Supplementary Information

for

Interaction Between Biimidazole Complexes of Ruthenium and Acetate: Hydrogen Bonding and Proton Transfer

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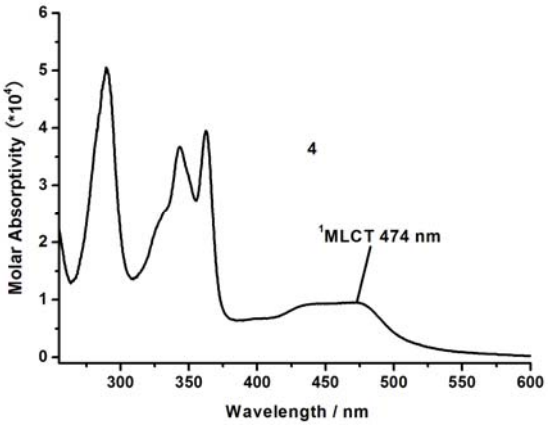

Fig. S1 Absorption spectra of **4** in acetonitrile at 298 K

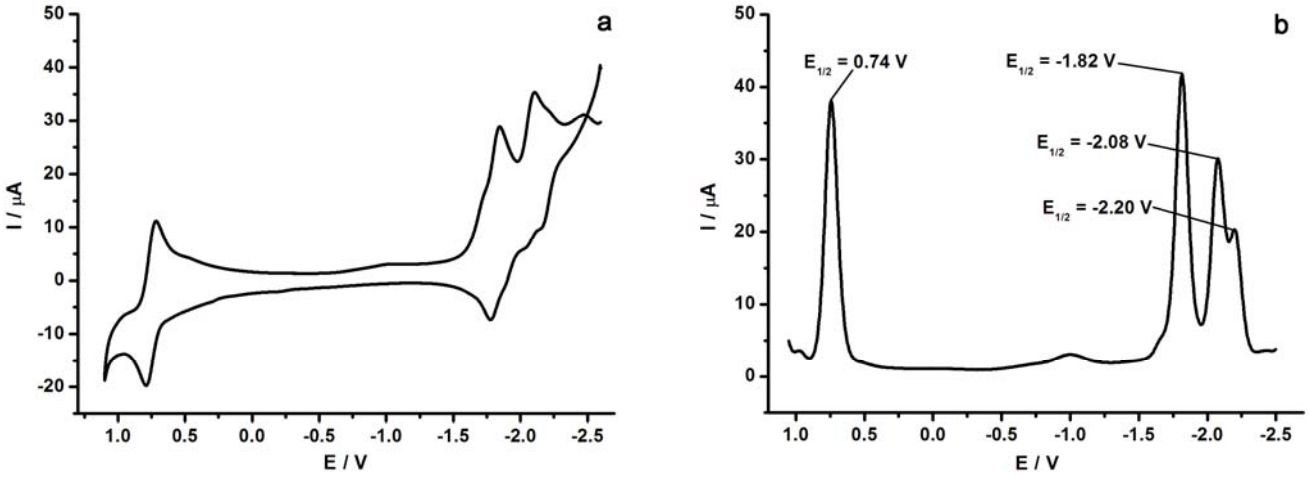

Fig. S2 (a) Cyclic voltammetric and (b) square wave voltammetric curves of **4** with a scan rate of 100 $mV \cdot s^{-1}$ in acetonitrile at 298 K (vs. $Ag/AgNO_3$).

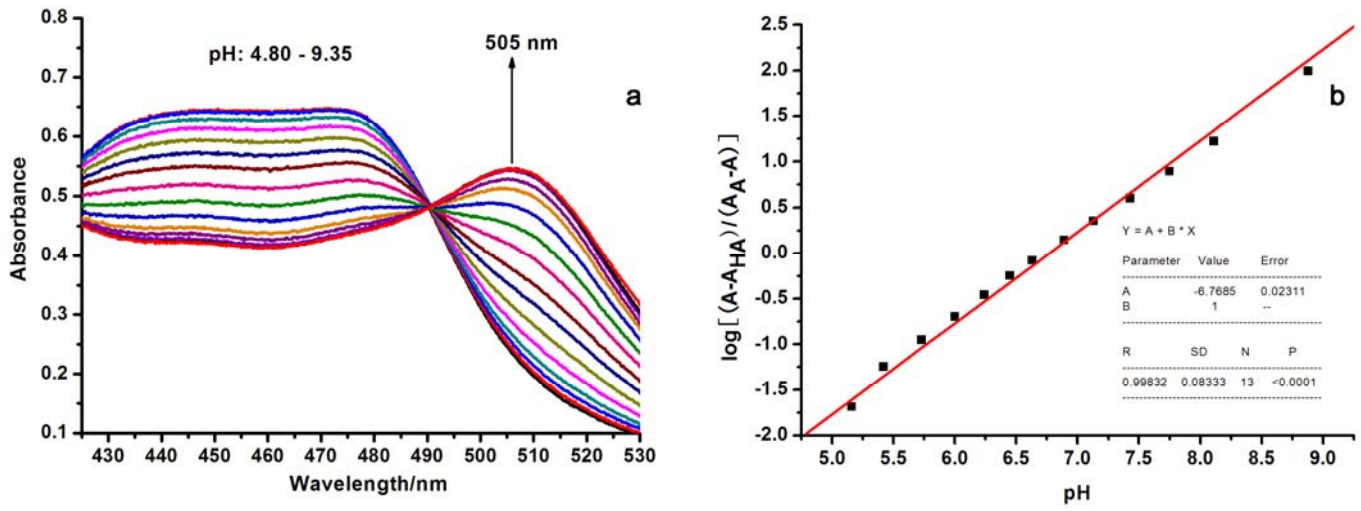

Fig. S3 Determination of pK_{a1} of **4** in acetonitrile-water mixture by UV method. (a) Absorption spectral change as pH value increases. (b) Linear fitting of pK_{a1}.

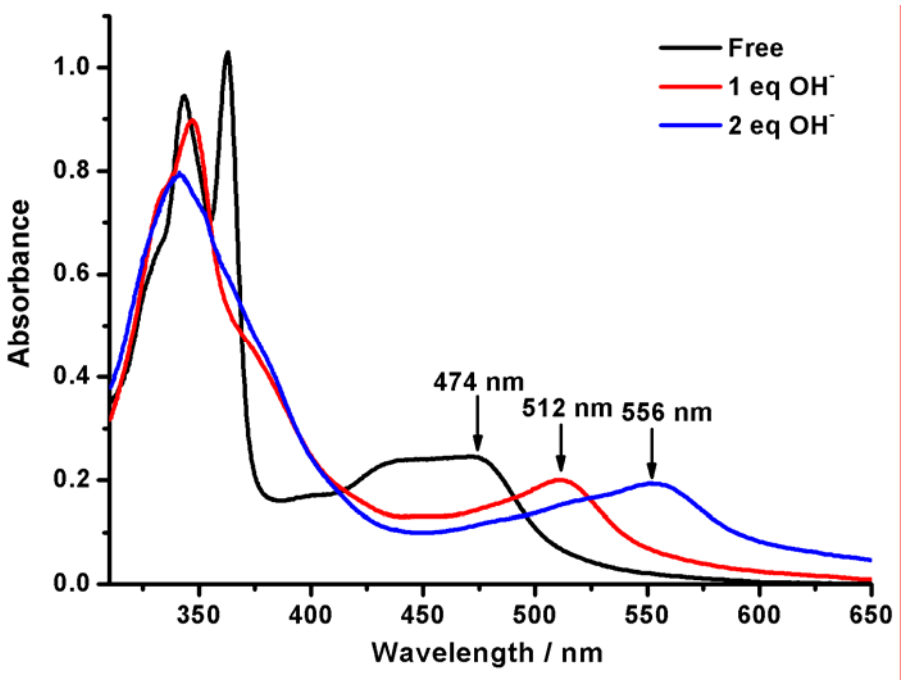

Fig. S4 Absorption spectra of **4** (2×10^{-5} mol·dm^{-3}) in acetonitrile in the absence and presence of 1 equiv and 2 equiv of OH^-.

