Electronic Supplementary Information (ESI)

Biometal Binding-Site Mimicry with Modular, Hetero-Bifunctionally Modified Architecture Encompassing a Trp/His Motif: Insights into Spatiotemporal Noncovalent Interactions from a Comparative Spectroscopic Study

Chi Ming Yang

（Nankai University）

Contents

Steady-state fluorescence titration spectra (λ_{ex} /λ_{em} 278/355 nm)

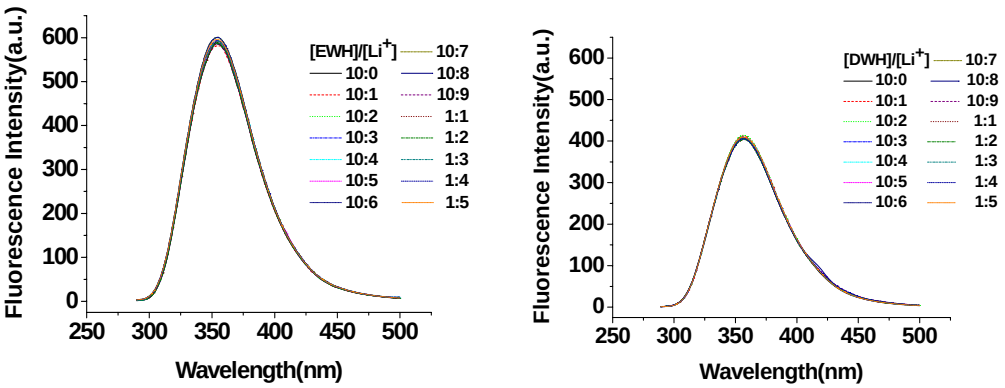
Aqueous solutions of EWH and DWH, respectively, each at a constant concentration (100 μM), were titrated with Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} , Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}, at buffered **pH 7.10**±0.05 and **pH 4.60**±0.03, respectively.

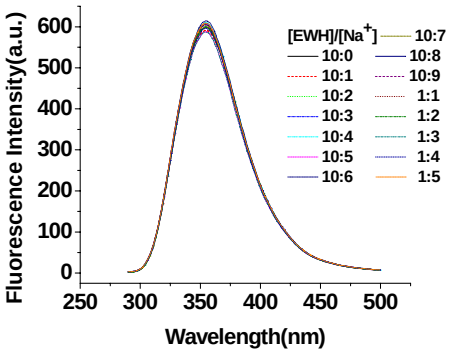
The amounts of metal ions added: [M^{n+}] = 0, 10 μM, 20 μM, 30 μM, 40 μM, 50 μM, 60 μM, 70 μM, 80 μM, 90 μM, 100 μM, 200 μM, 300 μM, 400 μM and 500 μM.

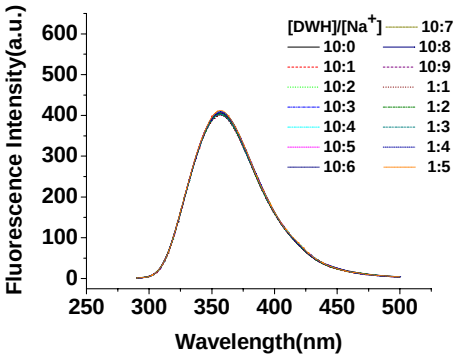
Color specifications: Molar ratios of [DWH] : [M^{n+}] = 10 : 0 (solid ——), 10 : 1 (dash - - -), 10 : 2 (dot ·····), 10 : 3 (dash dot -·-·-), 10 : 4 (dash dot dot -··-··-), 10 : 5 (dash – – – –), 10 : 6 (dot – – – –), 10 : 7 (dash dot -·-·-), 10 : 8 (solid ——), 10 : 9 (dash – – – –) 1 : 1 (dot ·····), 1 : 2 (dash dot -·-·-), 1 : 3 (dash dot dot -··-··-), 1 : 4 (dash - - -), 1 : 5 (dot ·····).

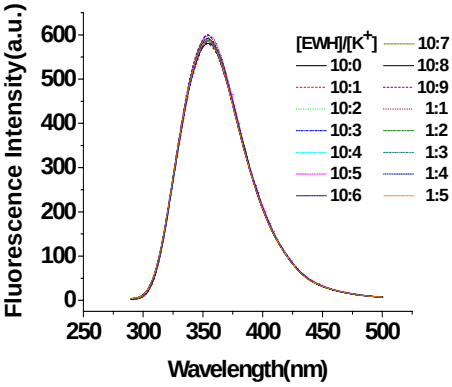
1. at pH 7.10

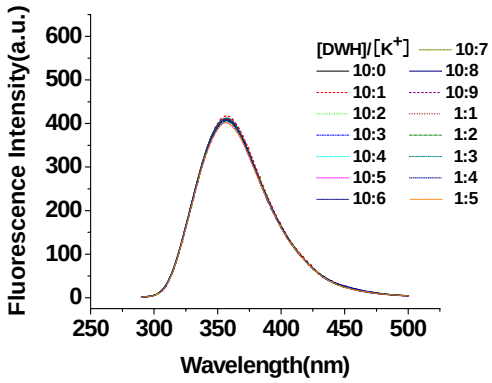
(1) For the titration with M^+ (Li^+, Na^+, K^+), 200 mM Tris-HCl buffer was used.
(2) For the titration with M^{2+} (Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}), 12.5 mM KH_2PO_4 / Na_2HPO_4 buffer was used.

