Supporting Information

Colorimetric and fluorescent detection of oxalate in water by a new macrocycle-based dinuclear Ni(II) complex: A remarkable red shift of fluorescence band

Md Mhahabubur Rhaman, Frank R. Fronczek, Douglas R. Powell and Md. Alamgir Hossain[*]

General

All reagents and solvents were purchased as reagent grade and were used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity INOVA 500 FT-NMR. Chemical shifts for samples were measured in $CDCl_3$ and calibrated with tetramethylsilane (TMS) as an internal reference. NMR data were processed and analyzed with MestReNova Version 6.1.1-6384. Mass spectral data were obtained in the ESI-MS positive mode on a FINNIGAN LCQDUO. The melting point was determined on a Mel-Temp (Electrothermal 120 VAC 50/60 Hz) melting point apparatus. Elemental analysis was carried out by Columbia Analytical Services (Tucson, AZ 85714). The fluorescence was measured on a Fluoromax-4 spectrofluorometer (HORIBA Scientific) and the absorbance was measured on a UV-2600 UV-VIS spectrophotometer (SHIMADZU).

Synthesis

1: Terephthalaldehyde (1.3433 g, 10 mmol) and *N*-methyl-2,2′-diaminodiethylamine (1.1719 g, 10 mmol) were dissolved separately in methanol (250 mL). These solutions were added usly dropwise in methanol (500 mL) simultaneously with constant stirring at ice bath. After 24 hour stirring, $NaBH_4$ (1.4 g, 37 mmol) was added slowly and stirred another 24 hour. After the evaporation of the solvent, the sample was dissolved in 200 mL of distilled water. The pH of the solution was adjusted above 7 by adding NaOH(aq) and solution was partitioned in CH_2Cl_2 (150 mL). The product was extracted with CH_2Cl_2 (3 x 150 mL) and the combined organic layers were dried by adding anhydrous $MgSO_4$ (3 g). After filtration, the solvent was evaporated under reduced pressure to produce oily product. The crude product was purified by column chromatography on a neutral-alumina column (2% CH_3OH in CH_2Cl_2) to give macrocycle. Yield: 1.09 g, 43%. M.p 88ºC. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ7.19 (s, 8H, Ar*H*), 3.75 (s, 8H, ArCH_2), 2.78 (t, *J* = 5.0 Hz, 8H, HNCH_2), 2.54 (t, *J* = 5.0 Hz, 8H, NCH_2), 2.16 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ138.9 (Ar-*C*), 127.9 (Ar-*C*H), 56.5 (N*C*H_2), 53.9 (NH*C*H_2), 46.9 (HCH_2*C*H_2), 42.1 (N*C*H_3). ESI-MS: m/z (+) 439.5 $[M + H]^+$. Anal Calcd. For $C_{26}H_{42}N_6$: C, 71.19; H, 9.65; N, 19.16. Found: C, 71.31; H, 9.68; N, 19.22.

$[Ni_2(\mathbf{1})(H_2O)_6]^{4+}(NO_3)_4$, **L**: The dinuclear nickel complex **L** was synthesized from the reaction of **1** (60 mg, 0.14 mmol) with $Ni(NO_3)_2.6H_2O$ (82 mg, 0.28 mmol) in H_2O/CH_3OH mixture (3 ml, 5:1 v/v). The solution was stirred for 30 min. Diethyl ether was added to the solution and the precipitate obtained immediately. The solid product was collected, washed with diethyl ether and dried under vacuum. Yield 76 mg, 69% yield. Anal. Calcd. for $C_{26}H_{42}N_{10}Ni_2O_{12}$: C, 38.84; H, 5.26; N, 17.42; O, 23.88. Found: C, 38.89, H, 5.31; N, 17.45; O, 23. 91. The nickel complex **L** (20 mg) was dissolved in $H_2O/MeOH$ (2 mL, 5:1, v/v), and crystal suitable for X-ray analysis were grown after two weeks from slow evaporation of the solvent.