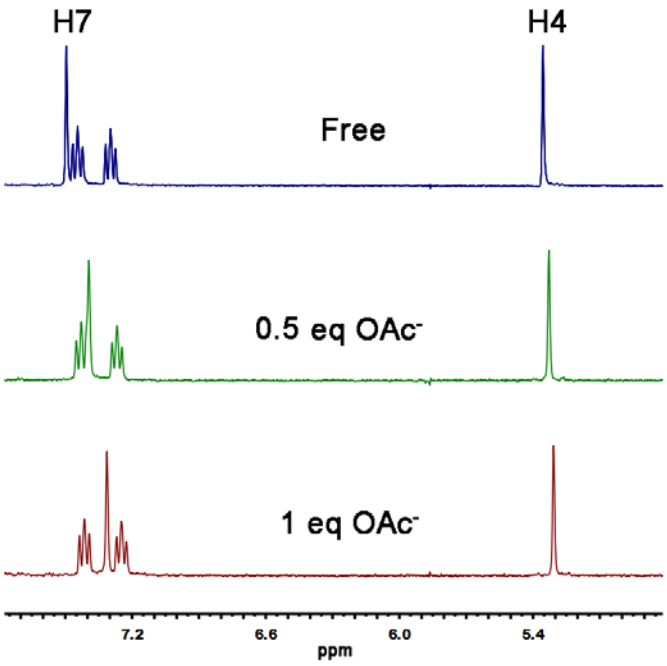

Fig. S5 ^{1}H NMR titration of **4** (0.003 mol·dm^{-3}) in acetonitrile-d_3 with OAc$^-$ (298 K, 300 MHz).

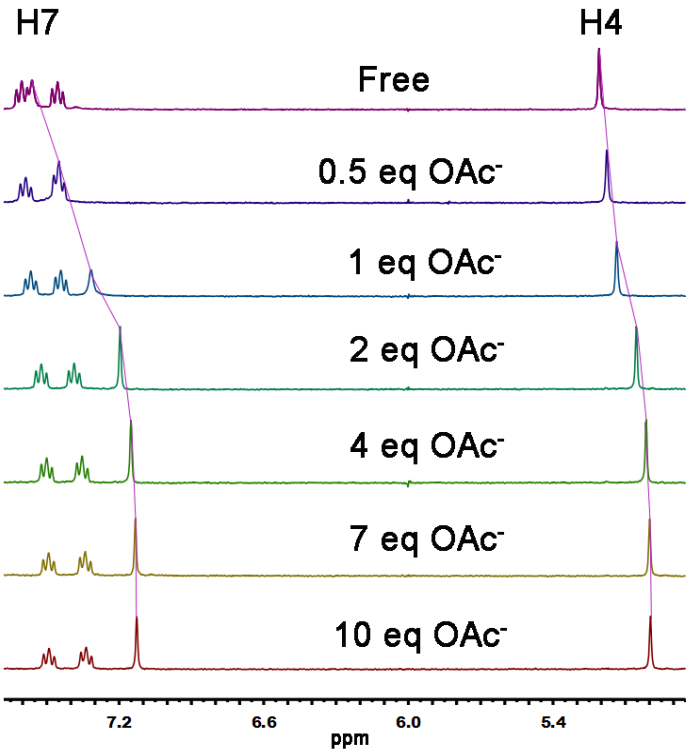

Fig. S6 ^{1}H NMR titration of **4** (0.003 mol·dm^{-3}) in DMSO-*d*6 with OAc$^-$ (298 K, 300 MHz).

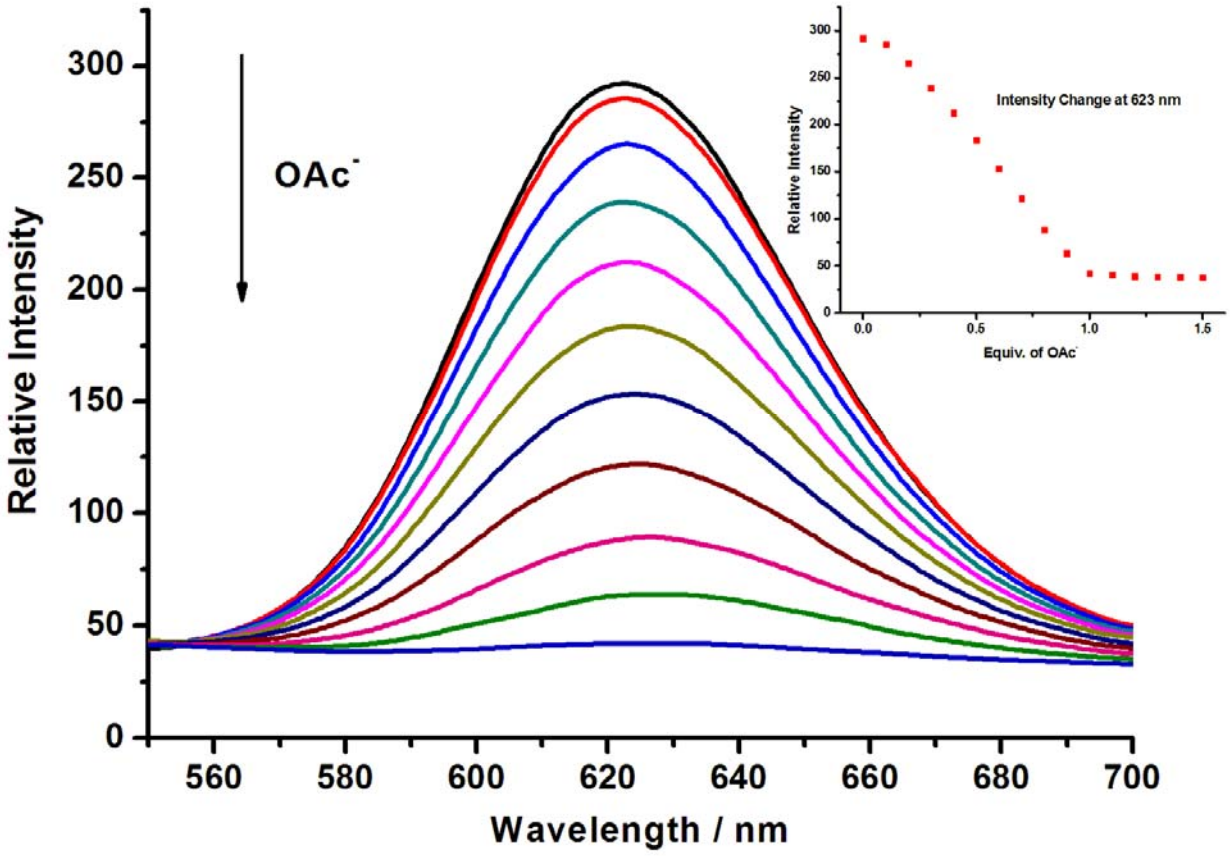

Fig. S7 Emission spectral response of **4** (2.0×10^{-5} mol·dm^{-3} in acetonitrile, 298K, λ_{ex} = 470 nm) upon addition of OAc^- anion. Inset: Intensity at 623 nm versus equiv of OAc^-.

