Supporting Information

Carboxylated Pillar[n]arene (n = 5-7) Host Molecules: High Affinity and Selective Binding in Water

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Determination of binding constant

Method for direct titration assay.

Binding constants K_a were calculated by nonlinear fitting with Origin 9 software based on 1:1 binding stoichiometry as the following equation:

$[H]_0$: initial host concentration; $[G]_0$: initial guest concentration; ΔA: change of Fluorescence intensity; Δε: change of coefficiency; K_a: binding constant.

$$\Delta_A = \Delta_\varepsilon \cdot \{\frac{1}{2}([H]^0 + [G]^0 + \frac{1}{K_a}) - \sqrt{\frac{1}{4}([H]^0 + [G]^0 + \frac{1}{K_a}) - [H]^0 \cdot [G]^0}\}$$

Method for indicator displacement assay.

Binding constants were measured with displacement assay and fitted with Scientist™ software based on the following model.

// MicroMath Scientist Model File
IndVars: ConcAntot
DepVars: Absorb
Params: ConcHtot, ConcGtot, Khg, Kha, AbsorbMax, AbsorbMin
Khg = ConcHG / (ConcH * ConcG)
Kha = ConcHAn / (ConcH * ConcAn)
Absorb = AbsorbMin + (AbsorbMax-AbsorbMin)*(ConcHG/ConcGtot)
ConcHtot = ConcH + ConcHG + ConcHAn
ConcGtot = ConcHG + ConcG
ConcAntot = ConcAn + ConcHAn
0 < ConcHG < ConcHtot
0 < ConcH < ConcHtot
0 < ConcG < ConcGtot
0 < ConcAn < ConcAntot

Direct Titration

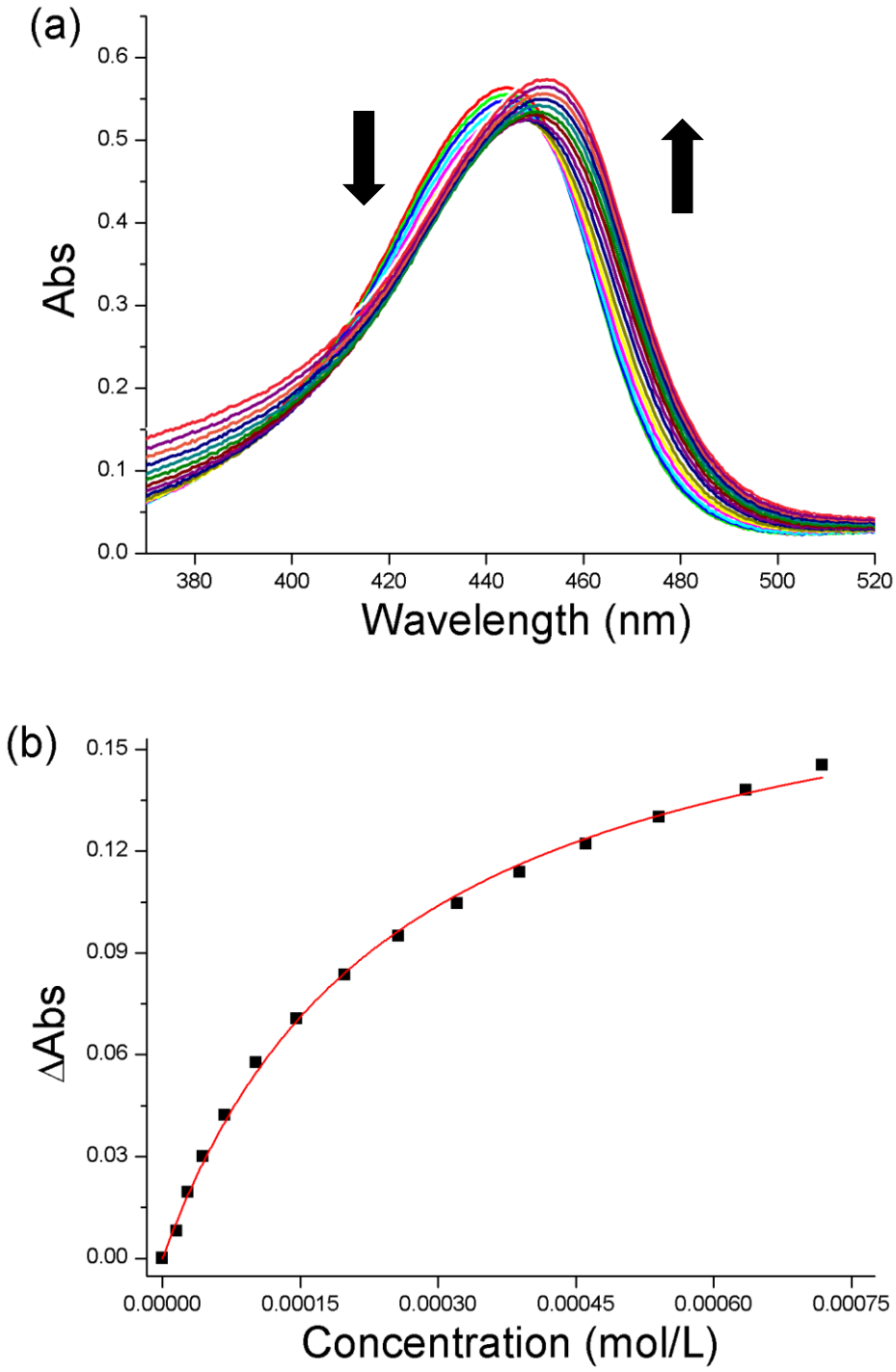

Figure S1. (a) UV-Vis spectra from the titration of dye **2** (10.0 μM) with **WP5** (0 – 718 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔAbs (A-A_0) at 475 nm as a function of the concentration of **WP5**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model (K_a = (4.1 ± 0.2) × 10^3 M^{-1}).

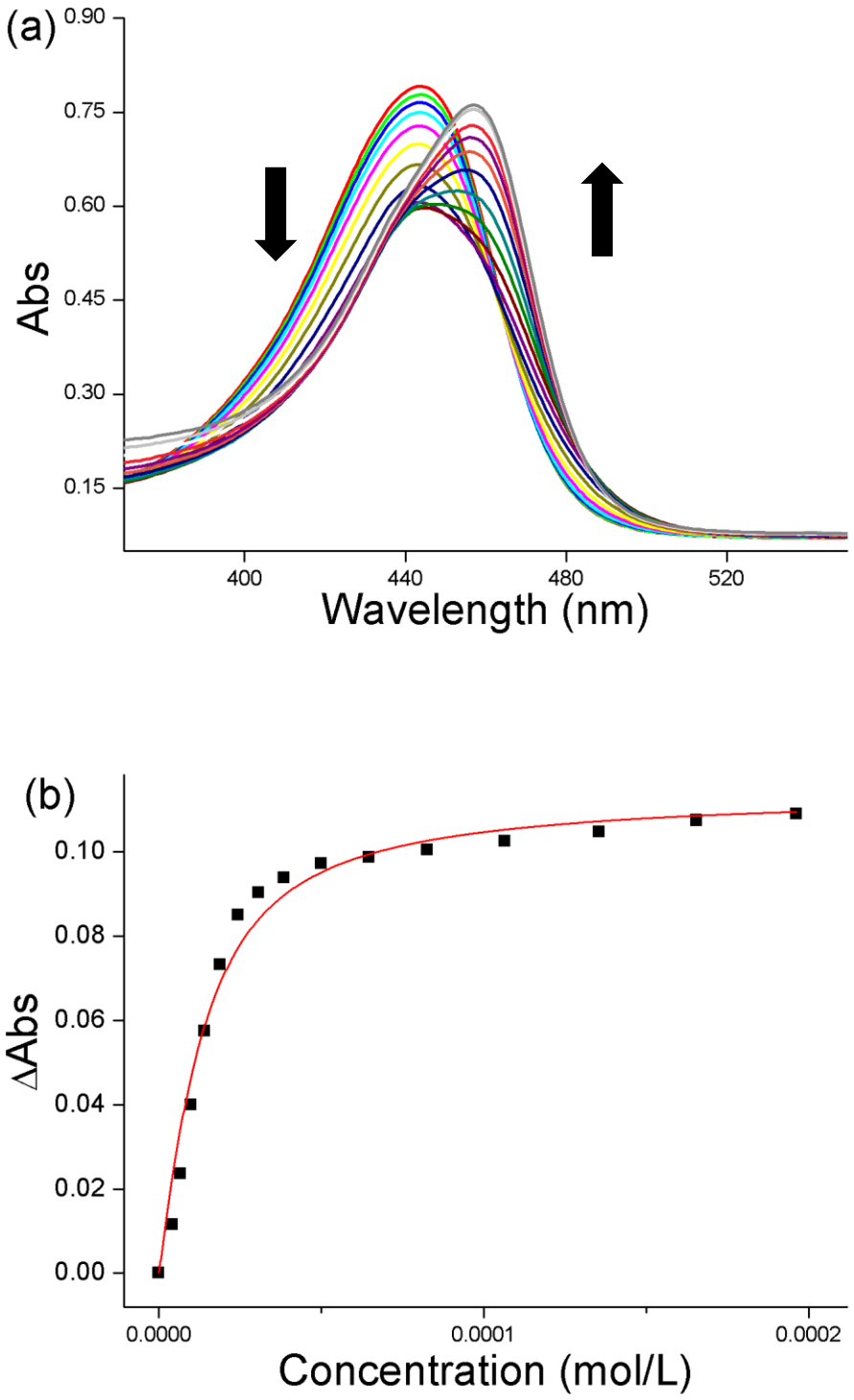

Figure S2. (a) UV-Vis spectra from the titration of dye **2** (15.0 μM) with **WP7** (0 – 196 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔAbs ($A-A_0$) at 480 nm as a function of the concentration of **WP7**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (1.1 \pm 0.2) \times 10^5\ M^{-1}$).

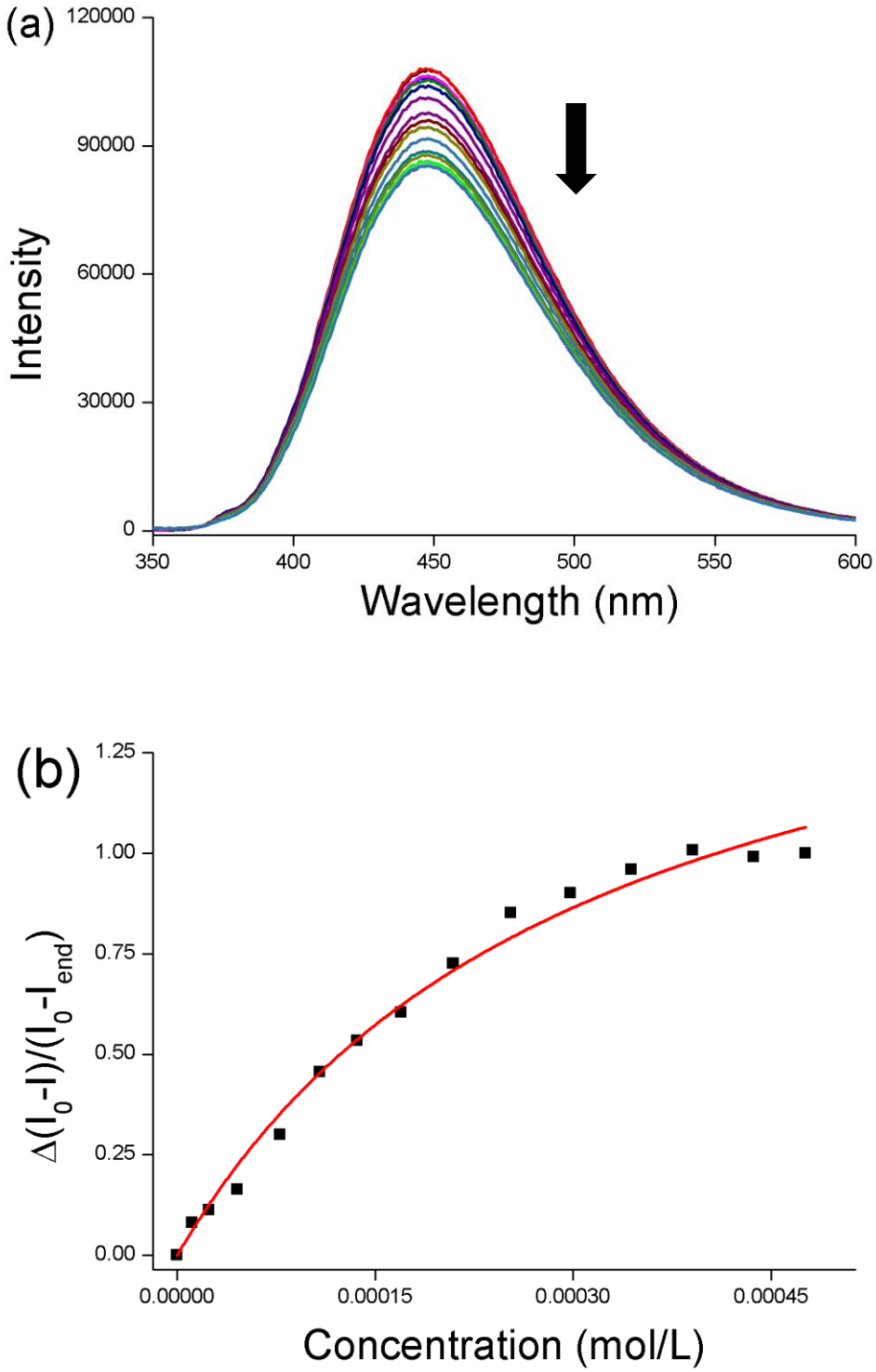

Figure S3. (a) Fluorescence spectra from the titration of guest **14** (10.0 μM) with **WP5** (0 – 476 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 460 nm as a function of the concentration of **WP5**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (3.3 \pm 0.5) \times 10^3\ M^{-1}$).