$[Ni_2(\mathbf{1})(H_2O)_2(ox)_2]$: The oxalate complex was synthesized from the reaction of **L** (50 mg, 0.06 mmol) with $K_2C_2O_4.H_2O$ (11 mg, 0.06 mmol) in $H_2O/MeOH$ mixture (2 ml, 5:1 v/v). The solution was stirred for 30 min. The sddition of ether made precipitate which was collected, washed with diethyl ether and dried under vacuum. Yield 40 mg, 66%. Anal. Calcd. for $C_{30}H_{42}N_6Ni_2O_8$: C, 49.22; H, 5.78; N, 11.48; O, 17.48. Found: C, 49.33, H, 5.87; N, 11.56; O, 17.54. The oxalate complex (20 mg) was dissolved in $H_2O/MeOH$ (2 mL, 5:1, v/v), and crystal suitable for X-ray analysis were grown after two weeks from slow evaporation of the solvent.

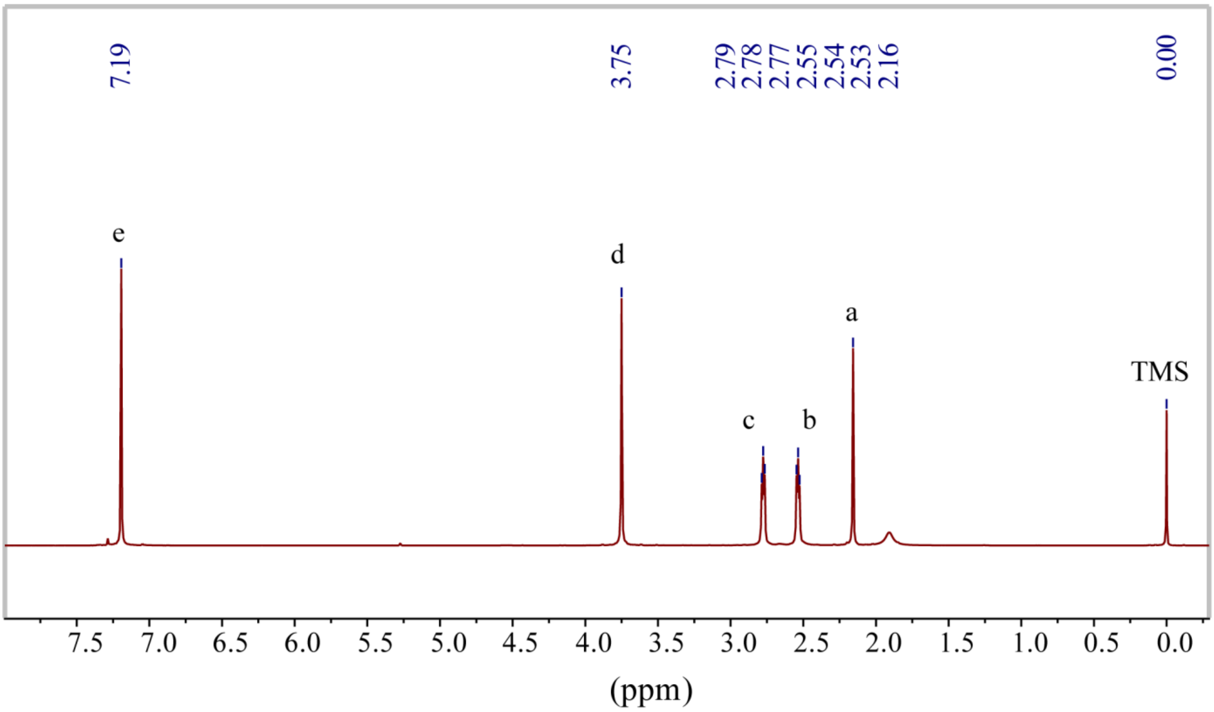

Figure S1. ^1H NMR spectrum of **1** in $CDCl_3$.