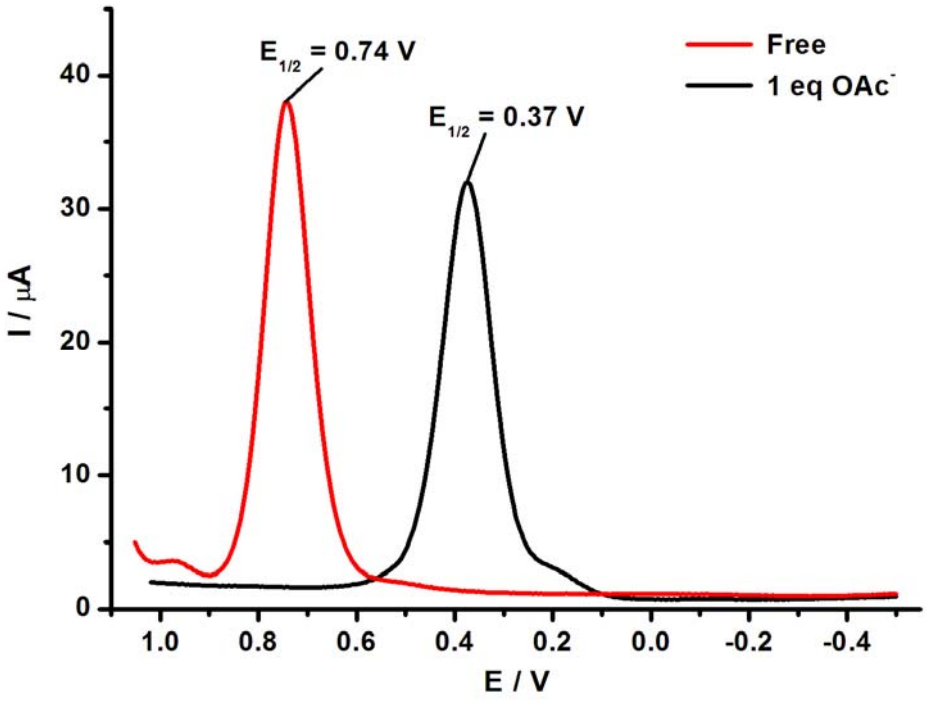

Fig. S8 SWV measurements of **4** in acetonitrile (0.001 mol·dm^{-3}) in the absence and presence of 1 equiv of OAc^- (*vs.* $Ag/AgNO_3$).

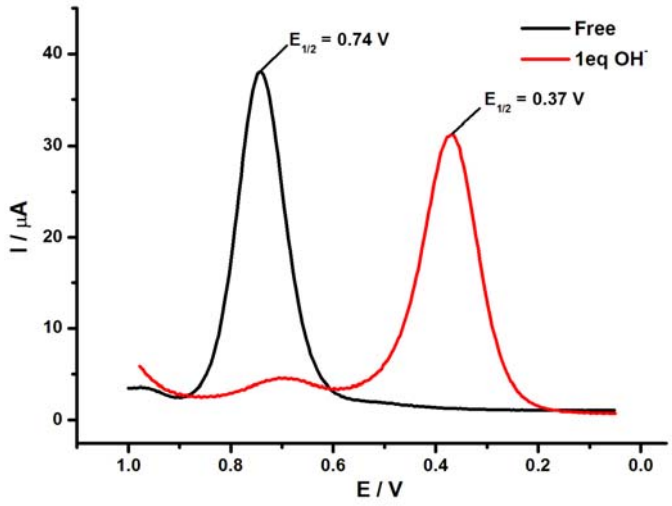

Fig. S9 SWV measurements of **4** in acetonitrile (0.001 mol·dm^{-3}) in the absence and presence of 1 equiv of OH^- (*vs.* $Ag/AgNO_3$).