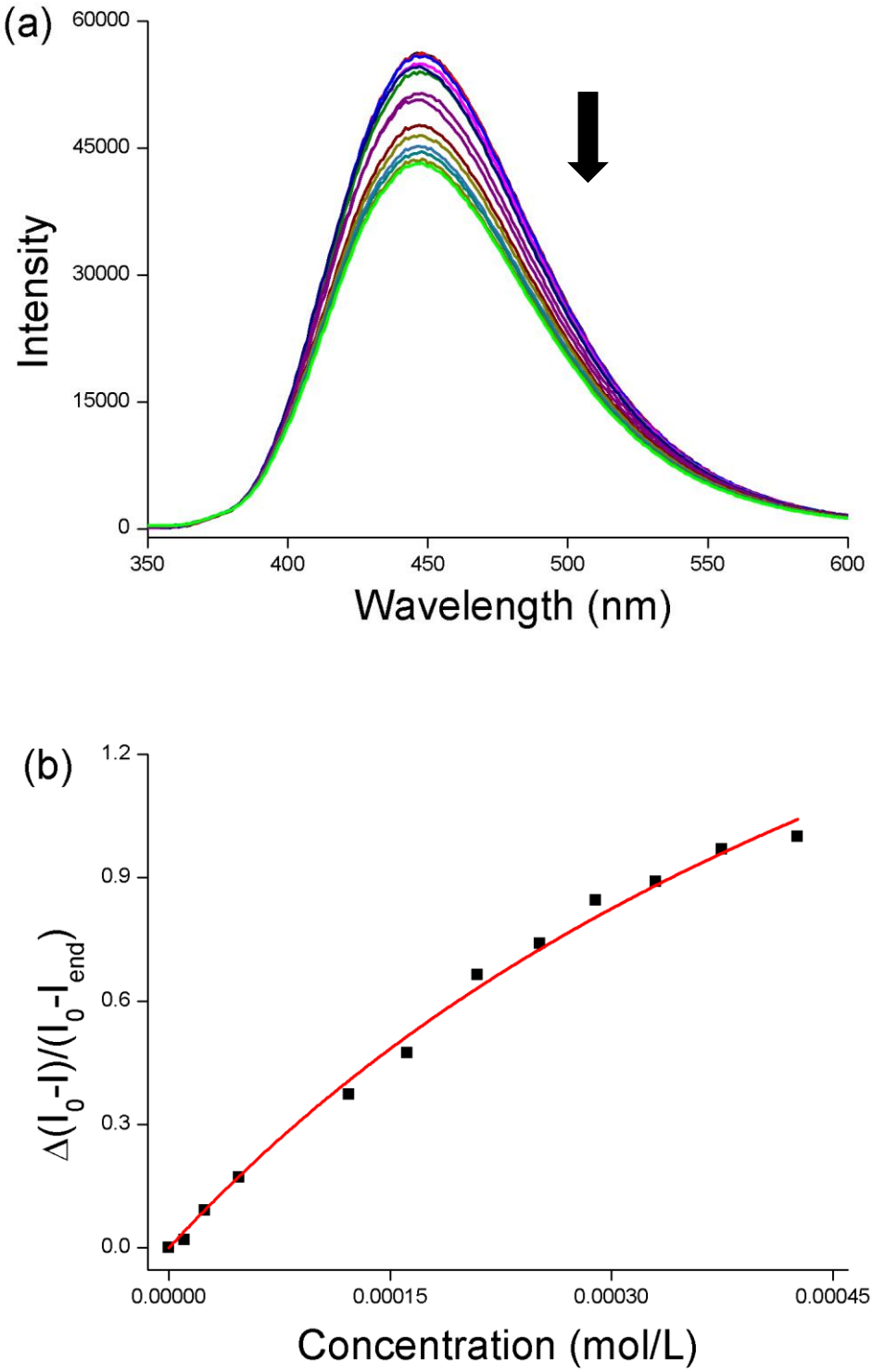

Figure S4. (a) Fluorescence spectra from the titration of guest **14** (5.0 μM) with **WP6** (0 – 426 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 460 nm as a function of the concentration of **WP6**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (1.4 \pm 0.3) \times 10^3\ M^{-1}$).

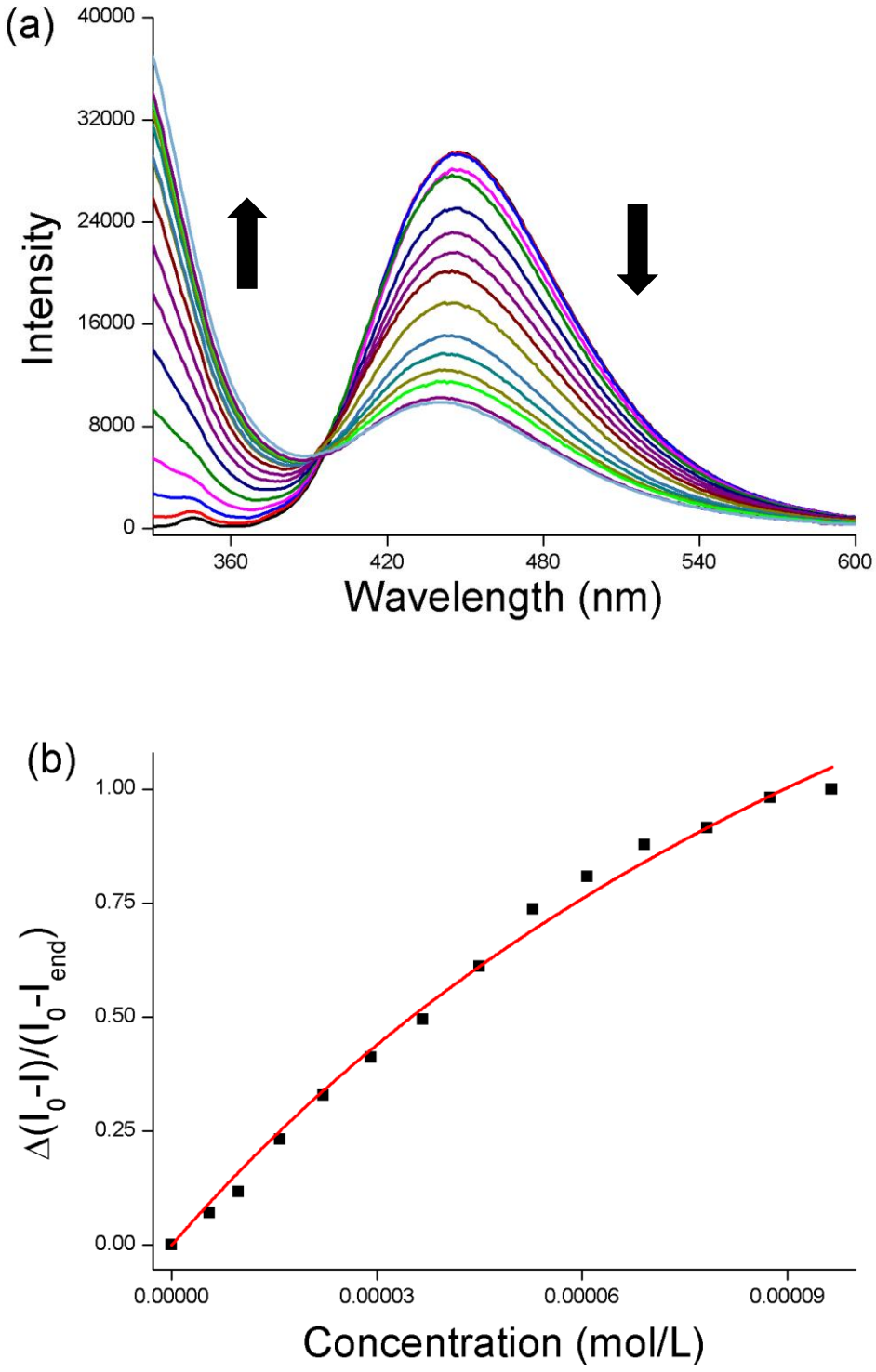

Figure S5. (a) Fluorescence spectra from the titration of guest **14** (1.0 μM) with **WP7** (0 – 96.5 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 460 nm as a function of the concentration of **WP7**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (6.3 \pm 1.1) \times 10^3\ M^{-1}$).

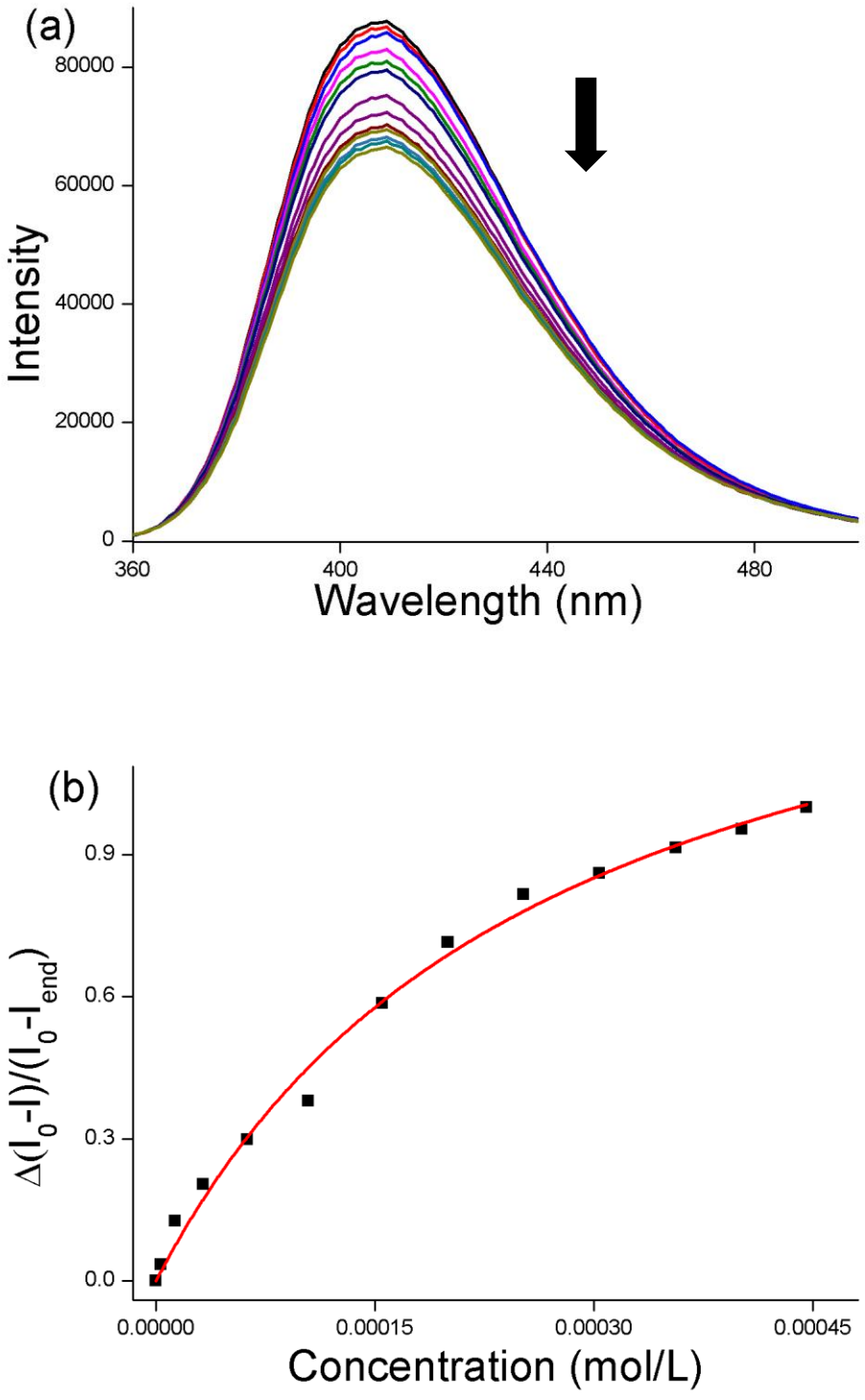

Figure S6. (a) Fluorescence spectra from the titration of guest **15** (10.0 μM) with **WP5** (0 – 445 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 390 nm as a function of the concentration of **WP5**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (3.9 \pm 0.5) \times 10^3\ M^{-1}$).

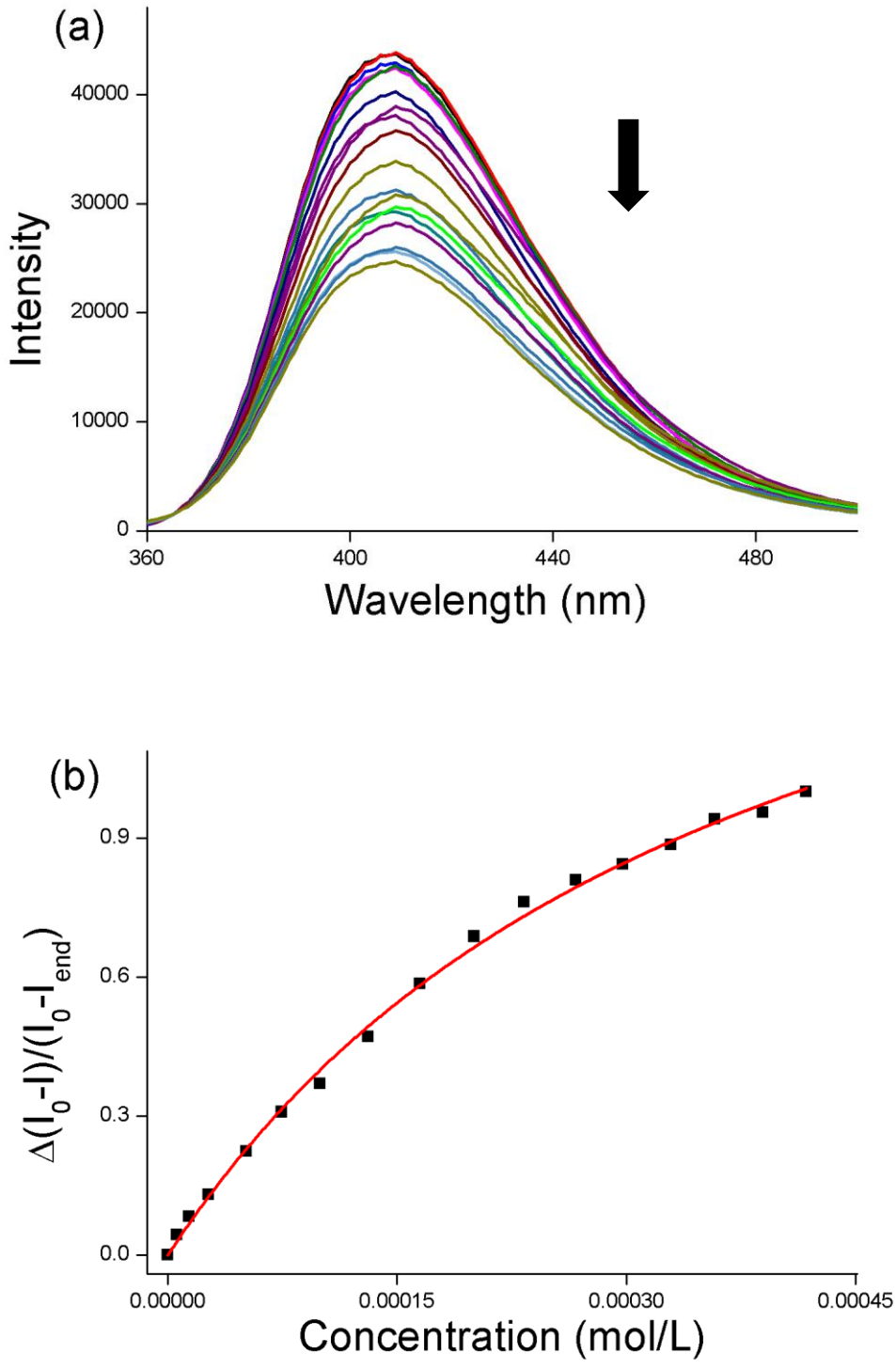

Figure S7. (a) Fluorescence spectra from the titration of guest **15** (5.0 μM) with **WP6** (0 – 418 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 390 nm as a function of the concentration of **WP6**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (2.7 \pm 0.2) \times 10^3\ M^{-1}$).