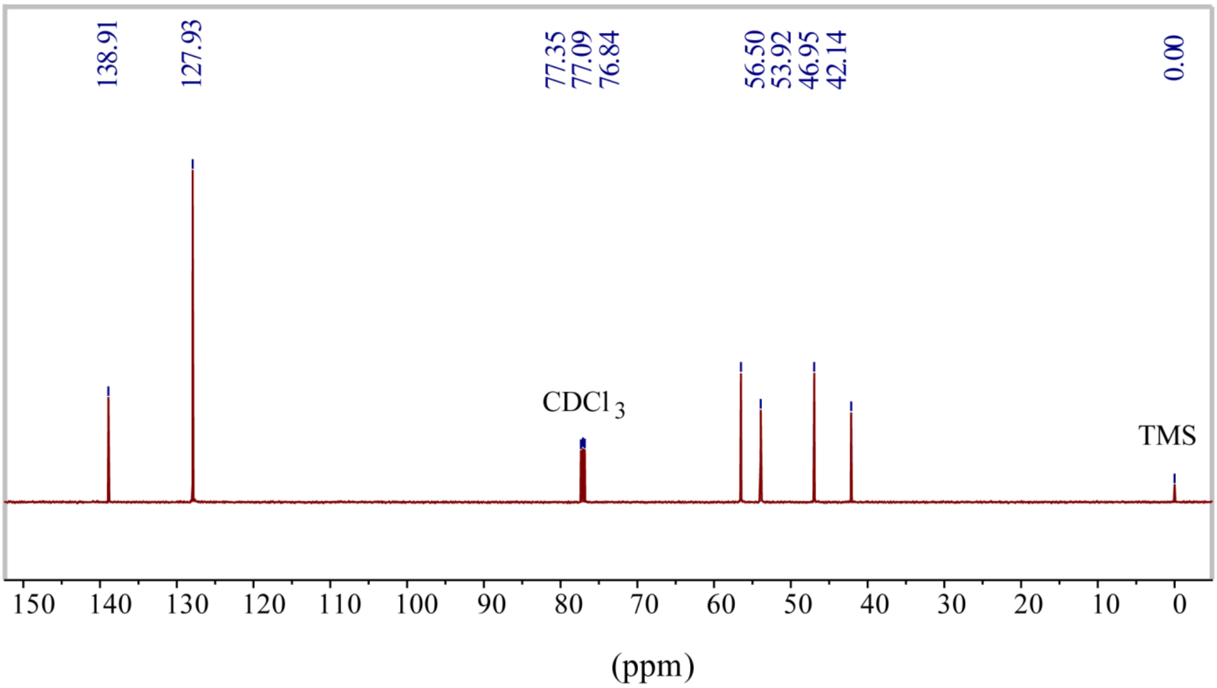

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

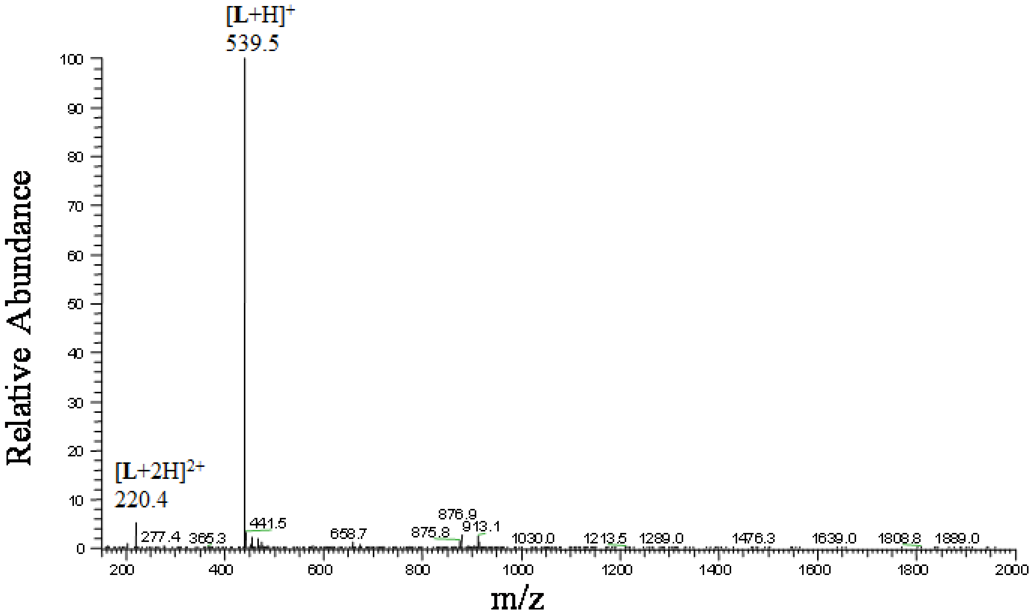

Figure S3. ESI-MS (positive ion mode) spectrum of 1 in MeOH.