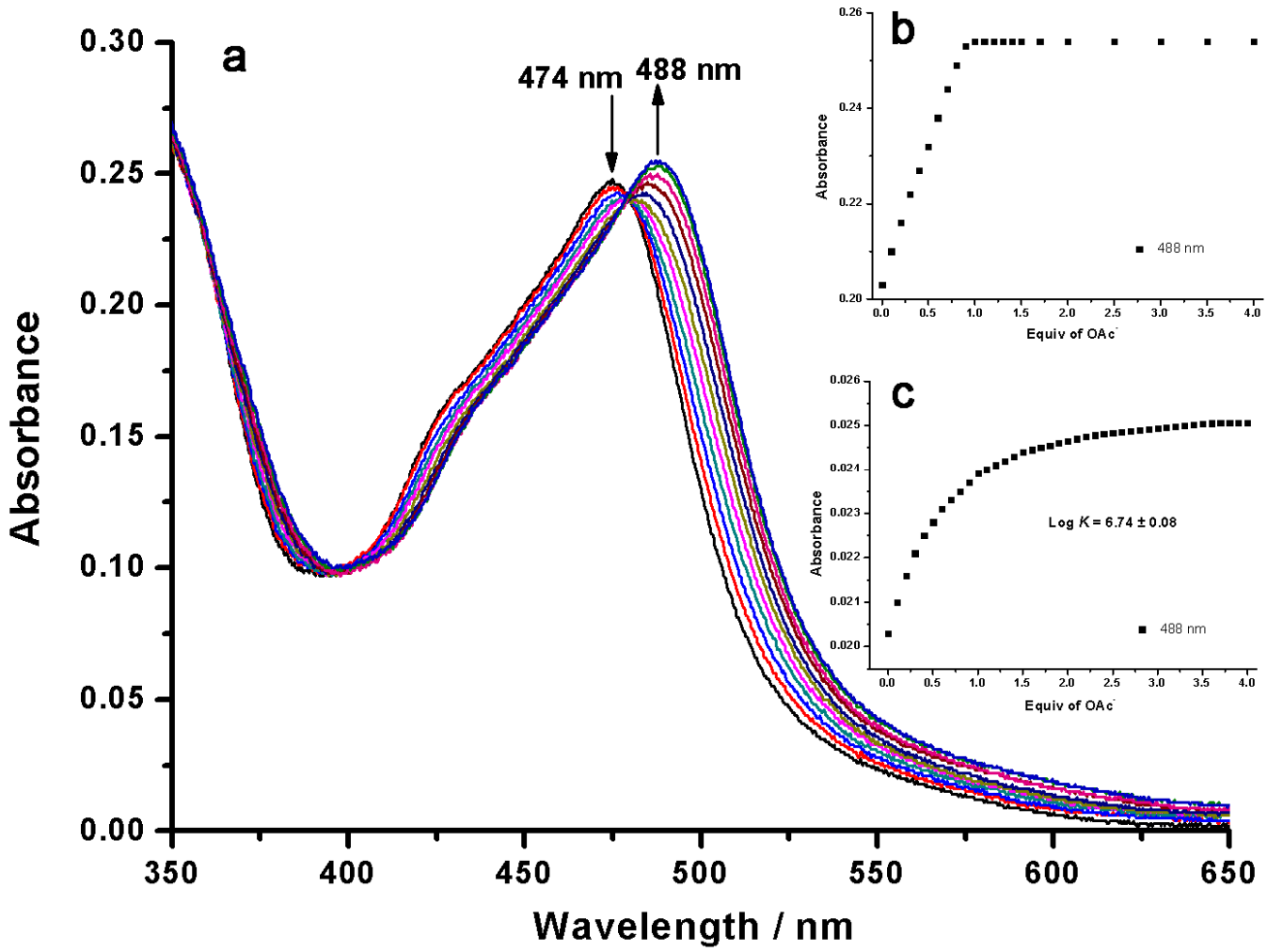

Fig. S10 (a) UV-vis titration of **1** (2.0×10^{-5} mol·dm^{-3}) in acetonitrile in the presence of 0.0016 mol·dm^{-3} HOAc upon addition of OAc^-. Absorbance change at 488 nm for a 2.0×10^{-5} mol·dm^{-3} solution (b) and for a 2.0×10^{-6} mol·dm^{-3} solution (c) of **1**.

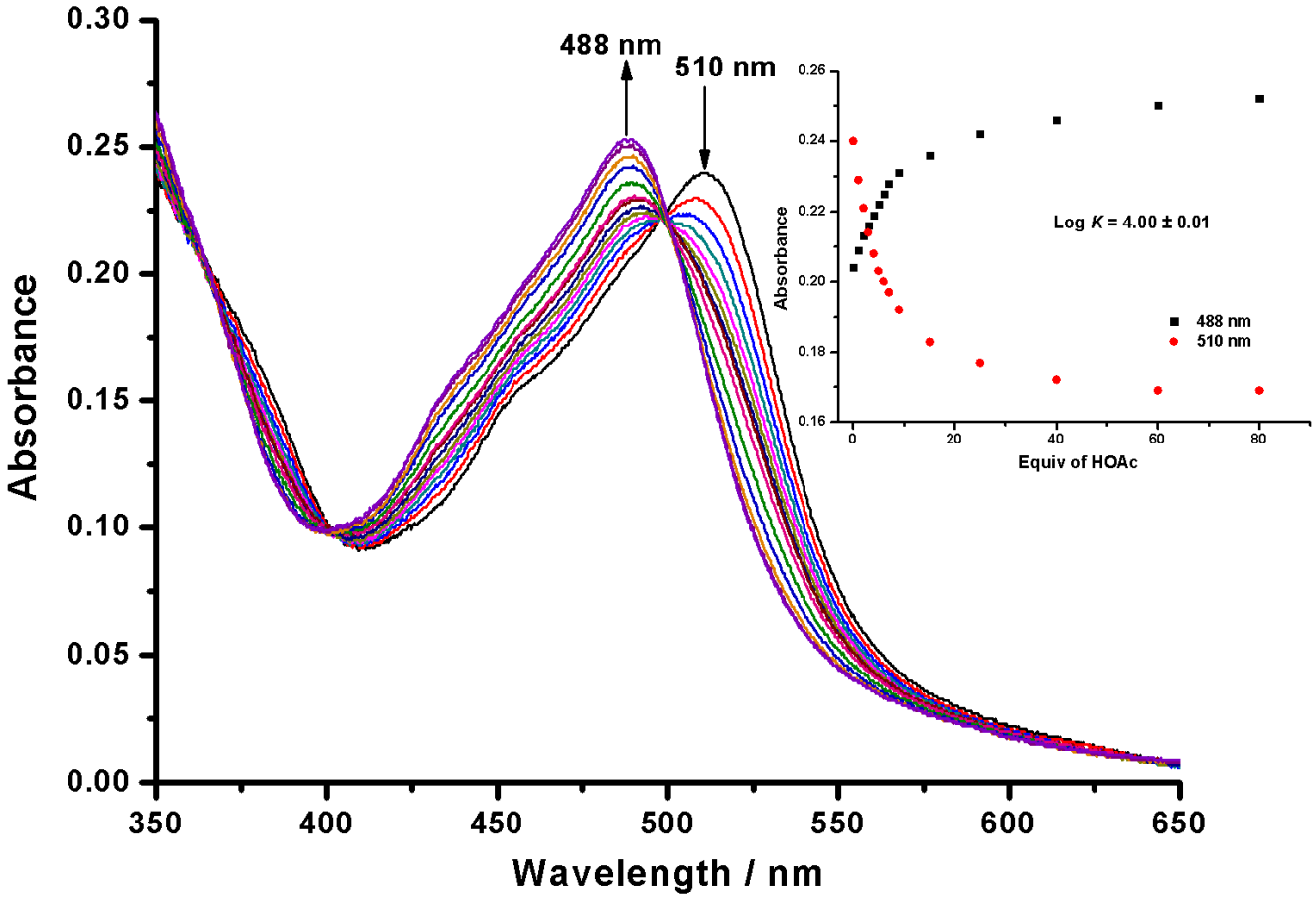

Fig. S11 UV-vis titration of mono-deprotonated **1** (2.0×10^{-5} mol·dm^{-3}) in acetonitrile upon addition of HOAc. Inset: Absorbance at 488 and 510 nm vs. equiv of HOAc.

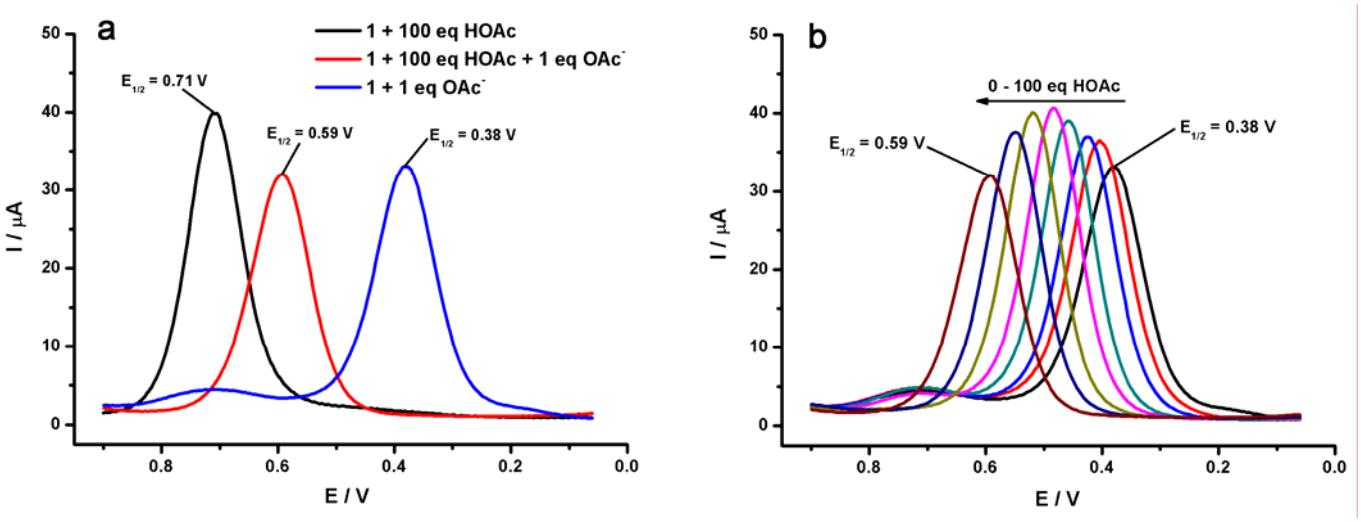

Fig. S12 (a) SWV curves of **1** (0.001 mol·dm^{-3}) and 100 equiv. of HOAc in acetonitrile in the absence and presence of 1 equiv. of OAc^-, and **1** in the presence of 1 equiv. of OAc^-. (b) Evolution of SWV curves of **1** (0.001 mol·dm^{-3}) and 1 equiv. of OAc^- in acetonitrile in the presence of increasing amount of HOAc from 0 to 100 equiv.