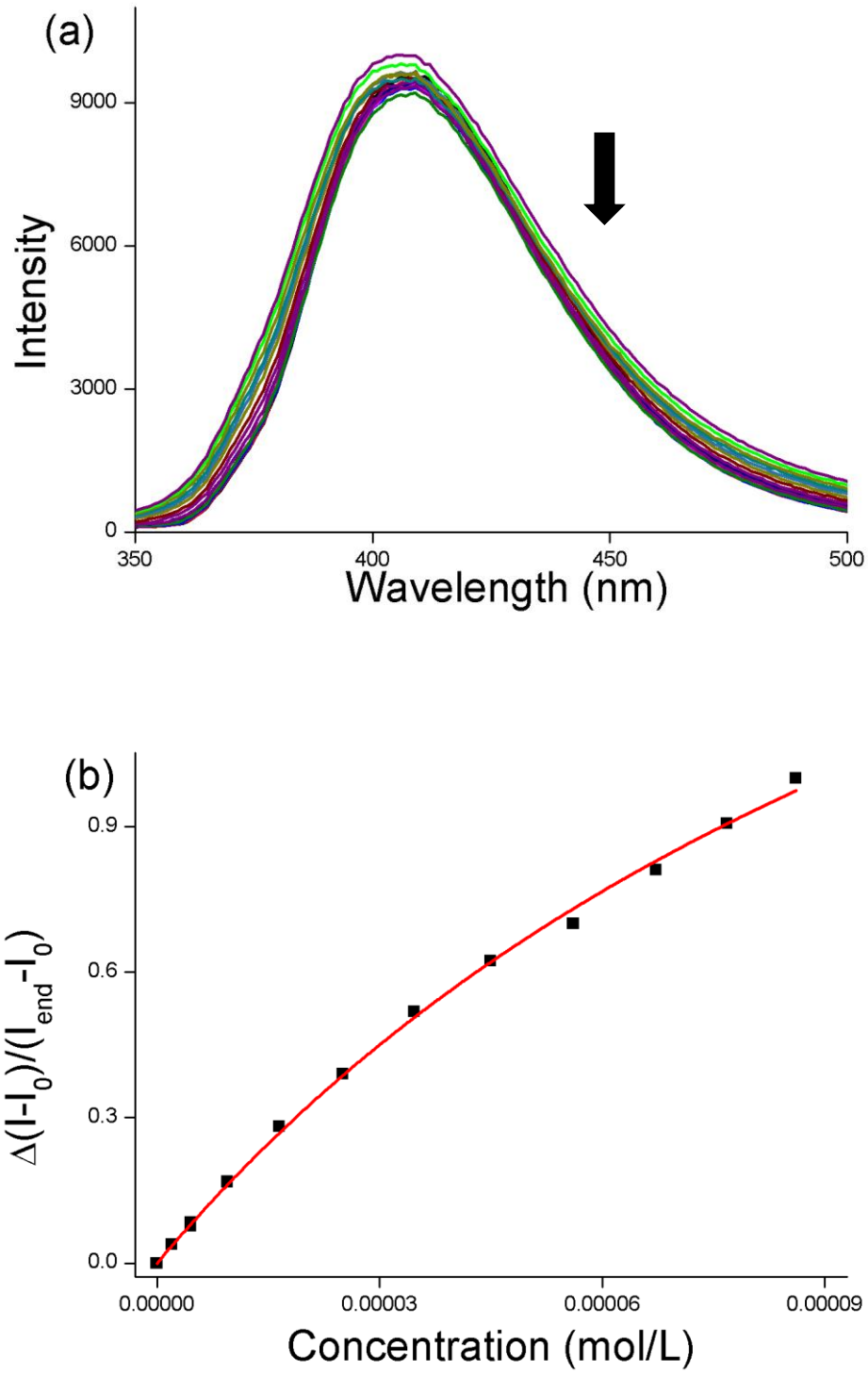

Figure S8. (a) Fluorescence spectra from the titration of guest **15** (1.0 μM) with **WP7** (0 – 86.1 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I- I_0)/(I_{end} -I_0)$ at 390 nm as a function of the concentration of **WP7**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (7.1 \pm 0.7) \times 10^3\ M^{-1}$).

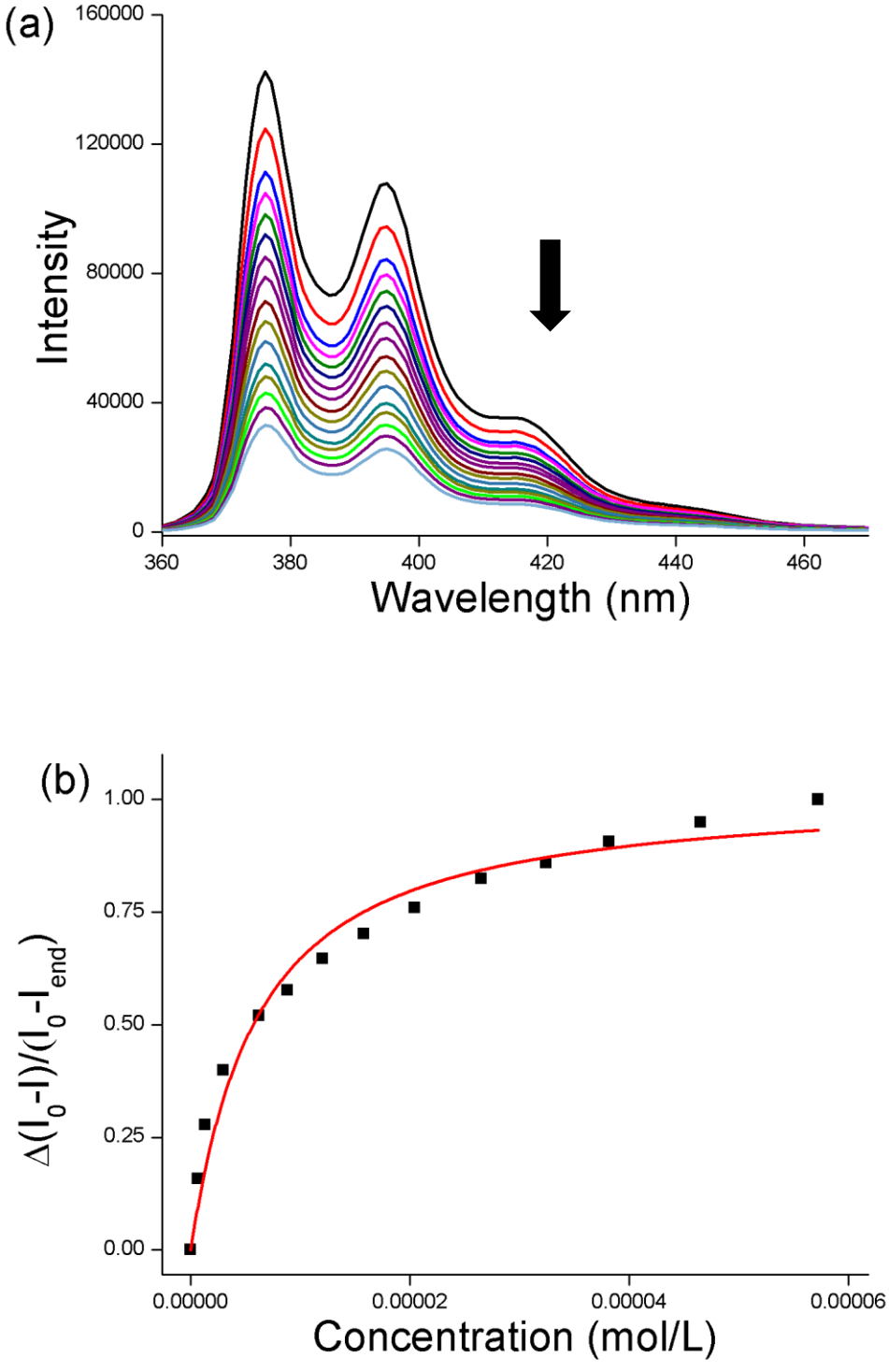

Figure S9. (a) Fluorescence spectra from the titration of guest **16** (1.0 μM) with **WP6** (0 – 57.3 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 378 nm as a function of the concentration of **WP6**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (1.8 \pm 0.3) \times 10^5\ M^{-1}$).

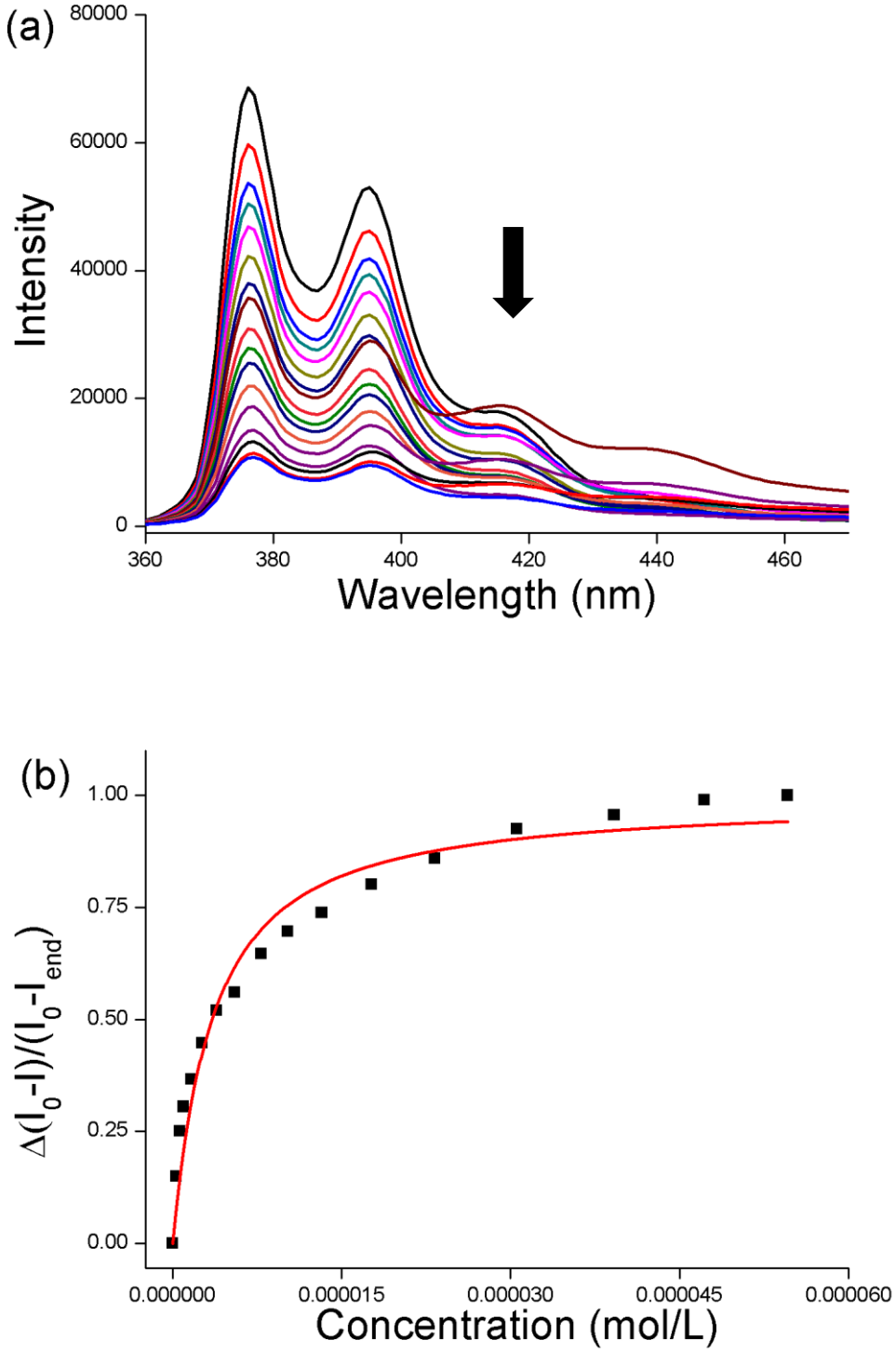

Figure S10. (a) Fluorescence spectra from the titration of guest **16** (1.0 μM) with **WP7** (0 – 54.6 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 378 nm as a function of the concentration of **WP7**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (3.3 \pm 0.5) \times 10^5\ M^{-1}$).

