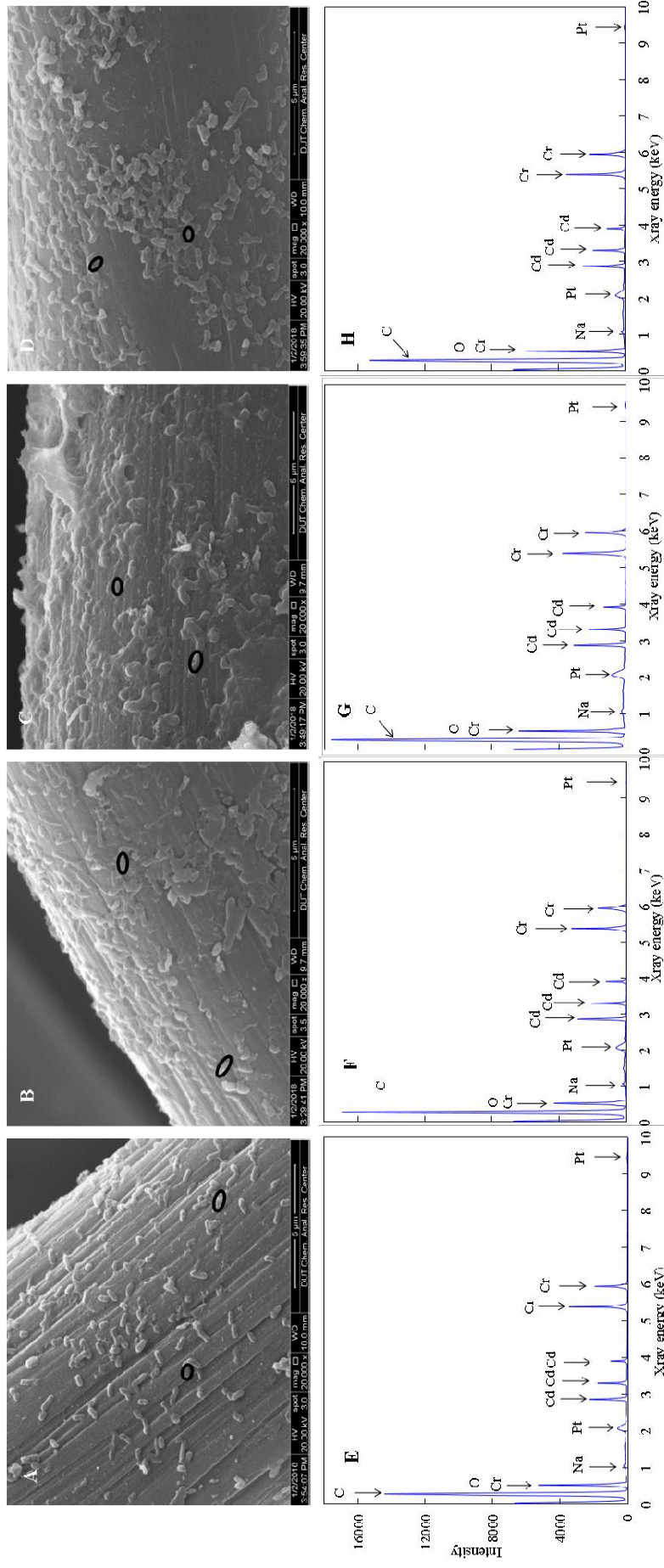


Fig. S11 SEM images (A, B, C and D) and EDS spectra (E, F, G and H) of electrochemically active bacteria of X1 (A and E), X3 (B and F), X5 (C and G), and X7 (D and H) on the cathodes at the end of five fed-batch cycles.