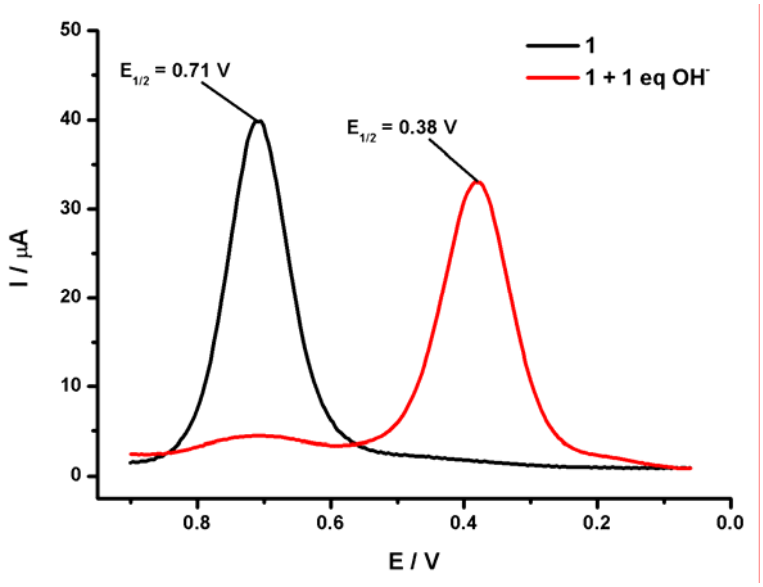

Fig. S13 SWV measurements of **1** in acetonitrile (0.001 mol·dm^{-3}) in the absence and presence of 1 equiv of OH^- (*vs.* $Ag/AgNO_3$).

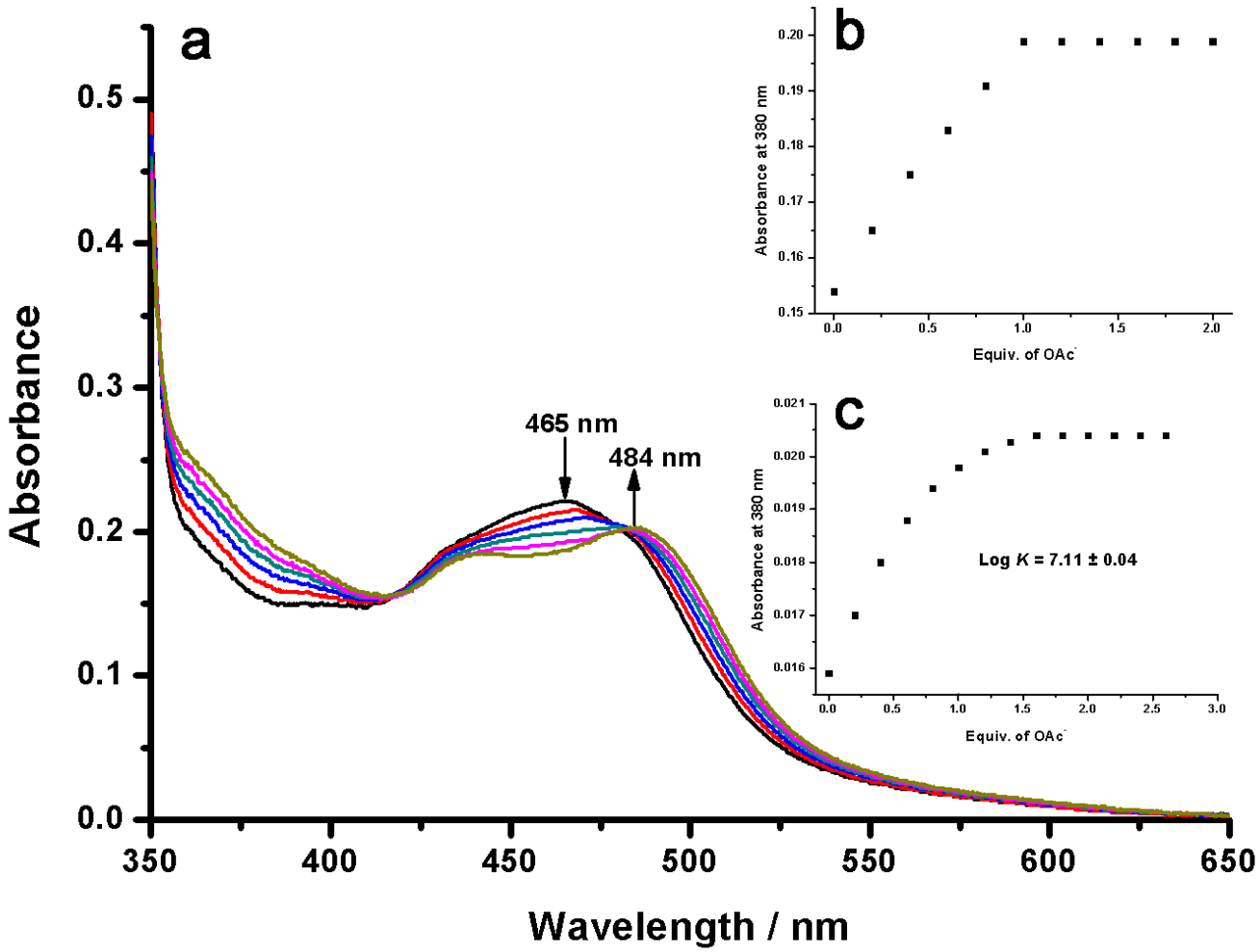

Fig. S14 (a) UV-vis titration of **2** (2.0×10^{-5} mol·dm^{-3}) in acetonitrile in the presence of 0.048 mol·dm^{-3} HOAc upon addition of OAc^-. Absorbance change at 380 nm for a 2.0×10^{-5} mol·dm^{-3} solution (b) and for a 2.0×10^{-6} mol·dm^{-3} solution (c) of **2**.