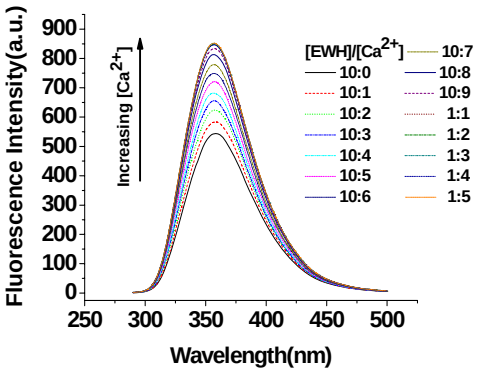


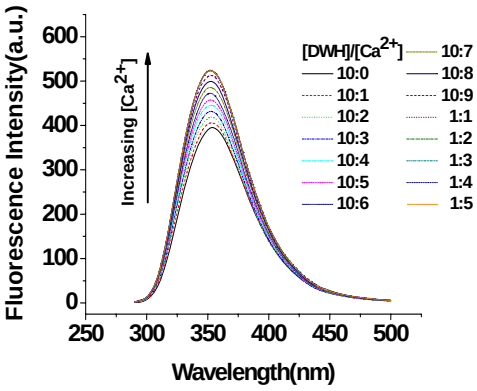


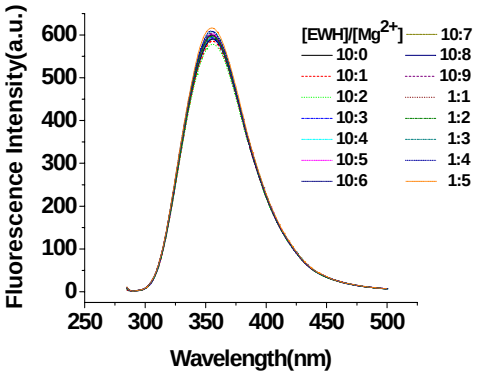


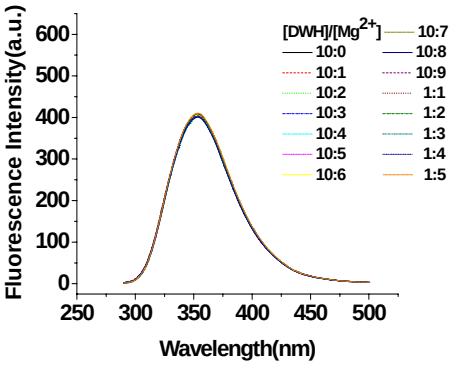


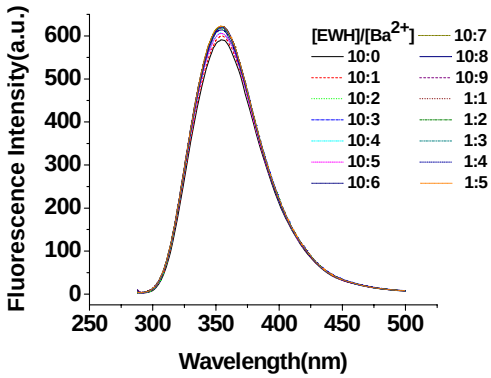


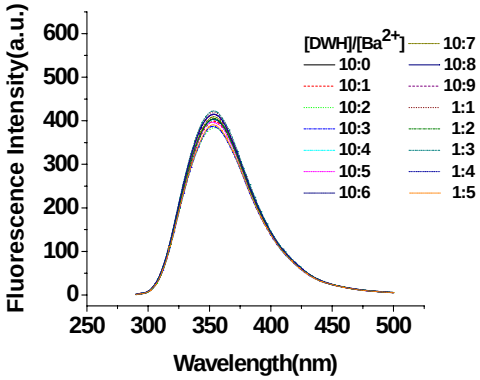


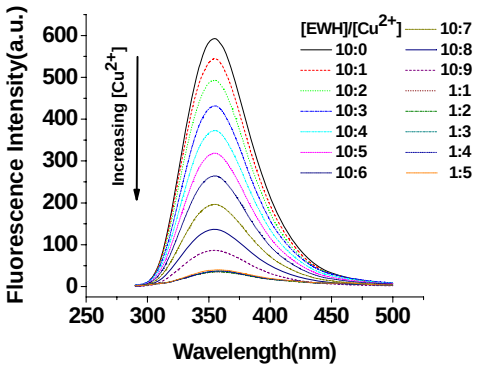


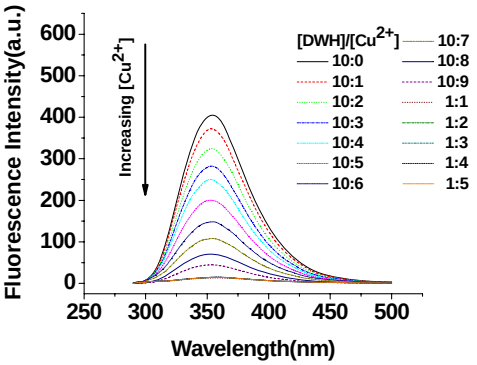


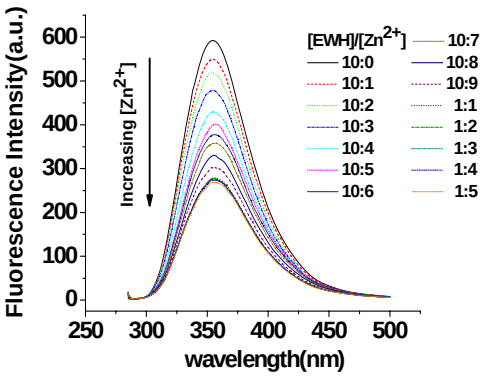