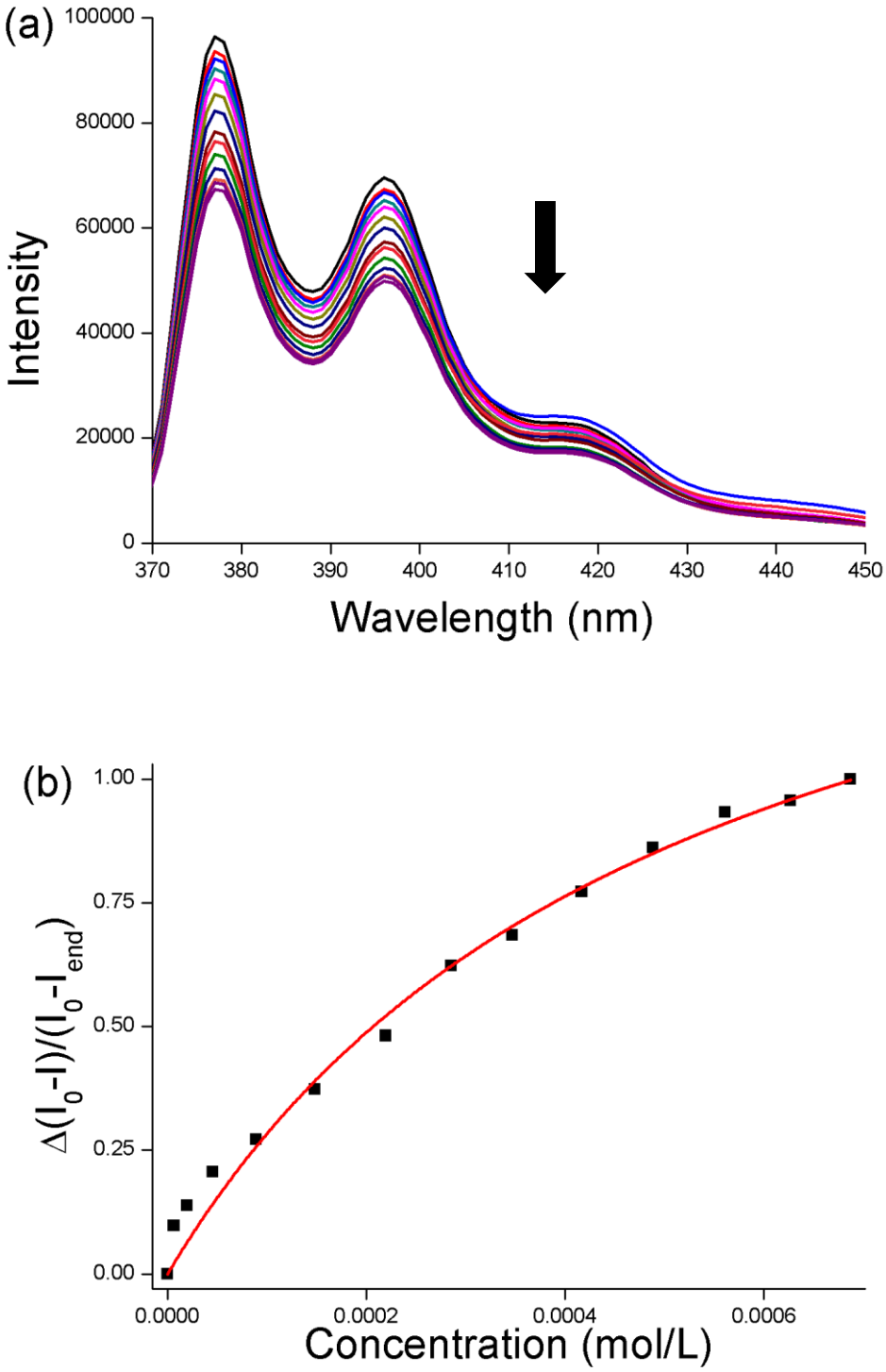

Figure S11. (a) Fluorescence spectra from the titration of guest **17** (5.0 μM) with **WP5** (0 – 687 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 378 nm as a function of the concentration of **WP5**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (2.0 \pm 0.3) \times 10^3\ M^{-1}$).

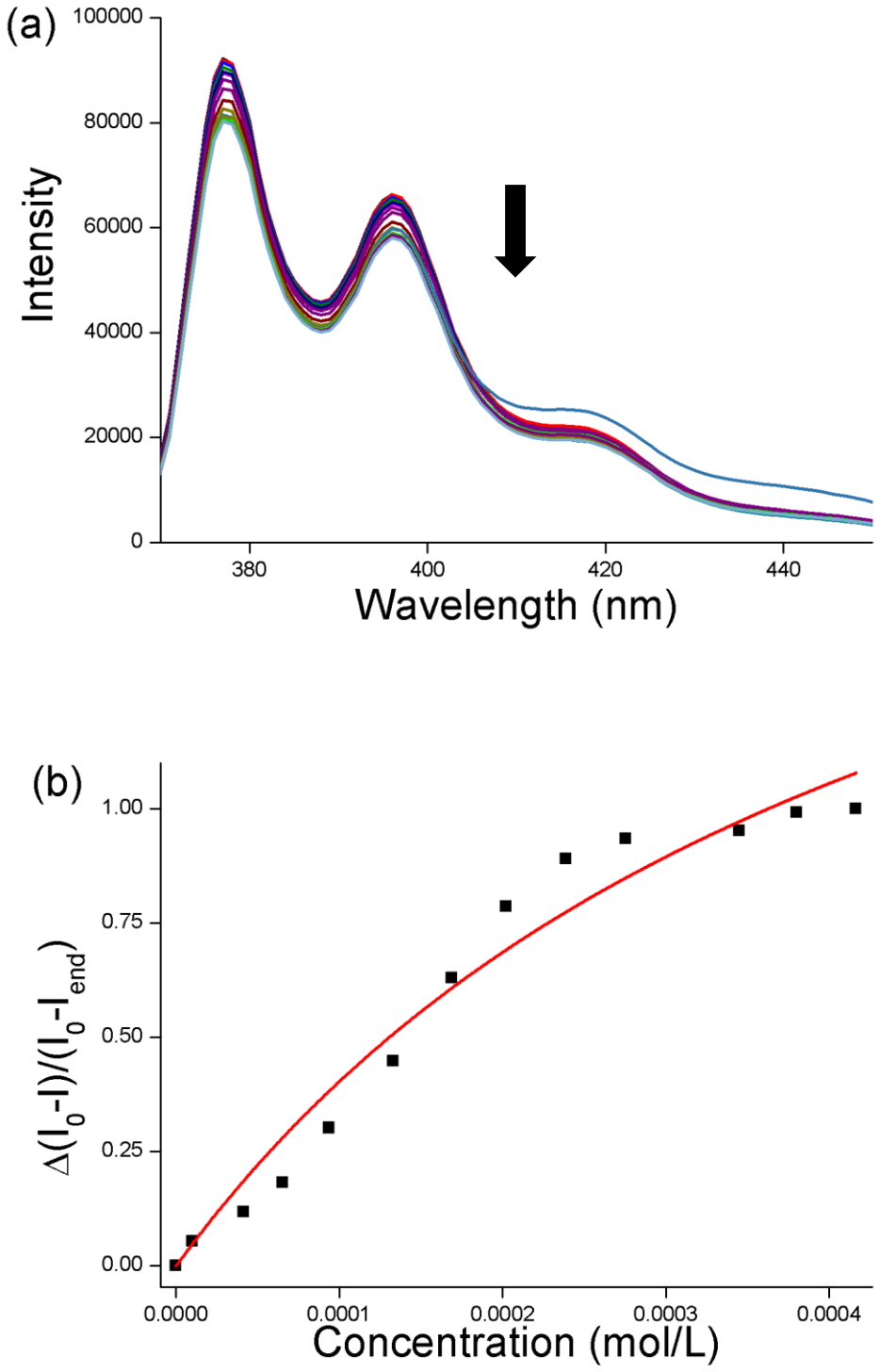

Figure S12. (a) Fluorescence spectra from the titration of guest **17** (5.0 μM) with **WP6** (0 – 416 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 378 nm as a function of the concentration of **WP6**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (2.2 \pm 0.7) \times 10^3\ M^{-1}$).

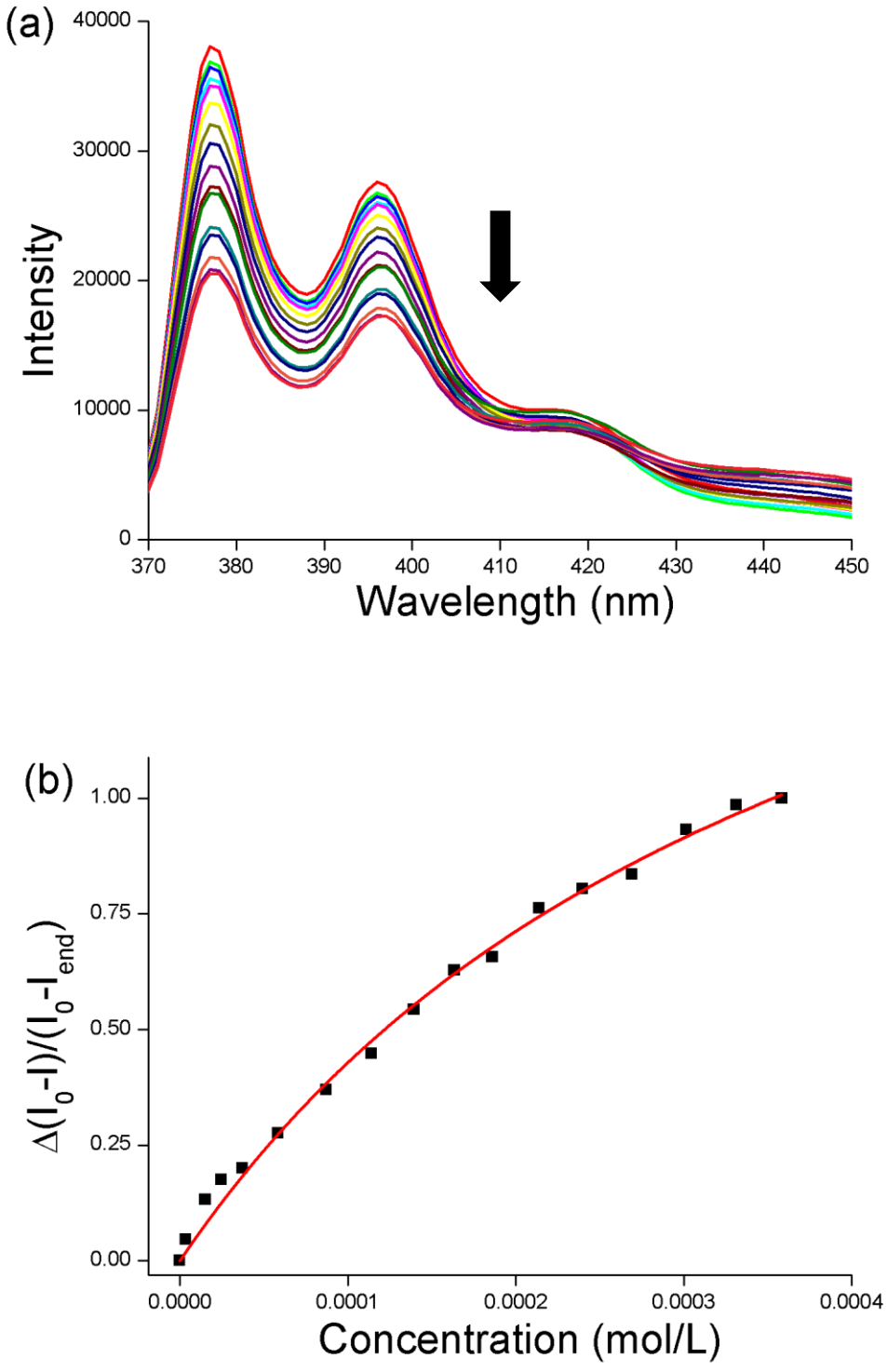

Figure S13. (a) Fluorescence spectra from the titration of guest **17** (2.0 μM) with **WP7** (0 – 358 μM) in sodium phosphate buffer (pH 7.4, 20 mM); (b) plot of the ΔIntensity $(I_0\text{-}I)/(I_0\text{-}I_{end})$ at 378 nm as a function of the concentration of **WP7**. The solid line represents the best non-linear fitting of the data based on a 1:1 binding model ($K_a = (2.6 \pm 0.3) \times 10^3\ M^{-1}$).

Indicator Displacement Assay

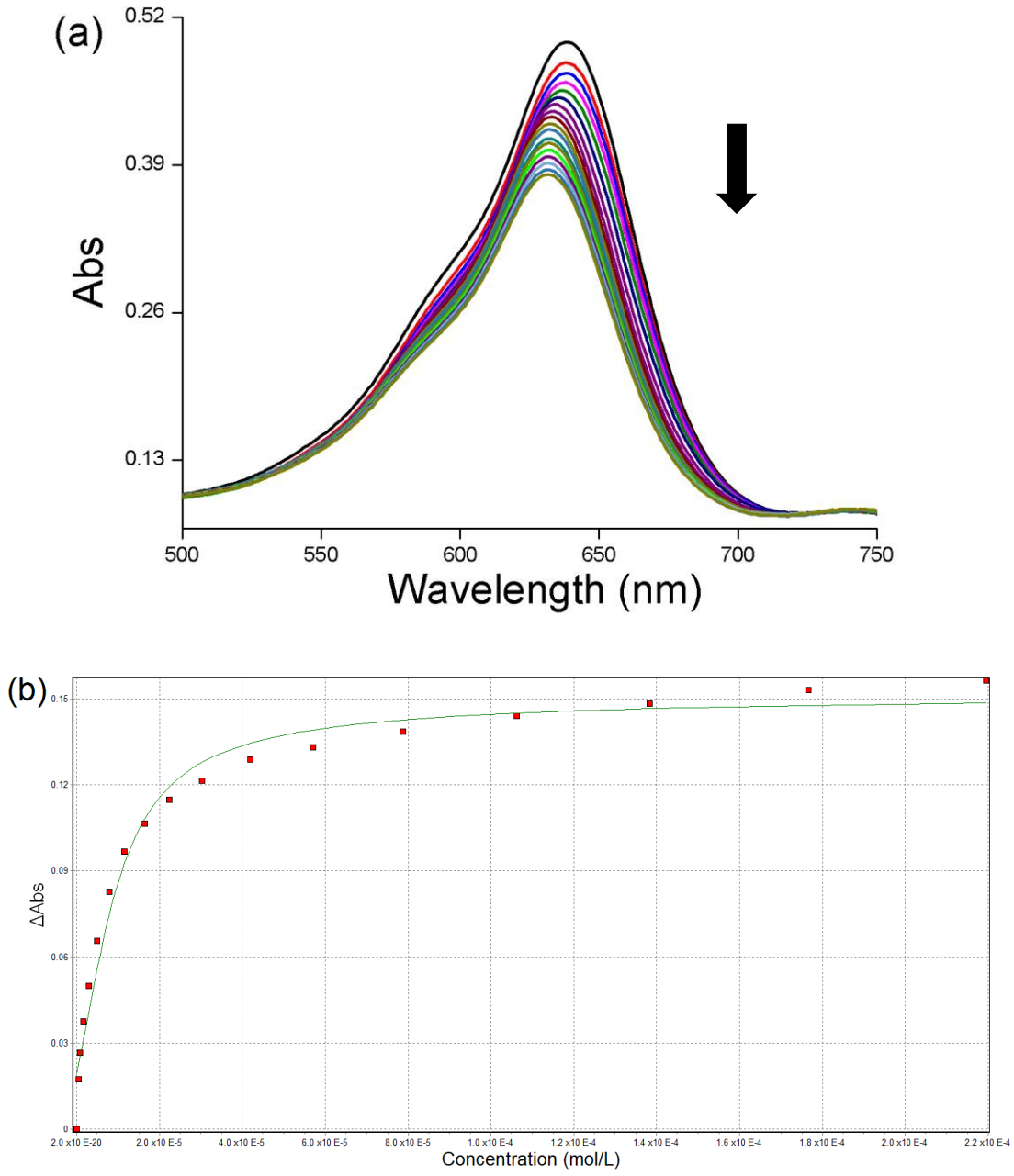

Figure S14. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **4** (0 – 220 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **4** with Scientist^{TM}. K_a was calculated to be (6.3 ± 1.7) × 10^5 M^{-1}.