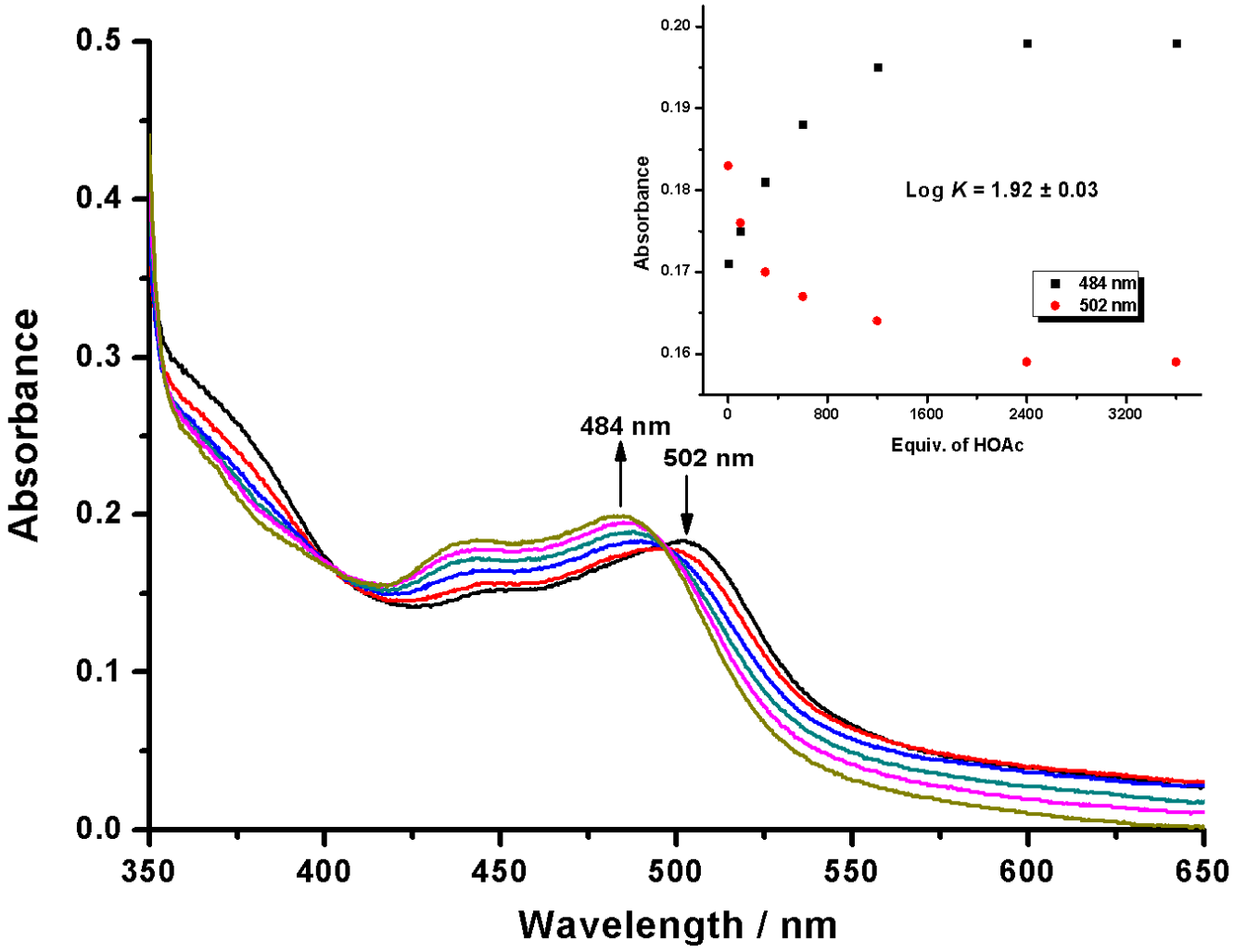

Fig. S15 UV-vis titration of mono-deprotonated **2** (2.0×10^{-5} mol·dm^{-3}) in acetonitrile upon addition of HOAc. Inset: Absorbance at 484 and 502 nm vs. equiv of HOAc.

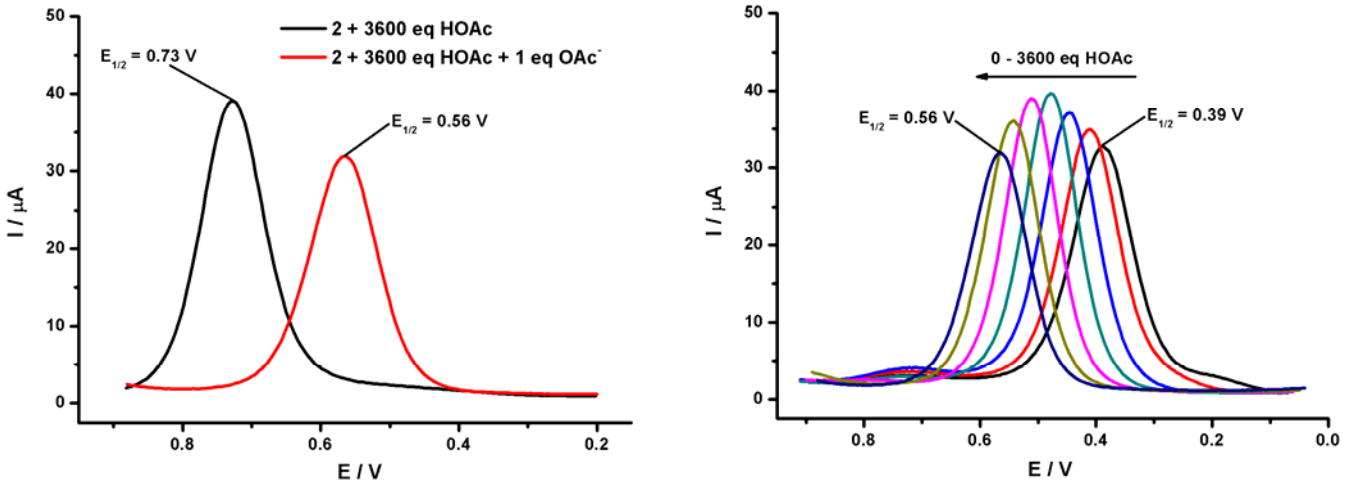

Fig. S16 (a) SWV curves of **2** (0.001 mol·dm^{-3}) and 3600 equiv. of HOAc in acetonitrile in the absence and presence of 1 equiv. of OAc^-. (b) Evolution of SWV curves of **2** (0.001 mol·dm^{-3}) and 1 equiv. of OAc^- in acetonitrile in the presence of increasing amount of HOAc from 0 to 3600 equiv.

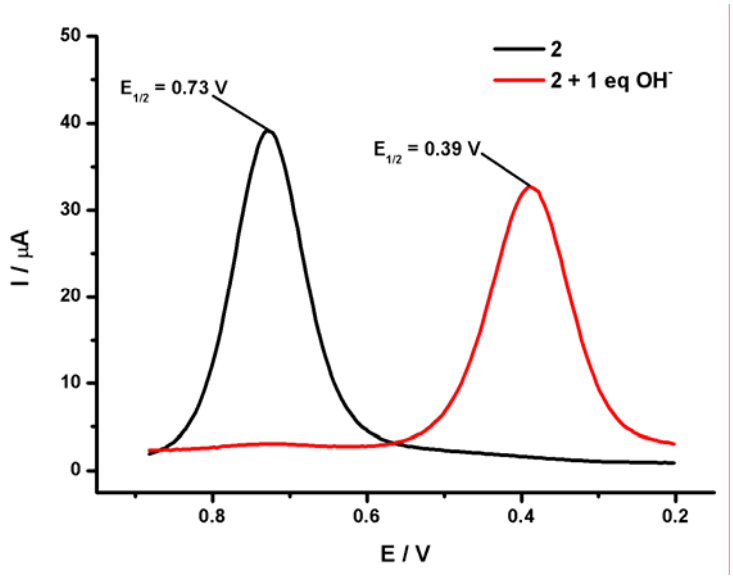

Fig. S17 SWV measurements of **2** in acetonitrile (0.001 mol·dm^{-3}) in the absence and presence of 1 equiv of OH^- (*vs.* $Ag/AgNO_3$).