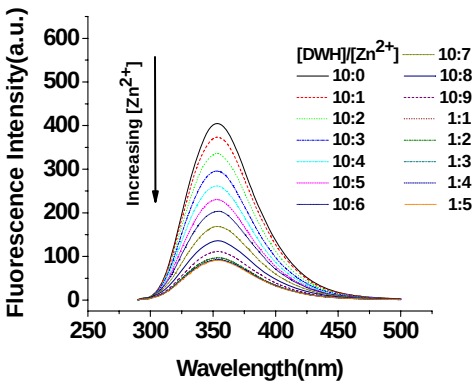


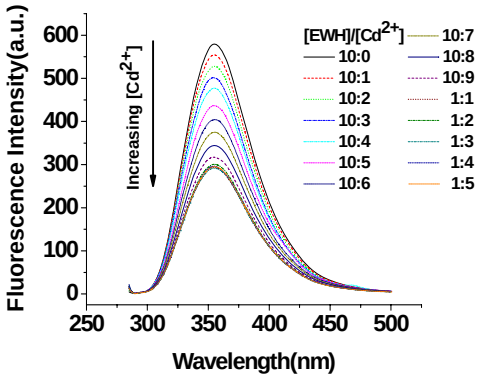


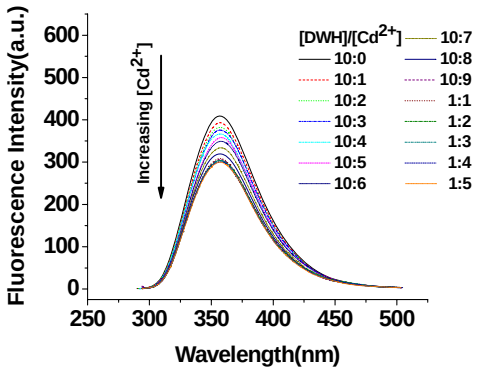


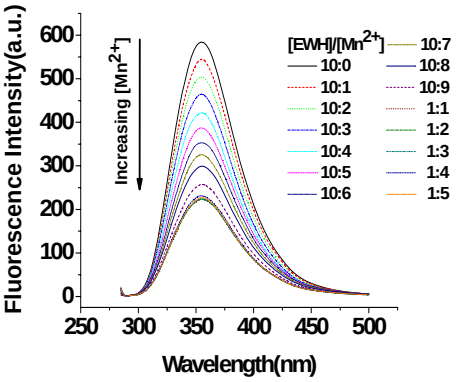


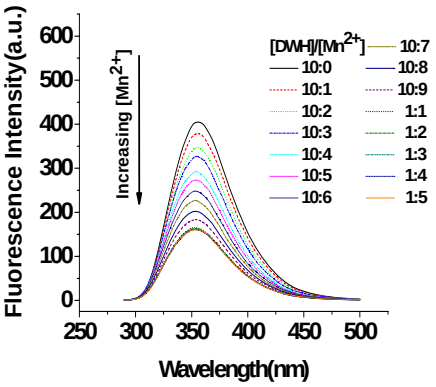


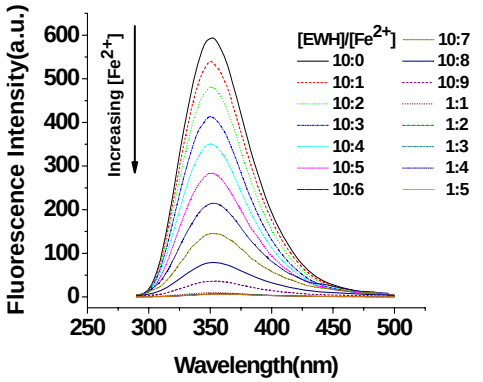


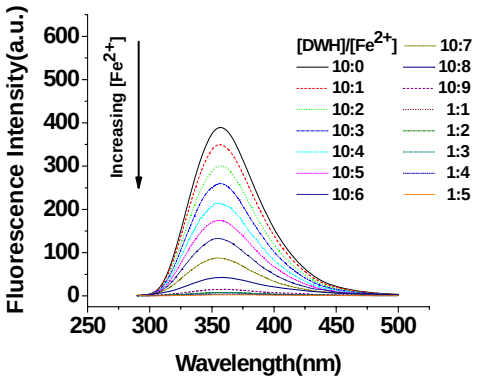


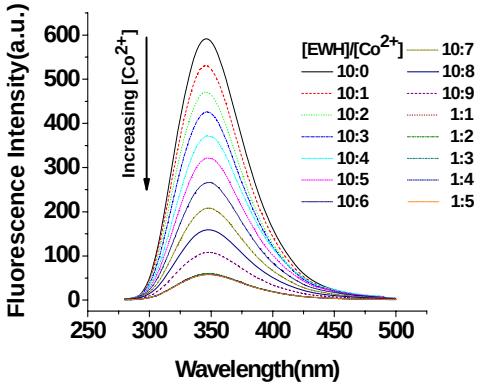


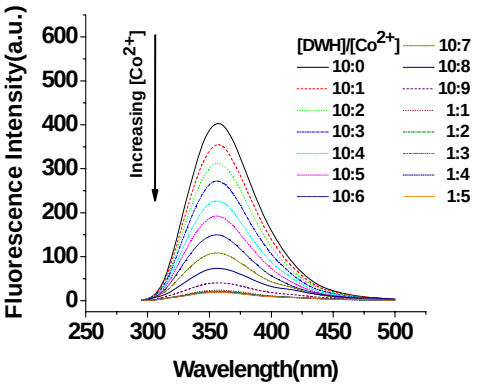