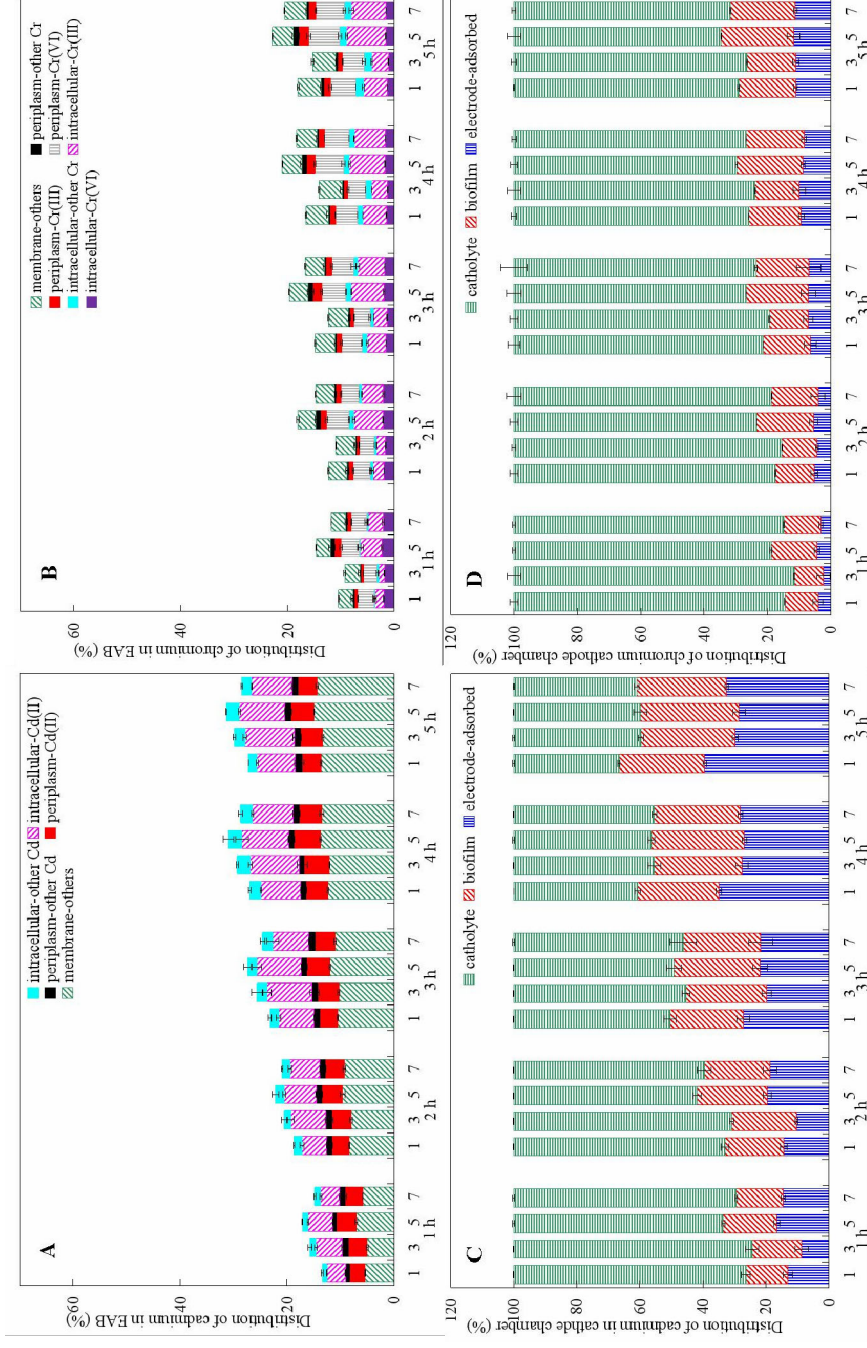


Fig. S12 Distribution of (A) Cd(II) in the intracellular or periplasmic fractions, or on the cell membrane, or other forms of cadmium (such as precipitates or complex), and (B) Cr(III) or Cr(VI) in the intracellular or periplasmic fractions, or on the cell membrane, or other forms of chromium (such as precipitates or complexes) in the open circuit controls (OCC). Measured concentrations of (C) cadmium and (D) chromium in the catholyte or in the biofilm, with the balance (based on the mass added) assumed to be adsorbed to the electrode (electrode-adsorbed) in the OCC.

Table S1 Values of R^2 and limits for linear relationships between fluorescence probes and Cd(II) or Cr(III) concentrations, and detection limits in periplasm and cytoplasm of the four electrotrophs.

Strain cytoplasm	Cr(III)			Cd(II)			Cr(III)			Cd(II)		
	Linear (μ M)	Detection (nM)	R^2	Linear (μ M)	Detection (nM)	R^2	Linear (μ M)	Detection (nM)	R^2	Linear (μ M)	Detection (nM)	R^2
X1	0.9960	176.1	419.5	0.9970	34.0	136.3	0.9946	128.0	399.4	0.9935	21.9	103.4
X3	0.9949	180.1	428.6	0.9980	32.6	112.3	0.9956	132.9	407.0	0.9967	21.6	91.7
X5	0.9957	168.8	402.5	0.9951	34.6	119.9	0.9946	124.7	385.2	0.9939	22.8	94.6
X7	0.9975	171.8	410.3	0.9978	36.5	129.8	0.9941	126.9	390.7	0.9970	23.3	99.8