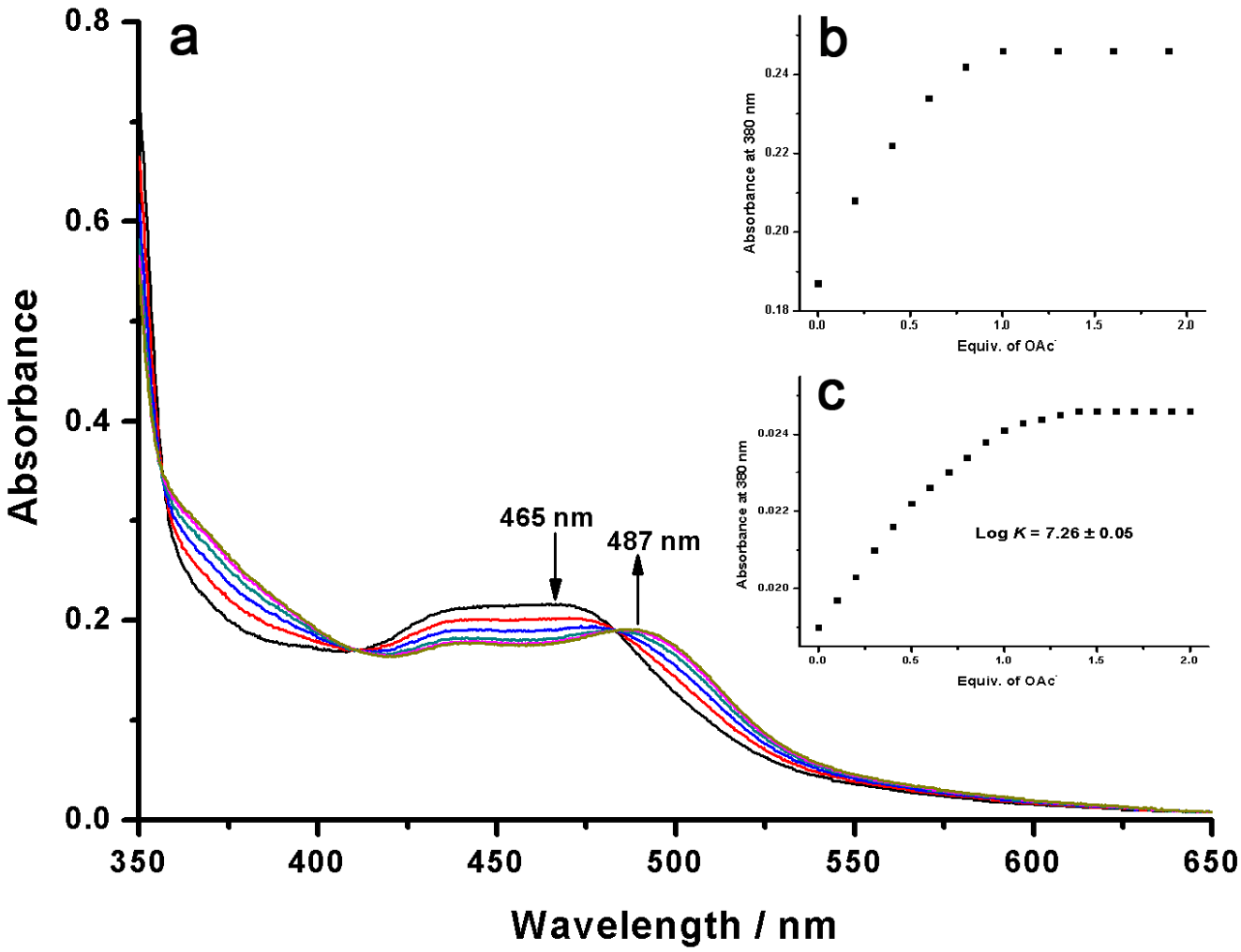

Fig. S18 (a) UV-vis titration of **3** (2.0×10^{-5} mol·dm^{-3}) in acetonitrile in the presence of 0.009 mol·dm^{-3} HOAc upon addition of OAc^-. Absorbance change at 380 nm for a 2.0×10^{-5} mol·dm^{-3} solution (b) and for a 2.0×10^{-6} mol·dm^{-3} solution (c) of **3**.

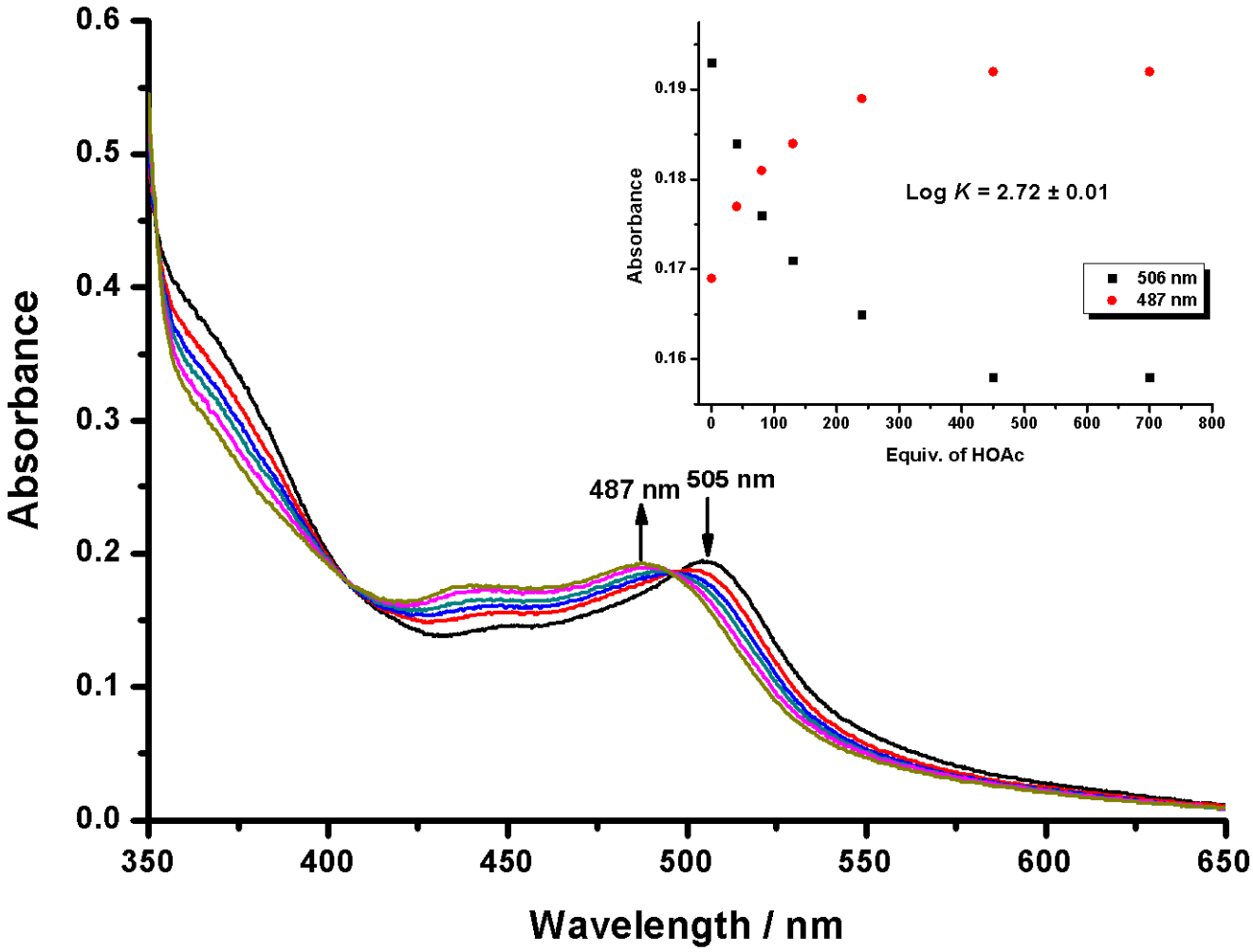

Fig. S19 UV-vis titration of mono-deprotonated **3** (2.0×10^{-5} mol·dm^{-3}) in acetonitrile upon addition of HOAc. Inset: Absorbance at 487 and 505 nm vs. equiv of HOAc.