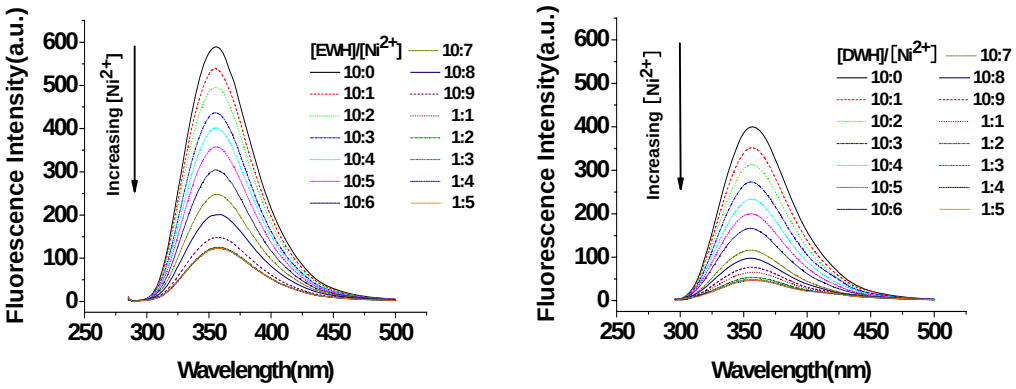








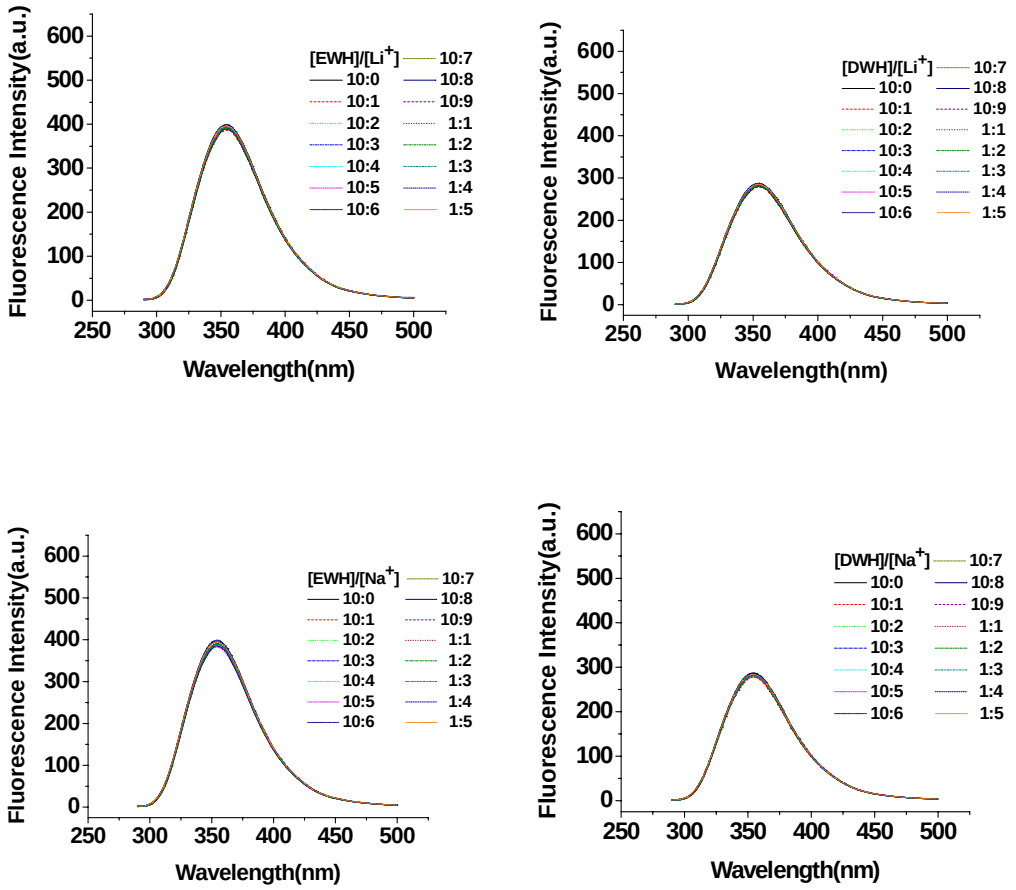


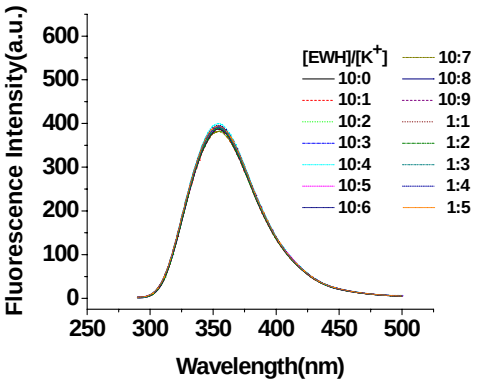


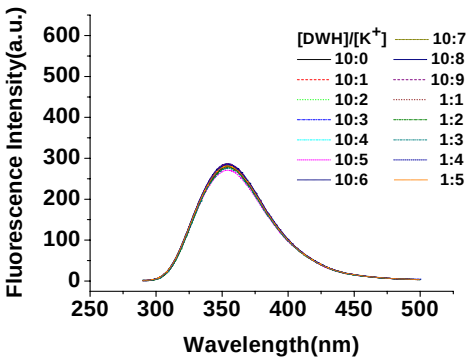
2. at pH 4.60

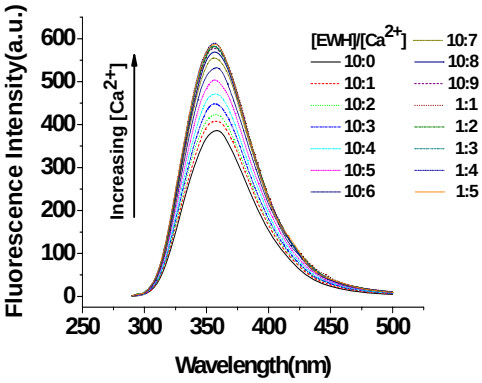
(1) For the titration with M^{n+} (Li^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} , Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}), 100 mM NaOAc / HOAc buffer was used.