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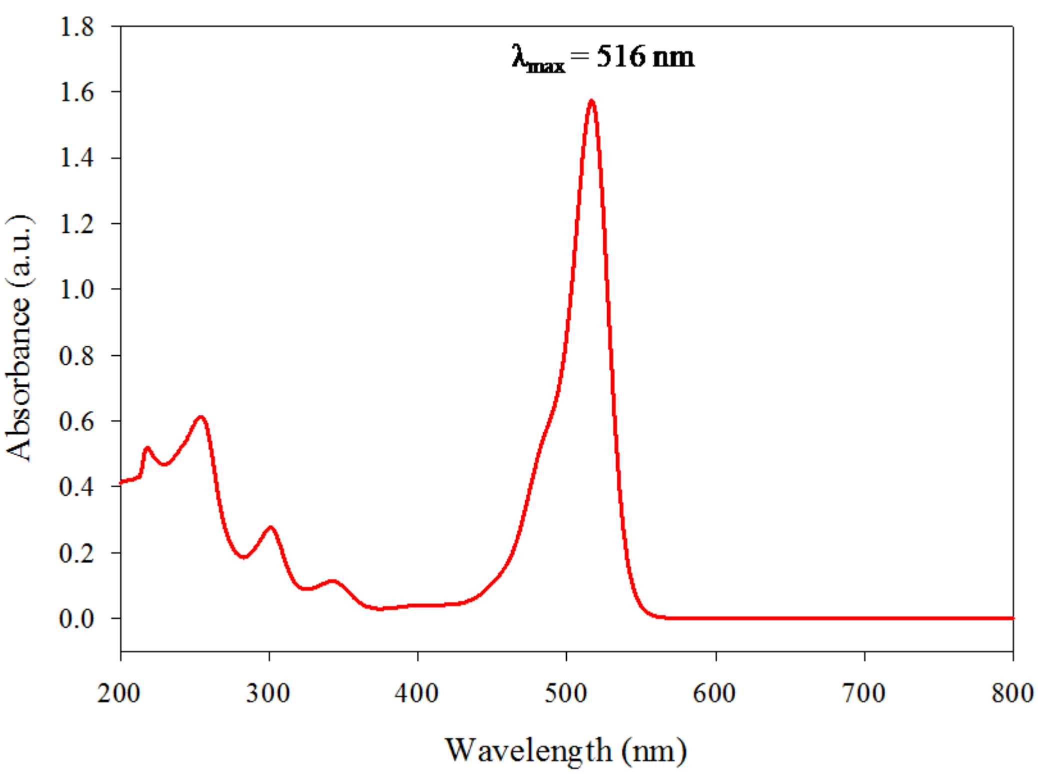