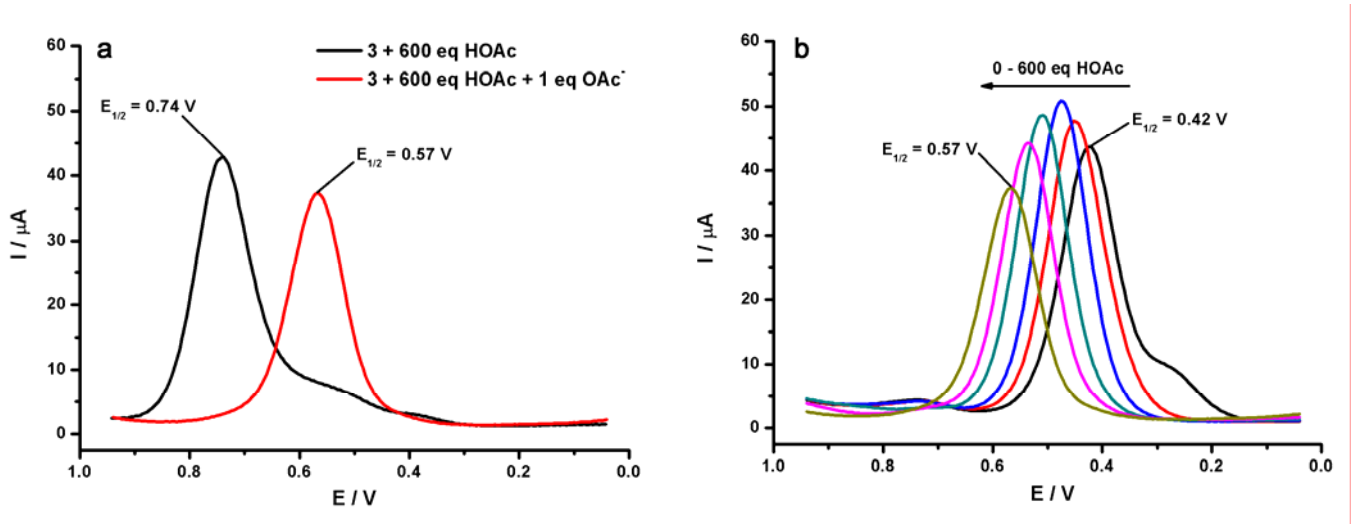

Fig. S20 (a) SWV curves of **3** (0.001 mol·dm^{-3}) and 600 equiv. of HOAc in acetonitrile in the absence and presence of 1 equiv. of OAc^-. (b) Evolution of SWV curves of **3** (0.001 mol·dm^{-3}) and 1 equiv. of OAc^- in acetonitrile in the presence of increasing amount of HOAc from 0 to 600 equiv.

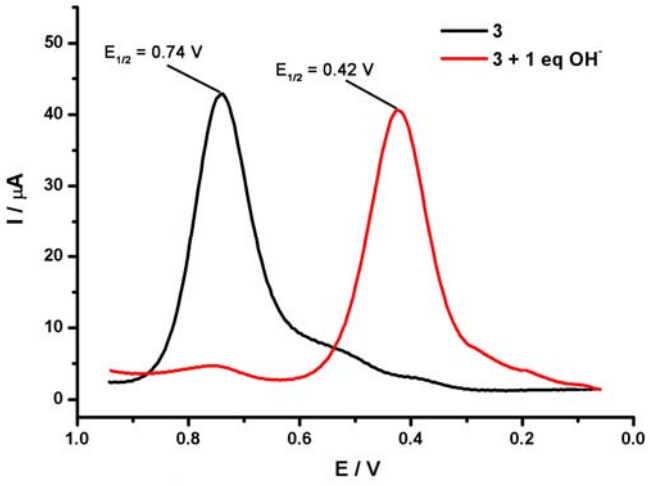

Fig. S21 SWV measurements of **3** in acetonitrile (0.001 mol·dm^{-3}) in the absence and presence of 1 equiv of OH^- (*vs.* $Ag/AgNO_3$).

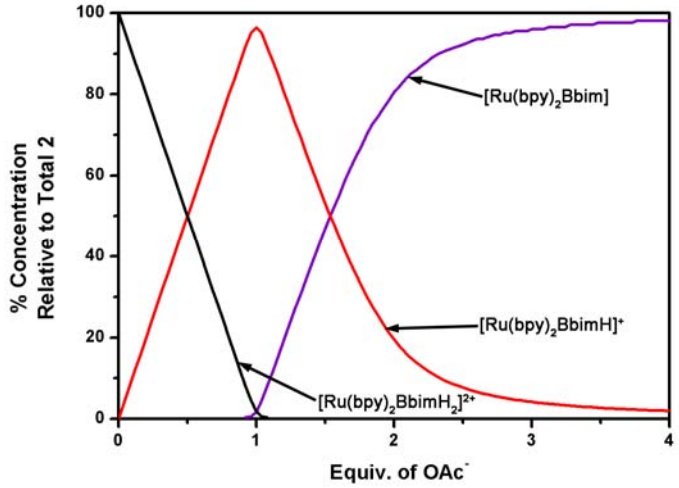

Fig. S22 Distribution diagram for **2** in acetonitrile upon addition of OAc^-.

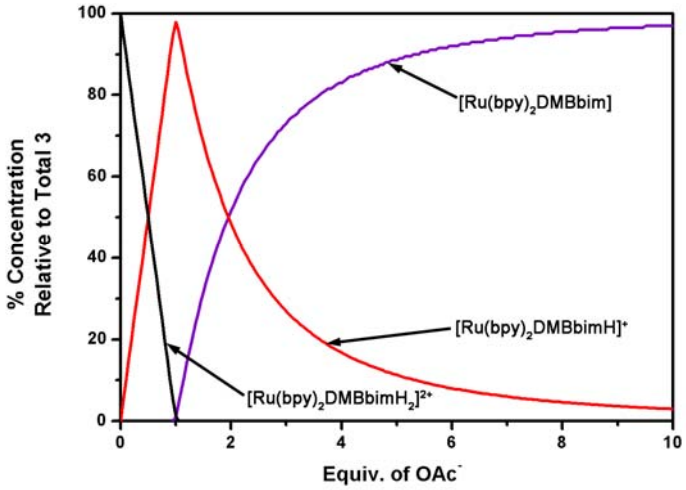

Fig. S23 Distribution diagram for **3** in acetonitrile upon addition of OAc^-.