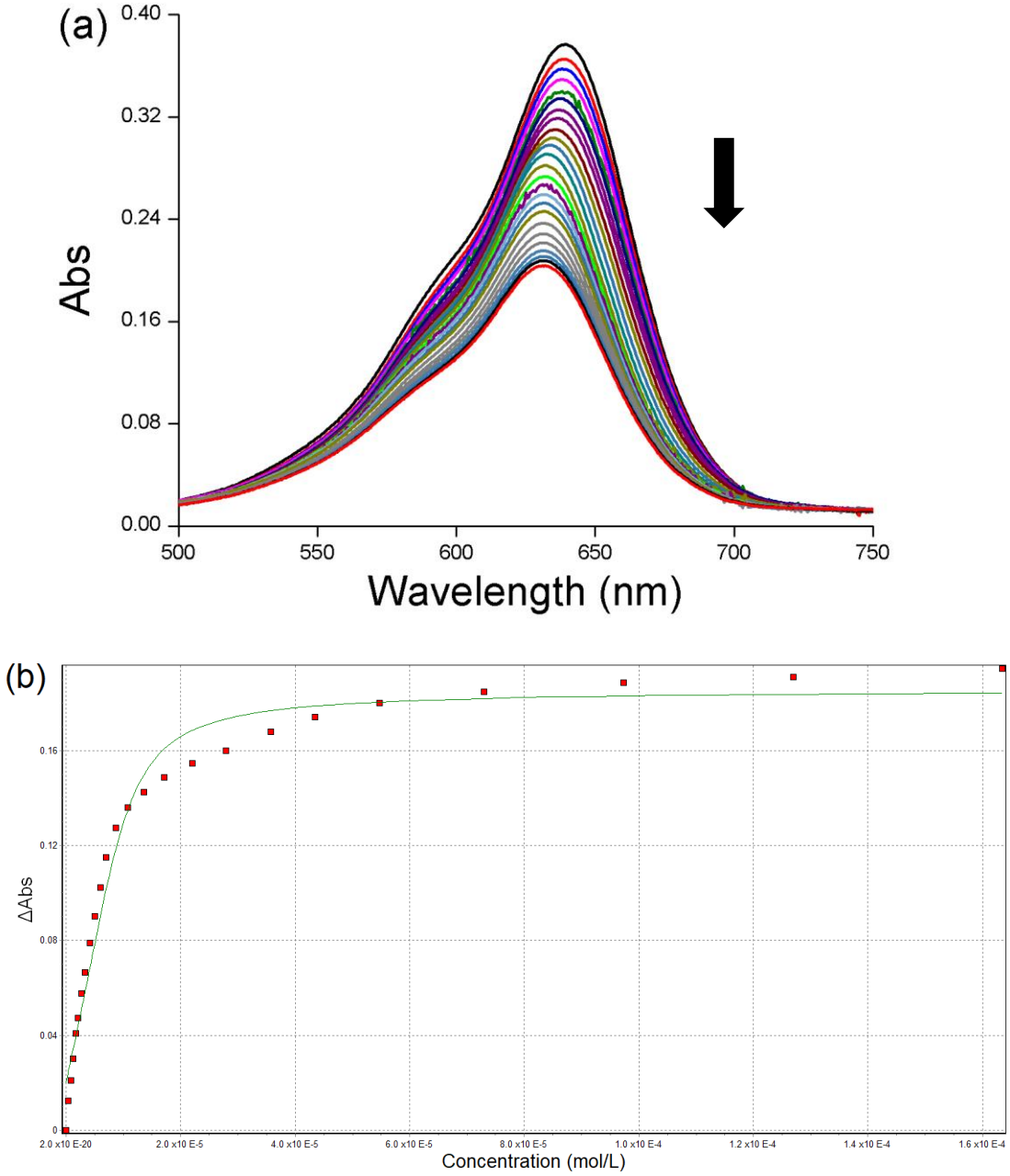

Figure S15. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **5** (0 – 163 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **5** with Scientist™. K_a was calculated to be (1.8 ± 0.6) × 10^6 M^{-1}.

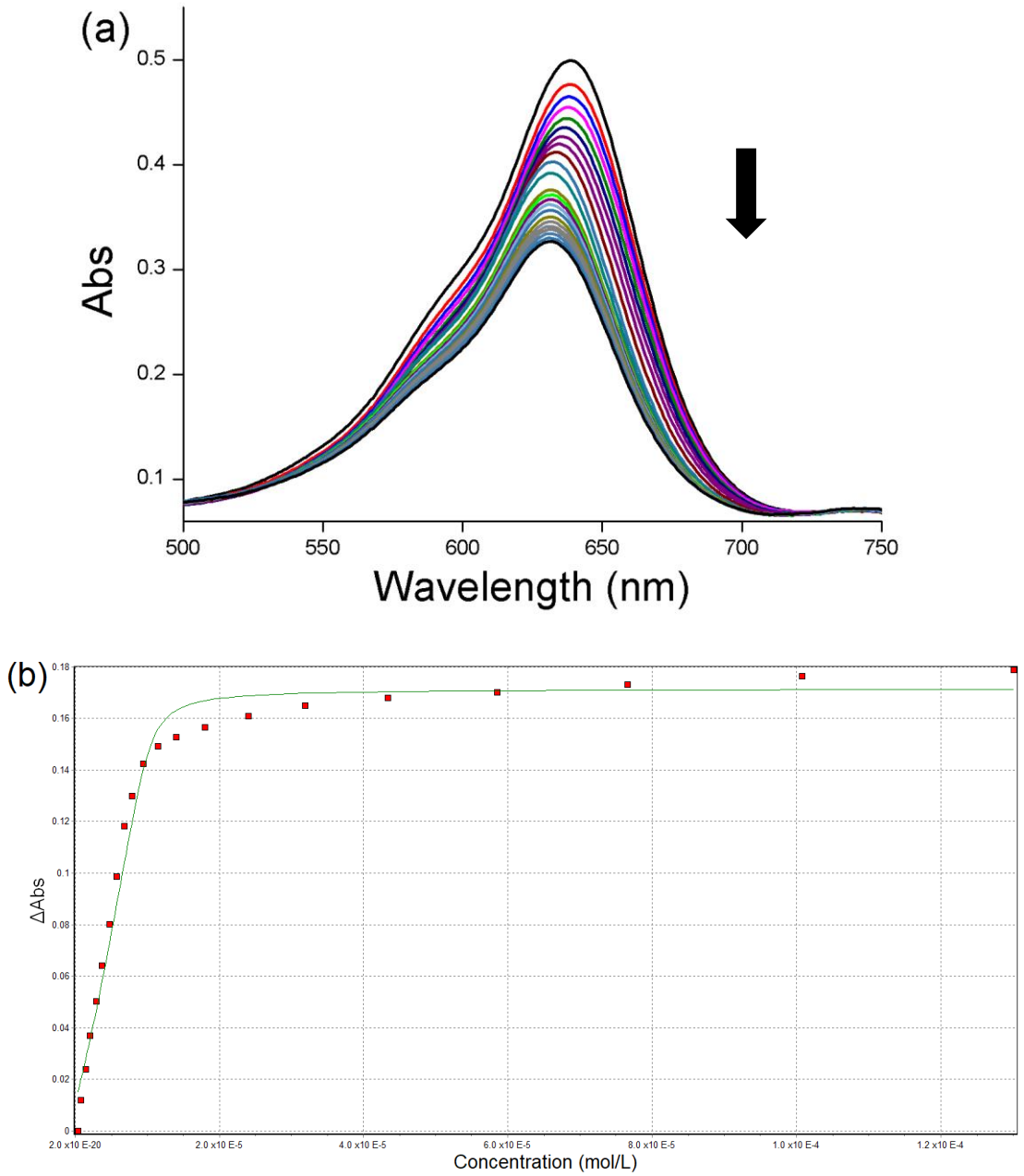

Figure S16. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **6** (0 – 130 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **6** with Scientist^{TM}. K_a was calculated to be (1.1 ± 0.6) × 10^7 M^{-1}.

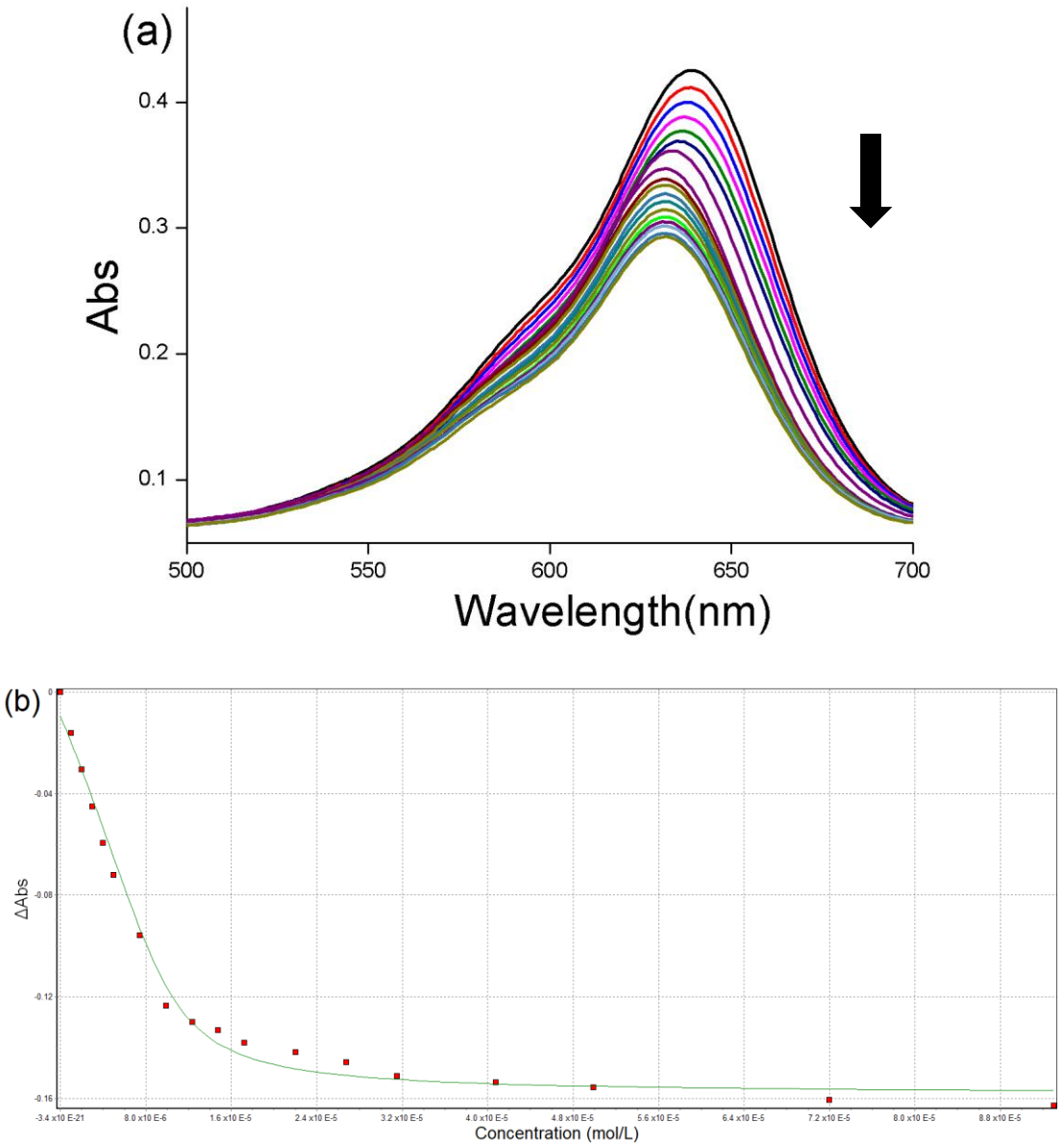

Figure S17. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **7** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **7** with Scientist™. K_a was calculated to be (3.0 ± 0.7) × 10^6 M^{-1}.