Figure S4. UV-vis spectrum of Eosin Y in 20 mM HEPES buffer at pH 7.0

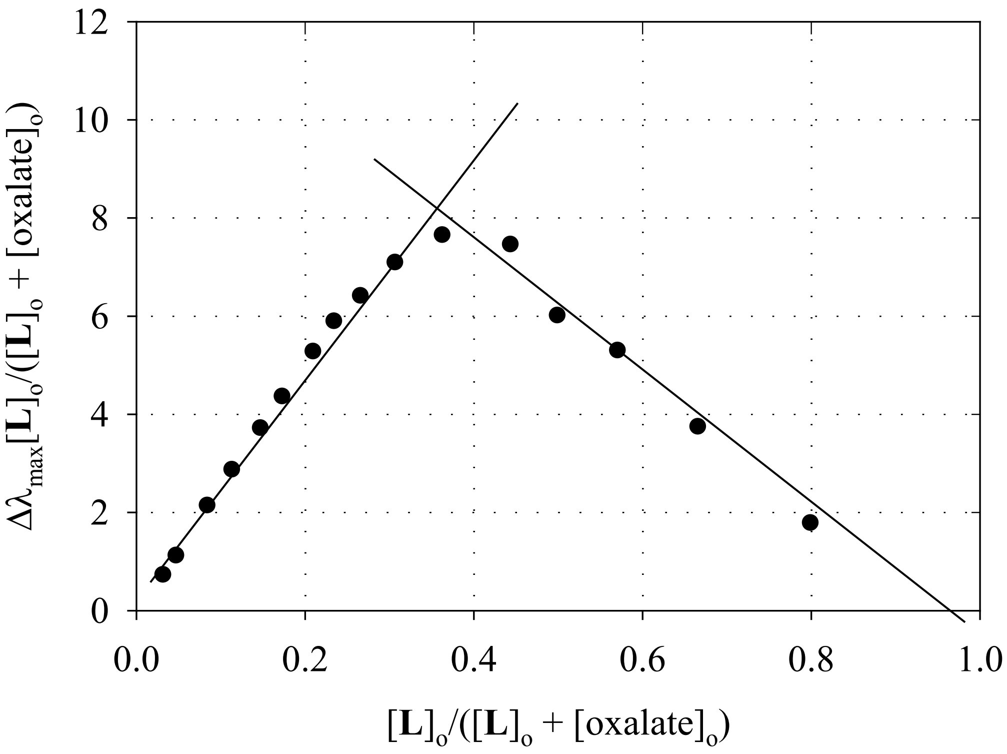

Figure S5. Job's plot of **L**.EY complex with potassium oxalate showing a maximum at 0.34 mole fraction of **L**, confirming a 1:2 (guest/host) complex formation.

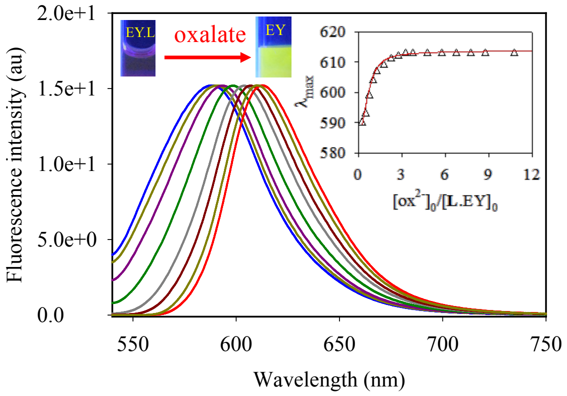

Figure S6. The change of emission λ_{max} (red shift) of [**L**.EY] (**L**:EY = 2:1) upon the addition of $K_2C_2O_4$ in water buffered with 20 mM HEPES at pH 7.4. $[\mathbf{L}]_o = 2 \times 10^{-6}$ M, $[K_2C_2O_4]_o = 2 \times 10^{-4}$ M. Excitation = 516 nm. Inset shows the plot of λ_{max} against the concentration of $K_2C_2O_4$.

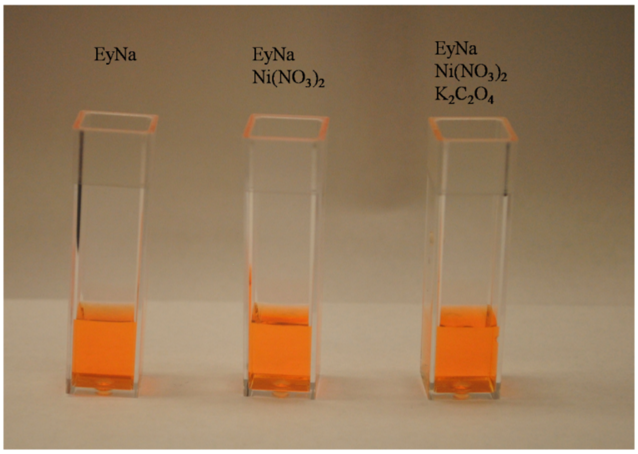

Figure S7. Control colorimetric experiment for oxalate using the mixture of $Ni(NO_3)_2$ (2×10^{-5} M) and Eosin Y (4×10^{-5} M) in water buffered with 20 mM HEPES at pH 7.4, showing no change in colour. Left: EY, middle: EY + $Ni(NO_3)_2$ (1:2, EY/$Ni(NO_3)_2$); right: EY + $Ni(NO_3)$ + $K_2C_2O_4$ (1:2:20).