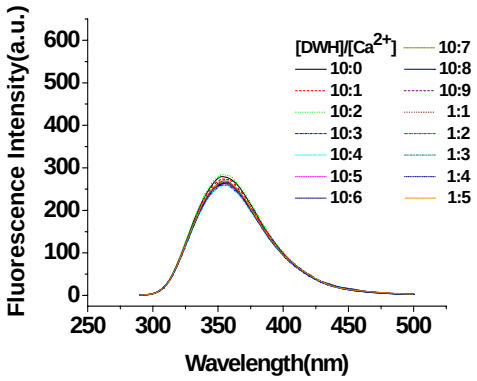
(2) For the titration with Na^+, 200 mM NH_4OAc / HOAc buffer was used.

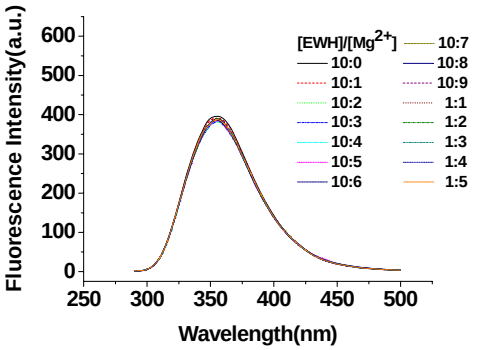


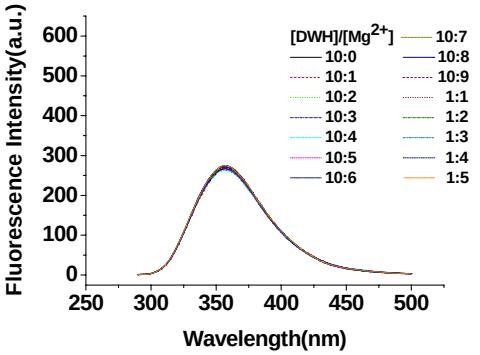


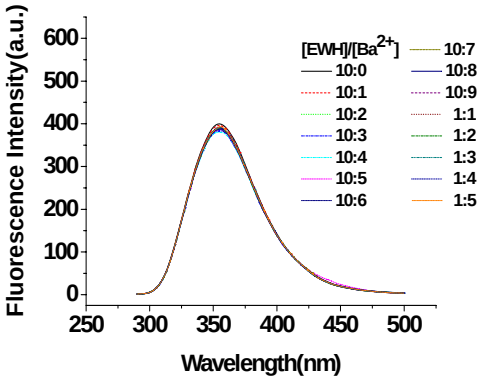


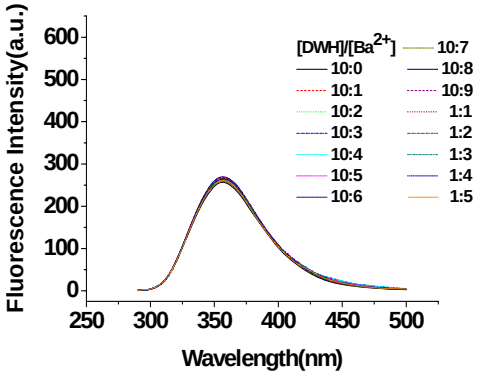


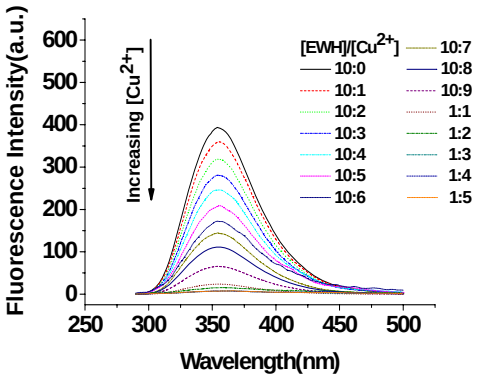


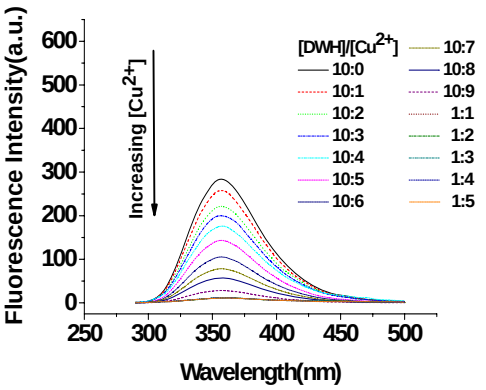


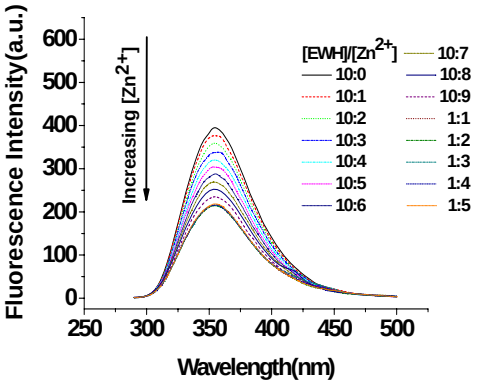


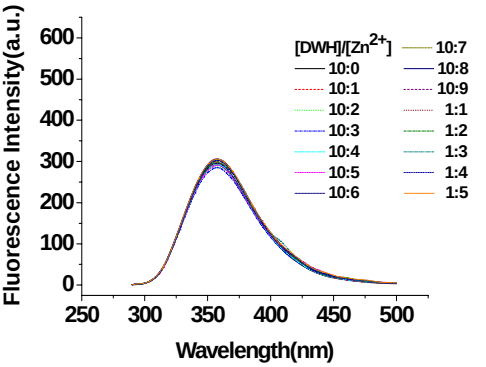


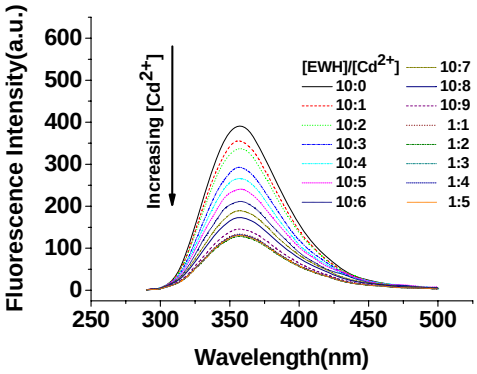


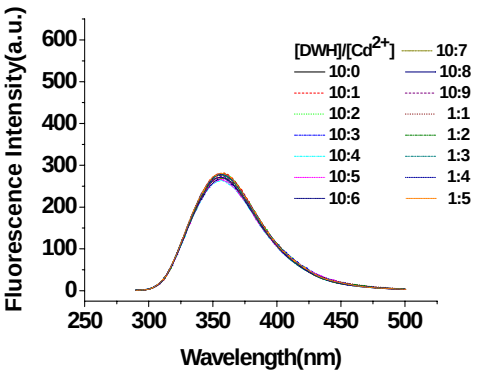


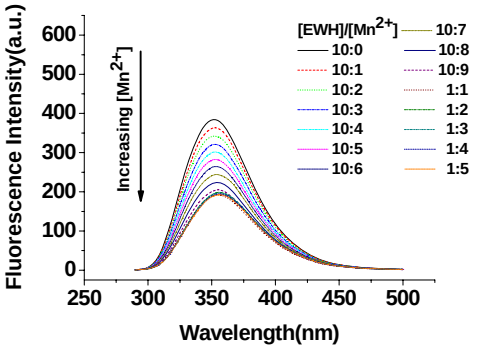