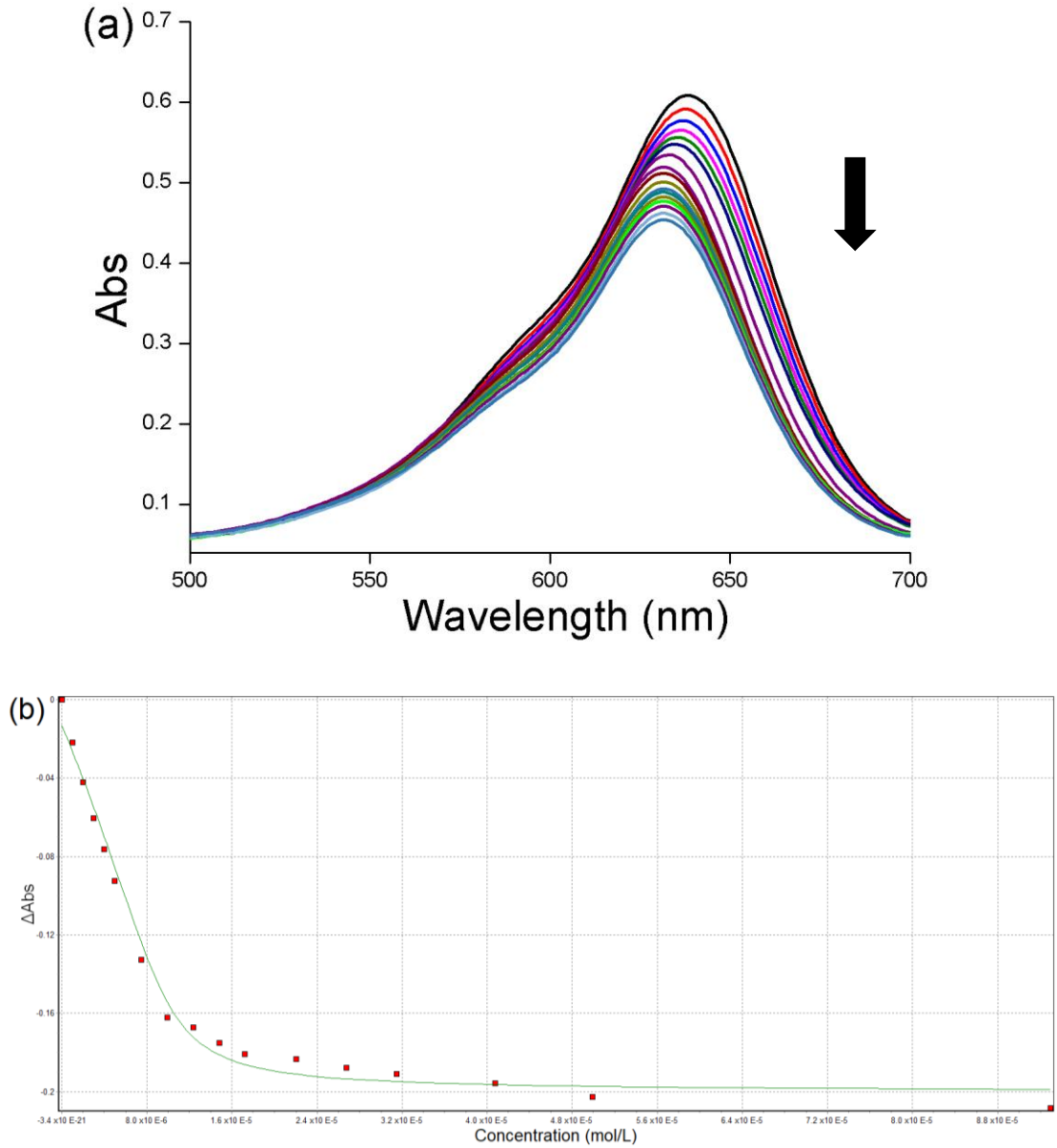

Figure S18. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **8** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **8** with Scientist™. K_a was calculated to be (4.3 ± 1.5) × 10^6 M^{-1}.

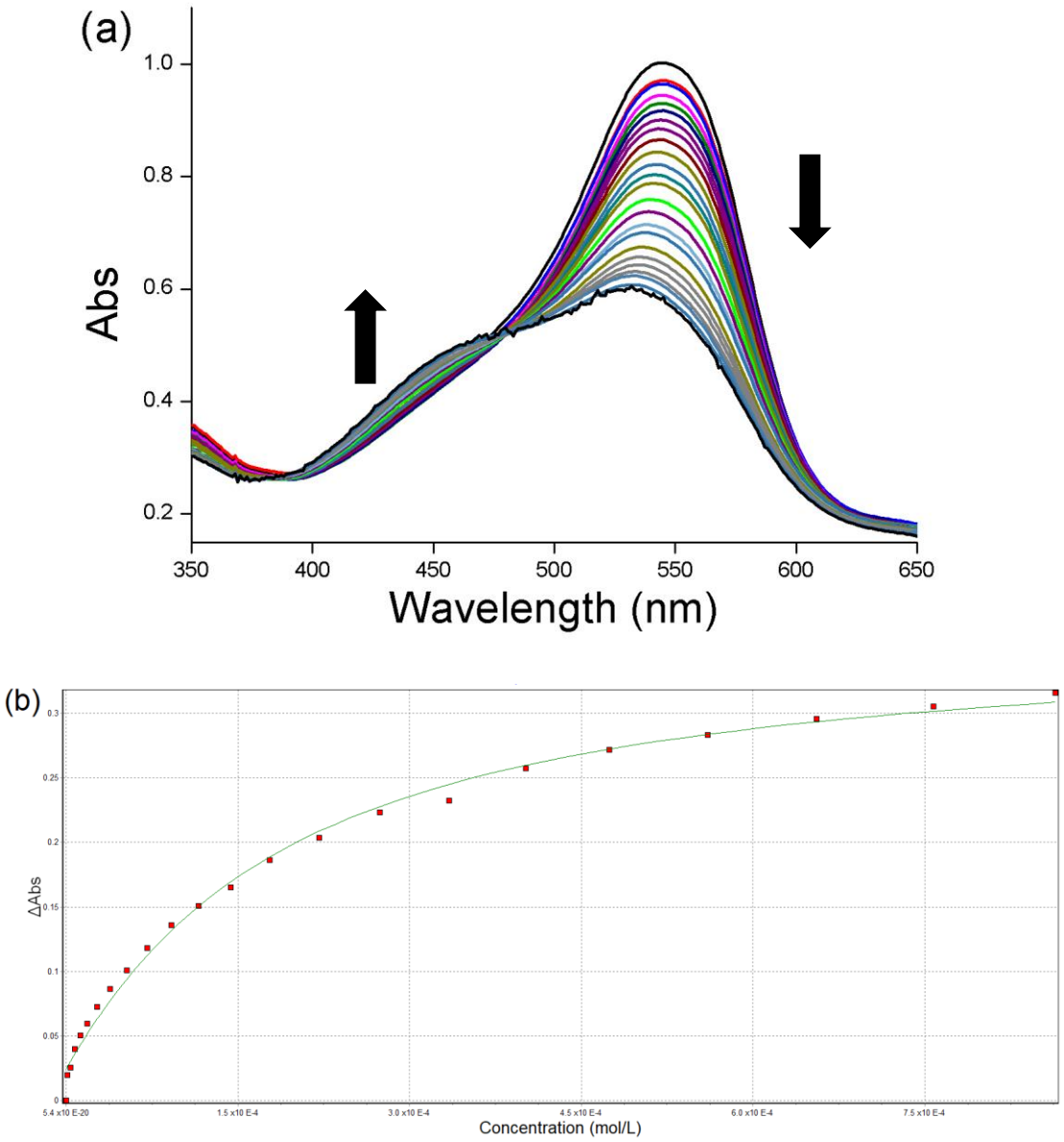

Figure S19. Displacement titration of a solution of dye **1** (50 μM) and **WP5** (50 μM) solution with guest **9** (0 – 978 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 575 nm *versus* concentration for the displacement titration of guest **9** with Scientist™. K_a was calculated to be (7.4 ± 0.7) × 10^3 M^{-1}.

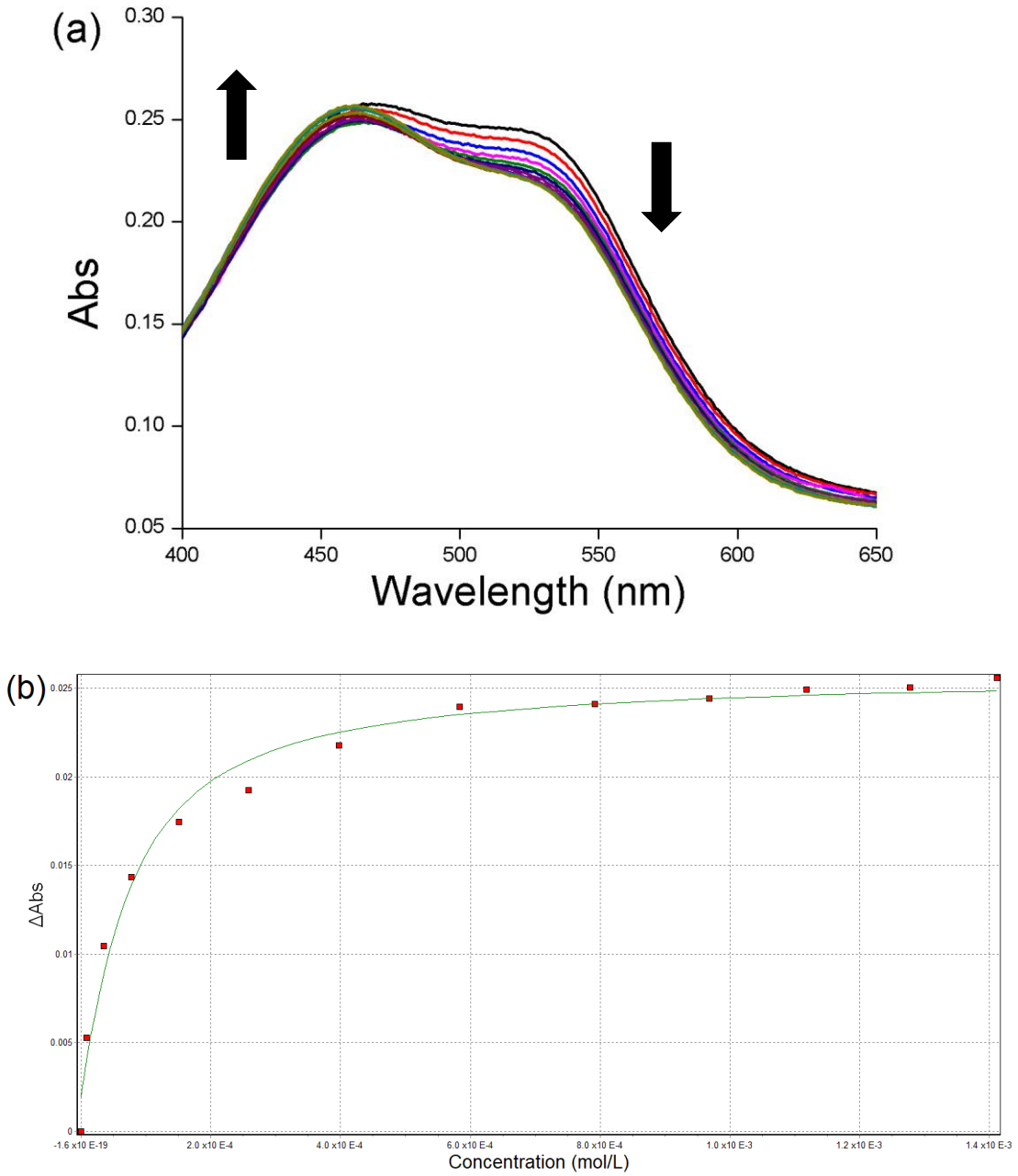

Figure S20. Displacement titration of a solution of dye **1** (30 μM) and **WP5** (35 μM) solution with guest **10** (0 – 1411 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 540 nm *versus* concentration for the displacement titration of guest **10** with Scientist^{TM}. K_a was calculated to be (2.0 ± 0.4) × 10^4 M^{-1}.

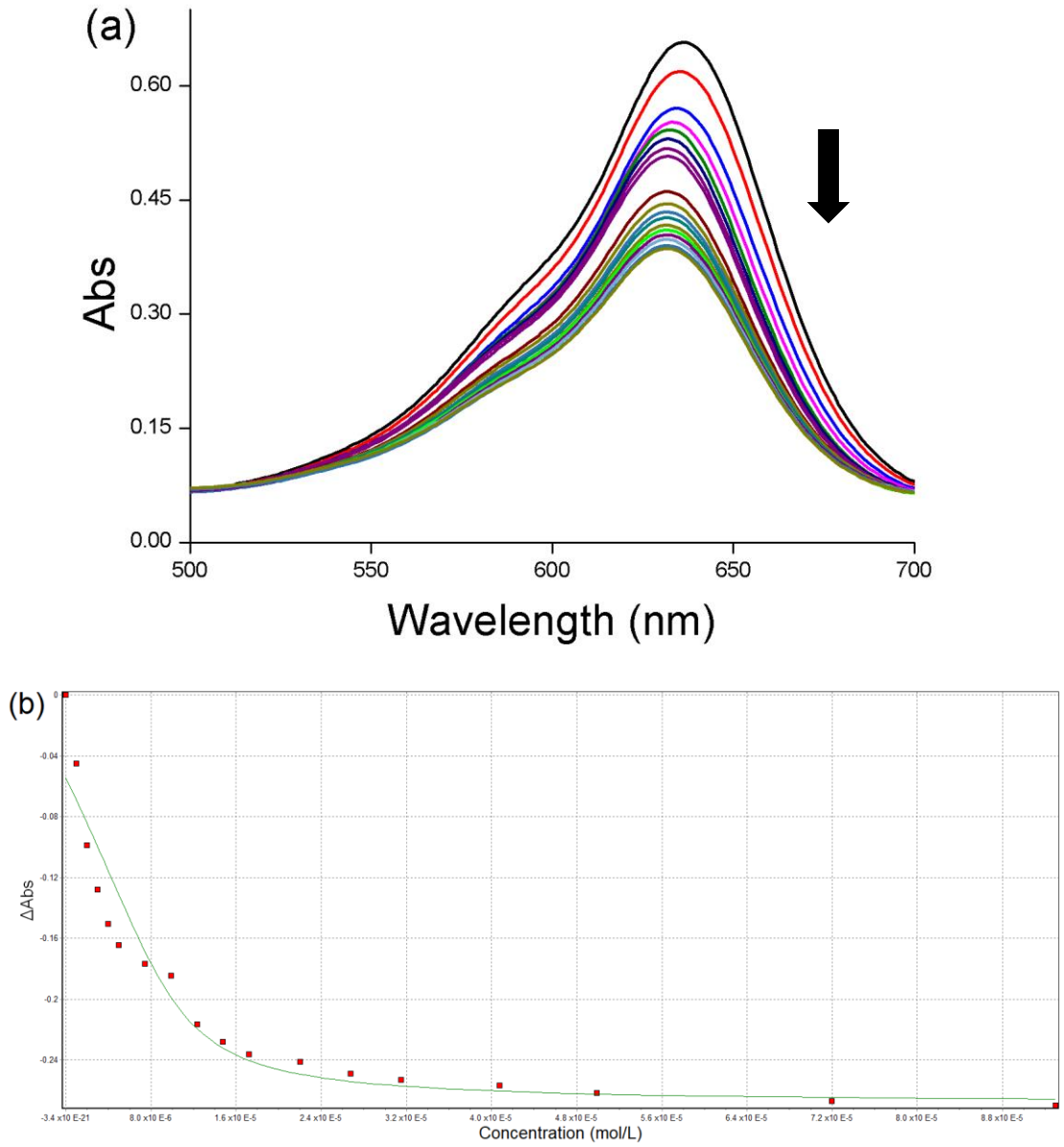

Figure S21. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **11** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A - A_0) at 650 nm *versus* concentration for the displacement titration of guest **11** with Scientist^{TM}. K_a was calculated to be (2.1 ±1.3) × 10^6 M^{-1}.