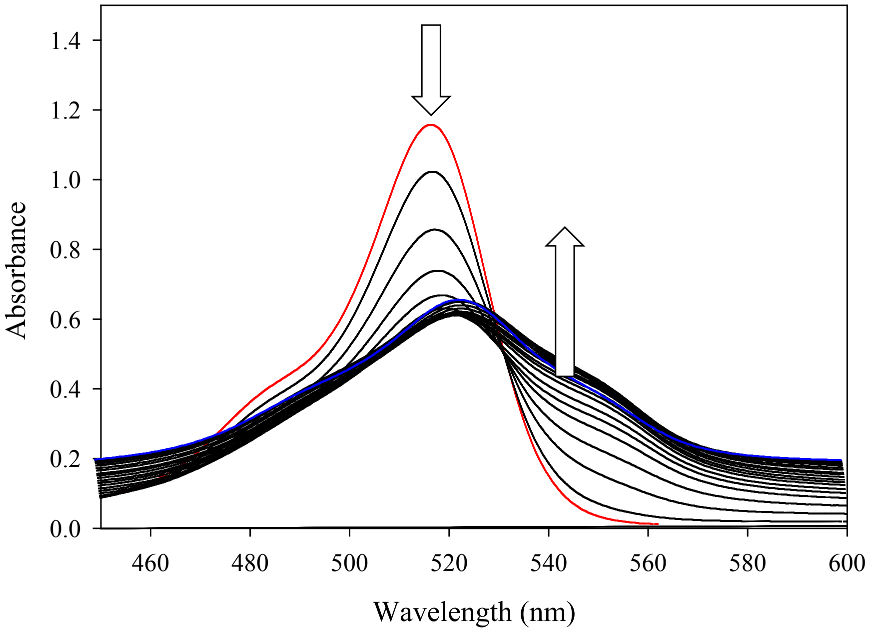

Figure S8. The change in absorbance spectra of Eosin Y dye (2 x 10^{-5} M) upon the addition of **L** (2 x 10^{-3} M) ($[dye]_o/[\mathbf{L}]_o = 0 - 25$) buffered with 20 mM HEPES at pH 7.4. Red curve is only dye and blue curve after addition of 25 equivalents of **L**

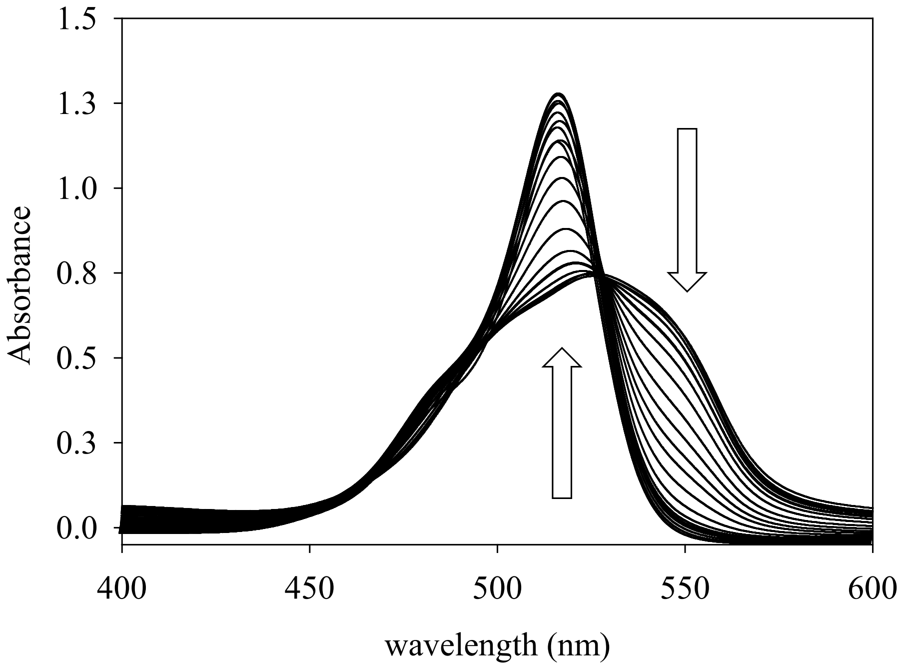

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Figure S9. The change in absorbance spectra of L.EY (L:EY = 1:2; $[L]_o = 2 \times 10^{-5}$ M) upon the addition of $K_2C_2O_4$ (2 x 10^{-3} M) ($[ox^{2-}]_o/[\mathbf{L}.EY]_o = 0 - 25$) buffered with 20 mM HEPES at pH 7.4.