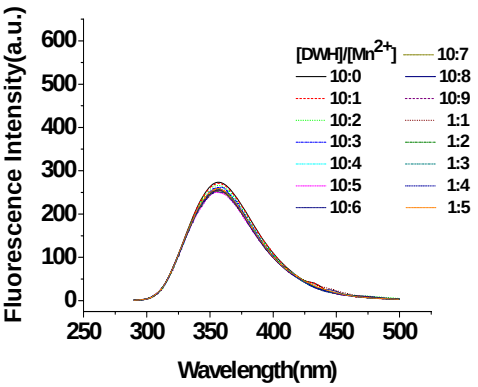


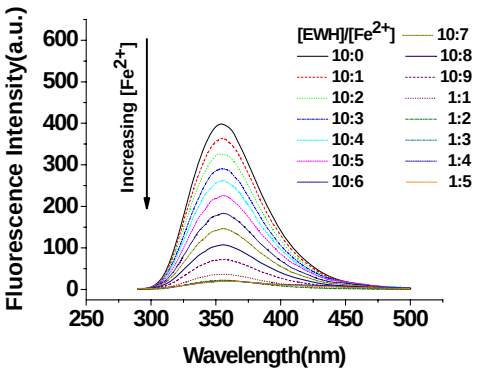


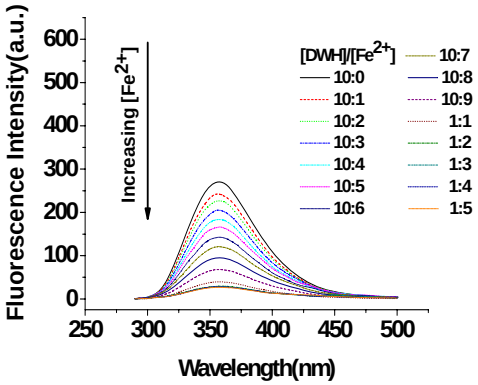


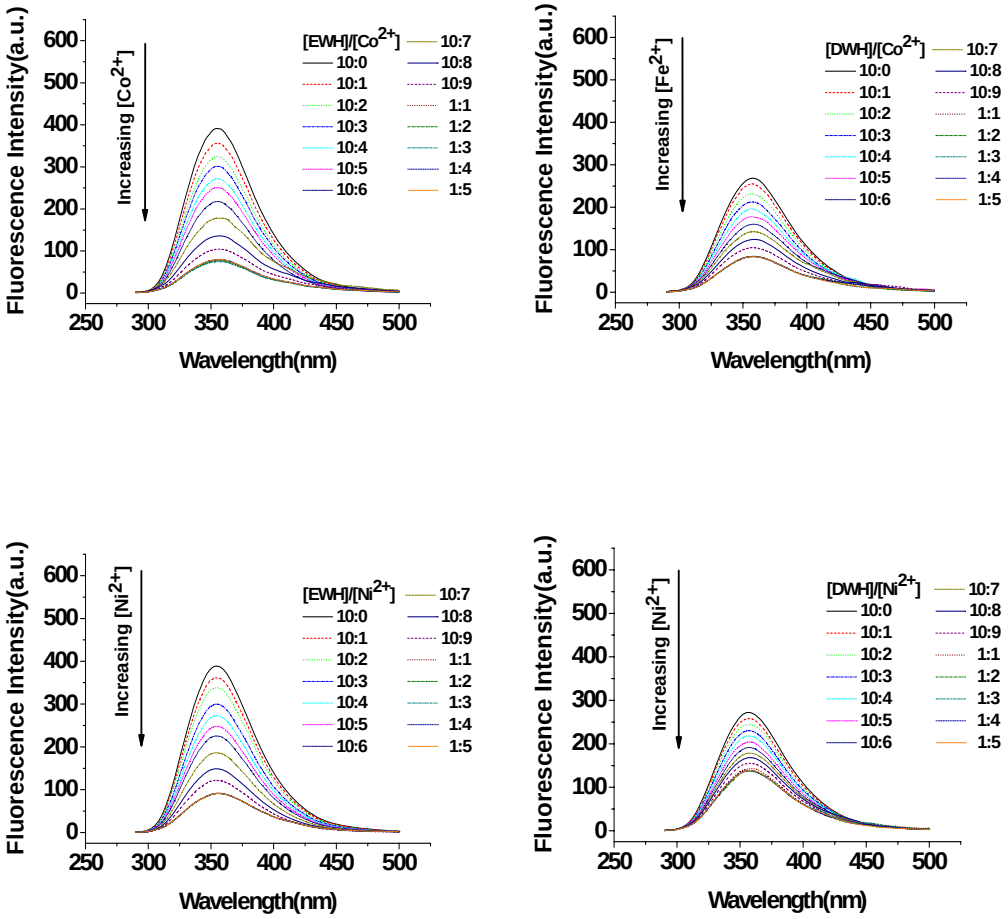




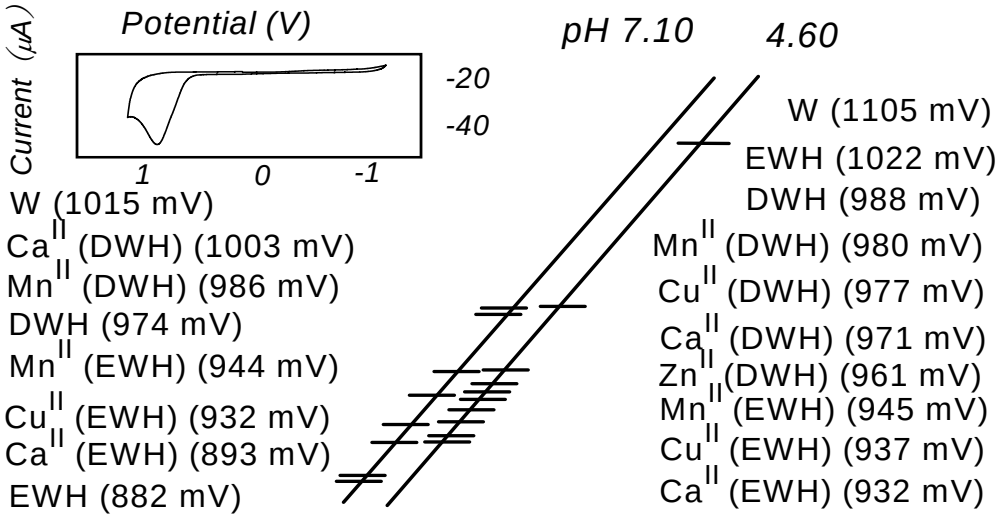








3. (1) Reduction potentials of the metallo-scaffolds. Inset: a typical cyclic voltammogram.



The effects of metal ions on the redox potential of the Trp(W) residue in the molecules, for example, metal-bound EWH, and DWH,

upon a change of pH from 7.0 to 4.6,

$\Delta\Delta\varepsilon\ (EWH)_{Ca(II)} = 932\text{-}893 = 39$ mV

$\Delta\Delta\varepsilon\ (DWH)_{Ca(II)} = 971\text{-}1003 = -32$ mV

$\Delta\Delta\varepsilon\ (EWH)_{Mn(II)} = 945\text{-}944 = 1$ mV

$\Delta\Delta\varepsilon\ (DWH)_{Mn(II)} = 980\text{-}986 = -6$ mV

At pH 7.0, $\Delta\varepsilon\ (EWH)_{Ca(II)} - \Delta\varepsilon\ (DWH)_{Ca(II)} = 893\text{-}1003 = -110$ mV

$\Delta\varepsilon\ (EWH)_{Mn(II)} - \Delta\varepsilon\ (DWH)_{Mn(II)} = 944\text{-}986 = -42$ mV

At pH 4.6, $\Delta\varepsilon\ (EWH)_{Ca(II)} - \Delta\varepsilon\ (DWH)_{Ca(II)} = 932\text{-}971 = -39$ mV

$\Delta\varepsilon\ (EWH)_{Mn(II)} - \Delta\varepsilon\ (DWH)_{Mn(II)} = 945\text{-}980 = -35$ mV