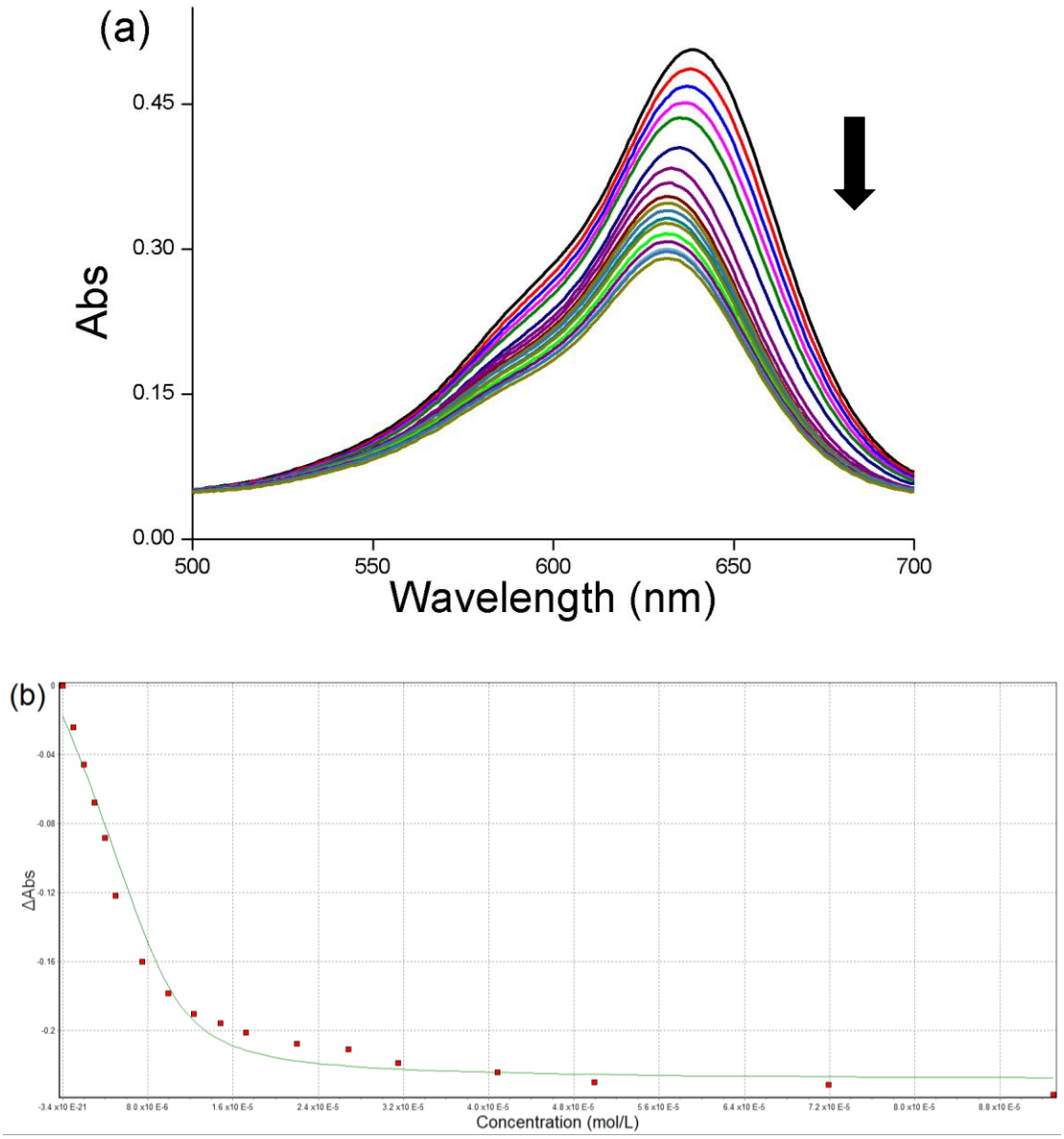

Figure S22. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **12** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A - A_0) at 650 nm *versus* concentration for the displacement titration of guest **12** with Scientist™. K_a was calculated to be (2.7 ± 0.5) × 10^6 M^{-1}.

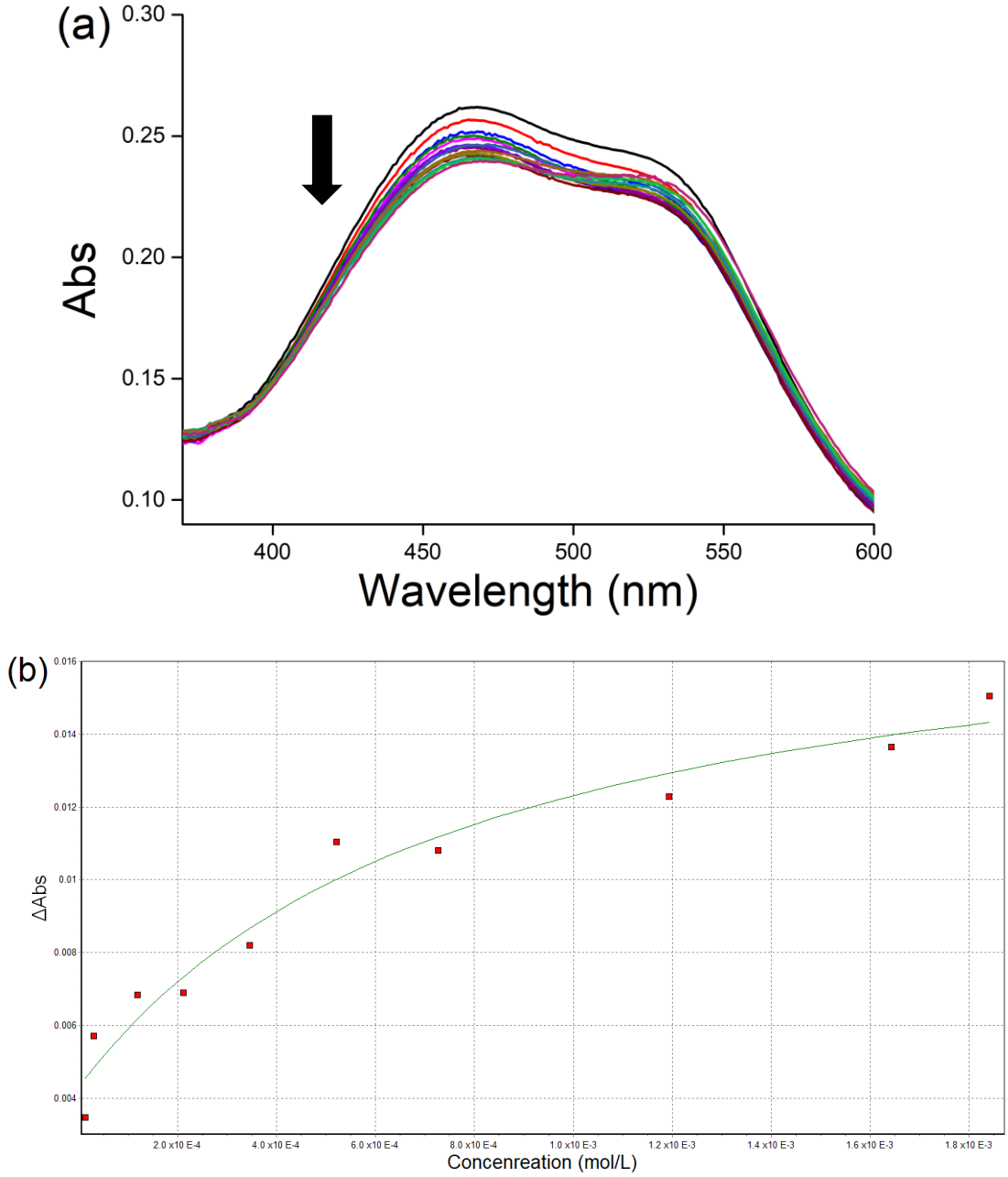

Figure S23. Displacement titration of a solution of dye **1** (30 μM) and **WP5** (30 μM) solution with guest **13** (0 – 1841 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 440 nm *versus* concentration for the displacement titration of guest **13** with Scientist^{TM}. K_a was calculated to be calculated to be $(1.5 \pm 0.6) \times 10^3$ M^{-1}.

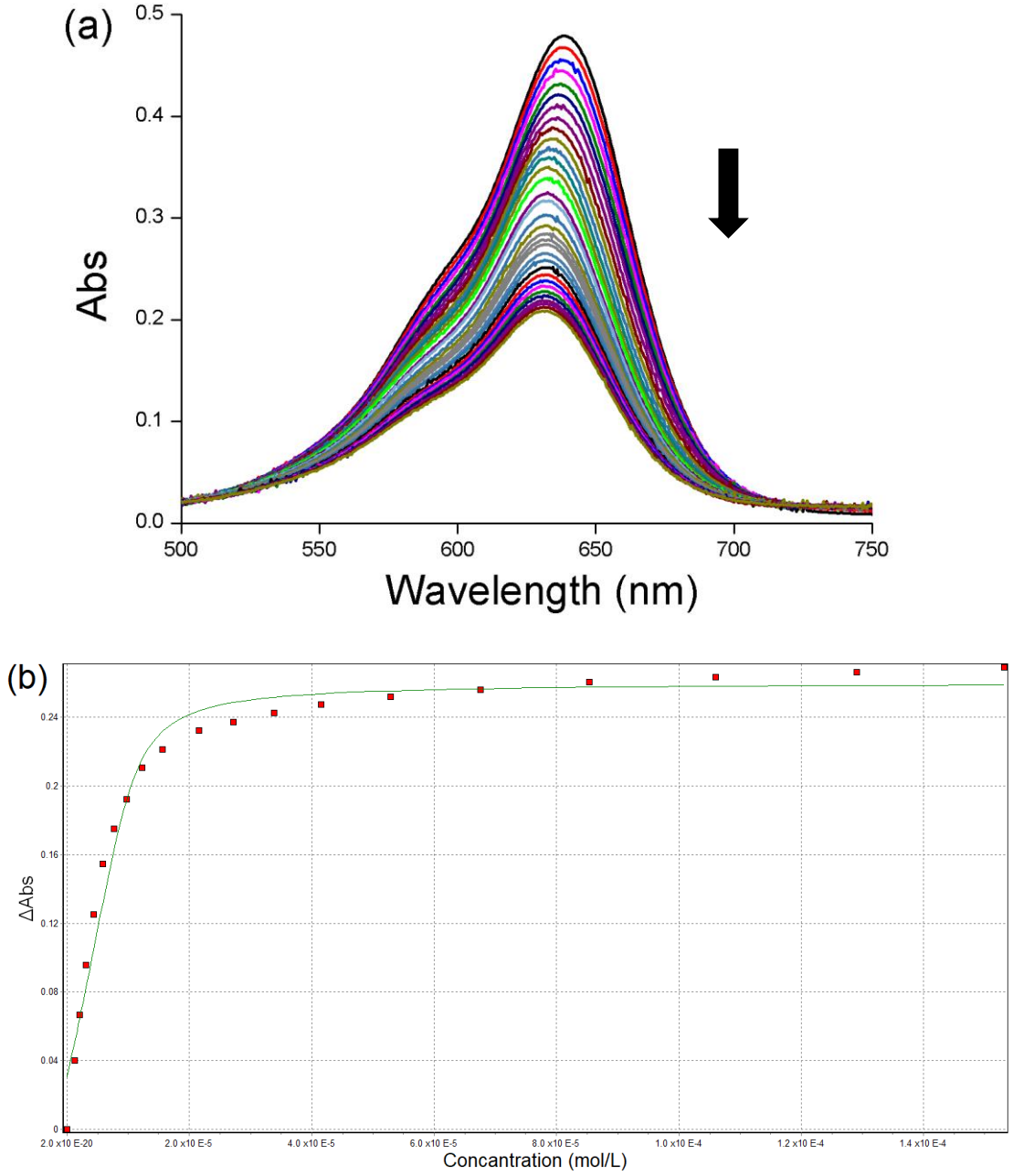

Figure S24. Displacement titration of a solution of dye **3** (10 μM) and **WP5** (10 μM) solution with guest **18** (0 – 206 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **18** with Scientist™. K_a was calculated to be (2.9 ± 1.0) × 10^6 M^{-1}.