free W, EWH, DWH, upon a change of pH from 7.0 to 4.6,

$\Delta\Delta\varepsilon\ (EWH) = 1022\text{-}882 = 140$ mV

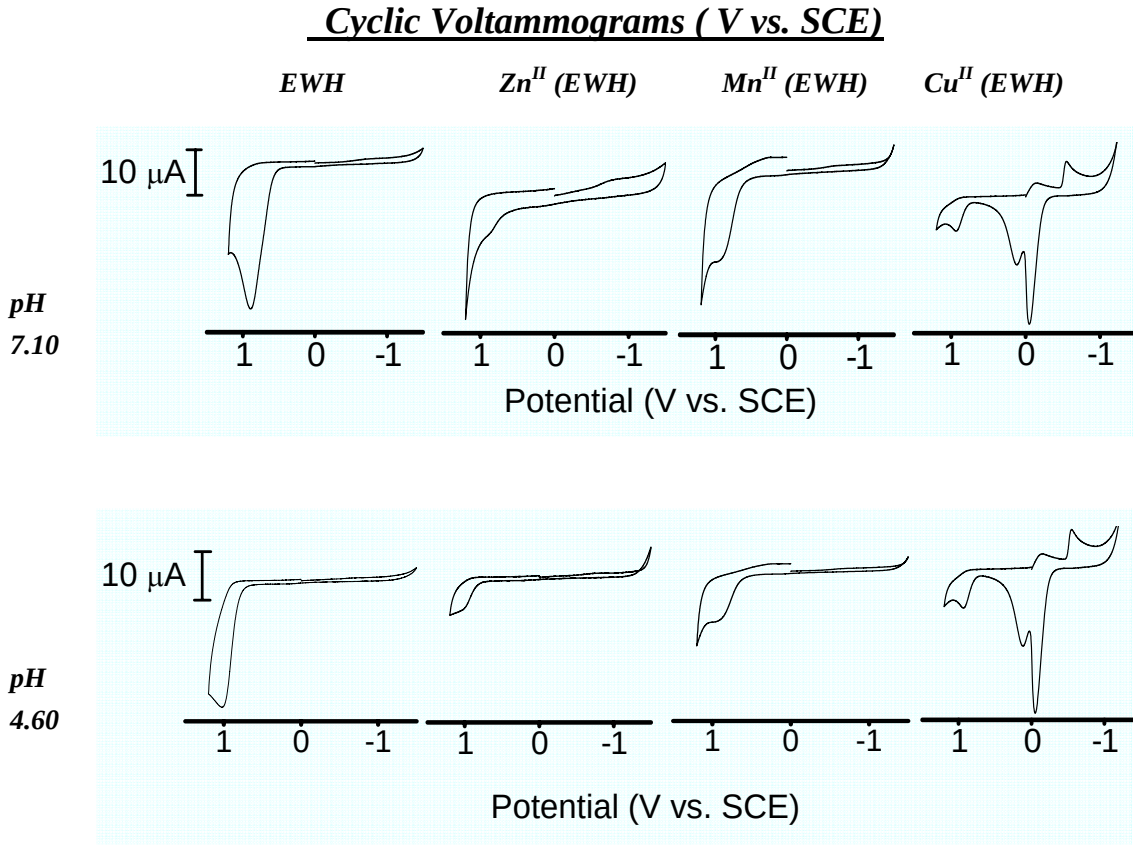
$\Delta\Delta\varepsilon\ (DWH) = 988\text{-}974 = 14$ mV

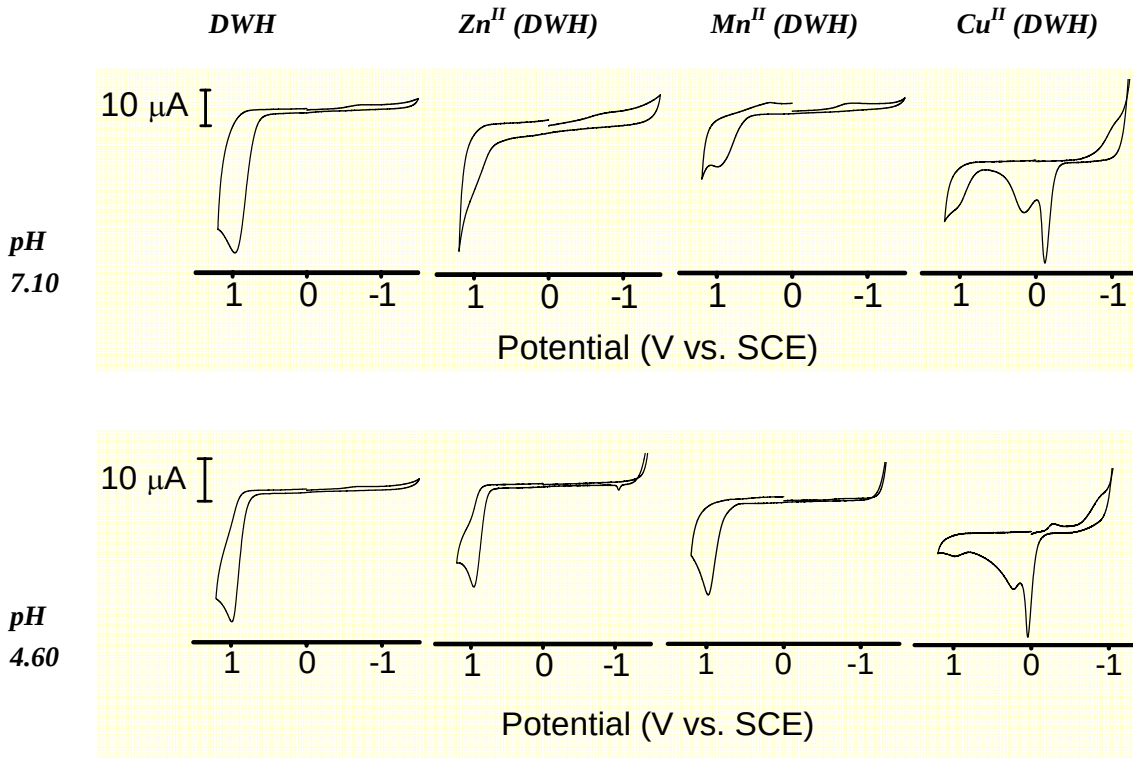
$\Delta\Delta\varepsilon\ (W) = 1105\text{-}1015 = 90$ mV

(2) Cyclic Voltammograms recorded for EWH, DWH, and their metal complexes

The complexes (1 mM) were prepared in aqueous solutions containing KC1 **(**0.2 M) and buffer (5 mM) and purged thoroughly with $\mathbf{N_2}$**.** Glassy carbon working electrode was used in conjunction with a Pt counter electrode and the reference was SCE.

Cyclic Voltammograms (V vs. SCE)





References:
(1) A. Harriman, *J. Phys. Chem.* 1987, **91**, 6102.
(2) B. J. Parsons, M. Al-Hakim, G. O. Phillips and A. J. Swallow, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 1575.