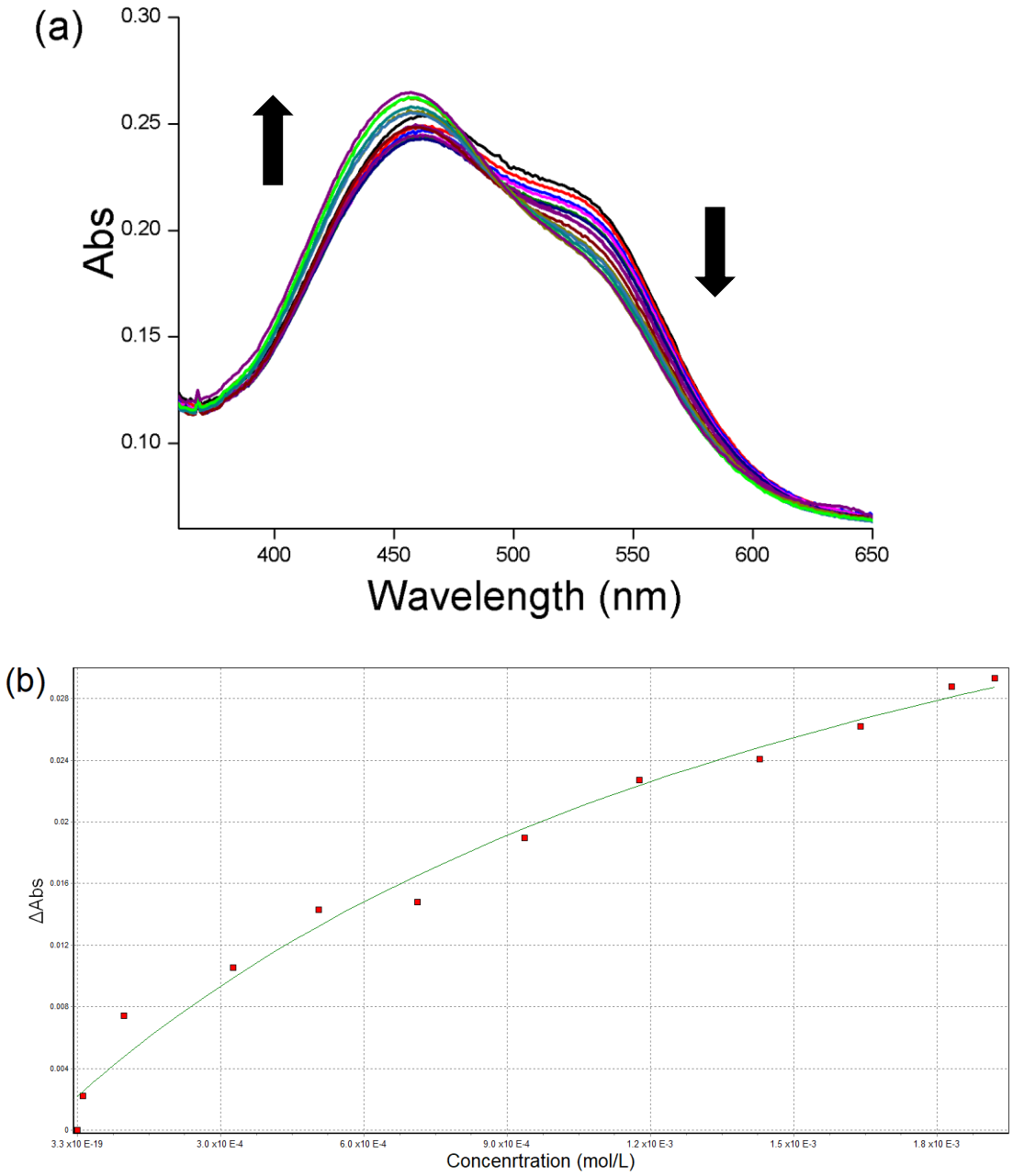

Figure S25. Displacement titration of a solution of dye **1** (30 μM) and **WP5** (35 μM) solution with guest **21** (0 – 1921 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 540 nm *versus* concentration for the displacement titration of guest **21** with Scientist™. K_a was calculated to be (6.1 ± 2.1) × 10^2 M^{-1}.

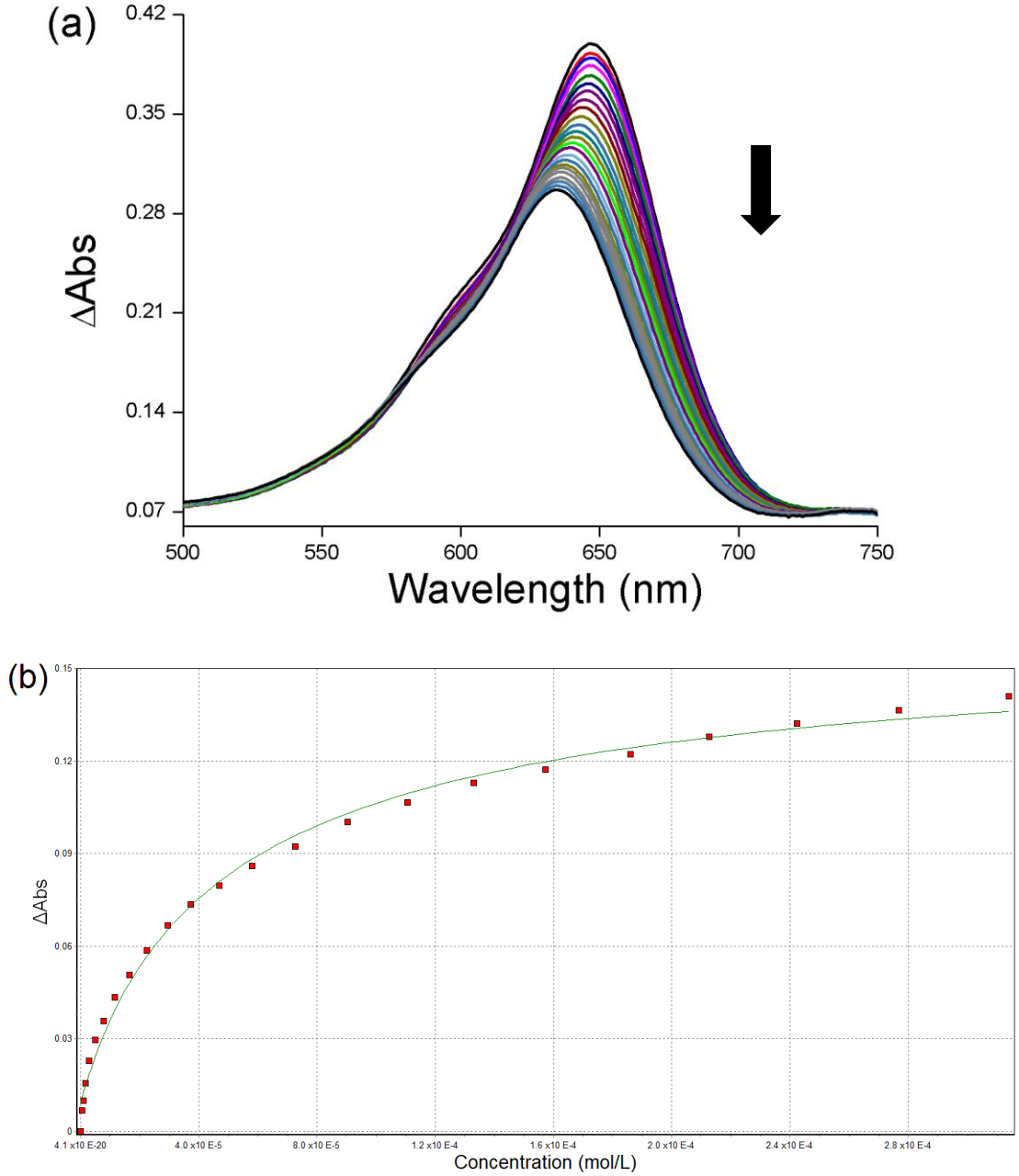

Figure S26. Displacement titration of a solution of dye **3** (15 μM) and **WP6** (15 μM) solution with guest **4** (0 – 314 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **4** with Scientist™. K_a was calculated to be (2.3 ± 0.3) × 10^5 M^{-1}.

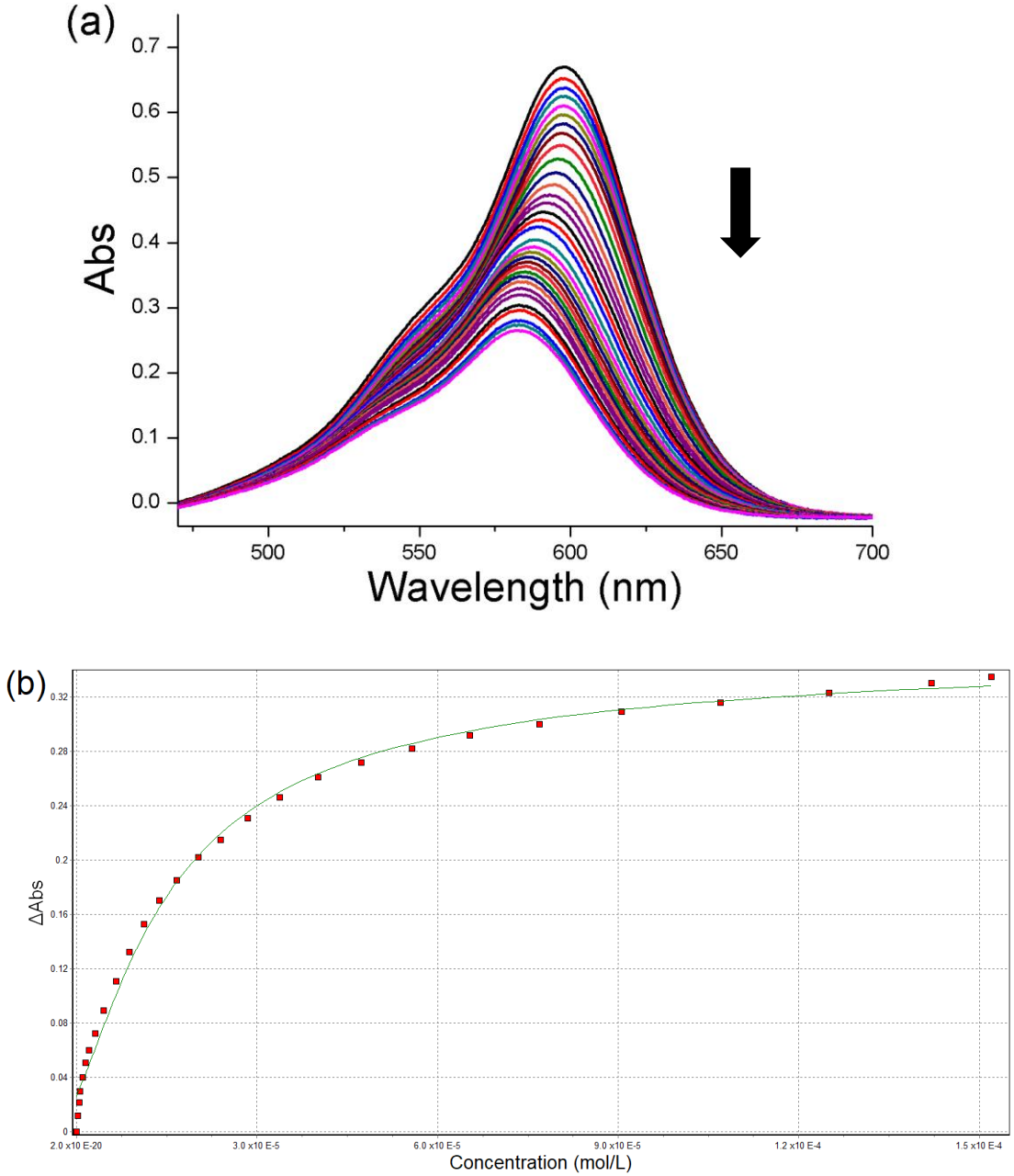

Figure S27. Displacement titration of a solution of dye **3** (15 μM) and **WP6** (15 μM) solution with guest **5** (0 – 243 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 620 nm *versus* concentration for the displacement titration of guest **5** with Scientist™. K_a was calculated to be (1.6 ± 0.2) × 10^6 M^{-1}.

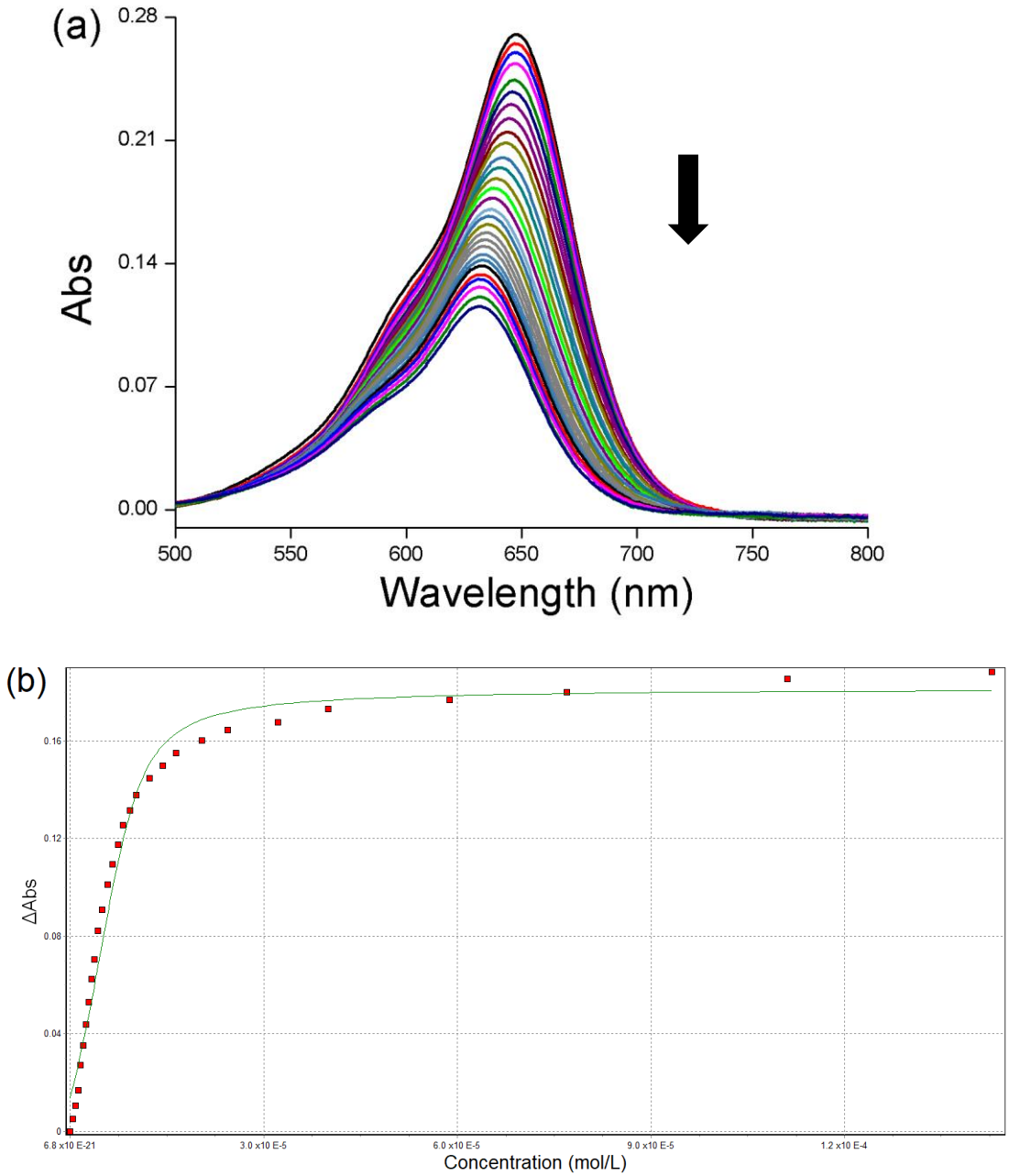

Figure S28. Displacement titration of a solution of dye **3** (15 μM) and **WP6** (15 μM) solution with guest **6** (0 – 143 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **6** with Scientist™. K_a was calculated to be (1.5 ± 0.5) × 10^7 M^{-1}.

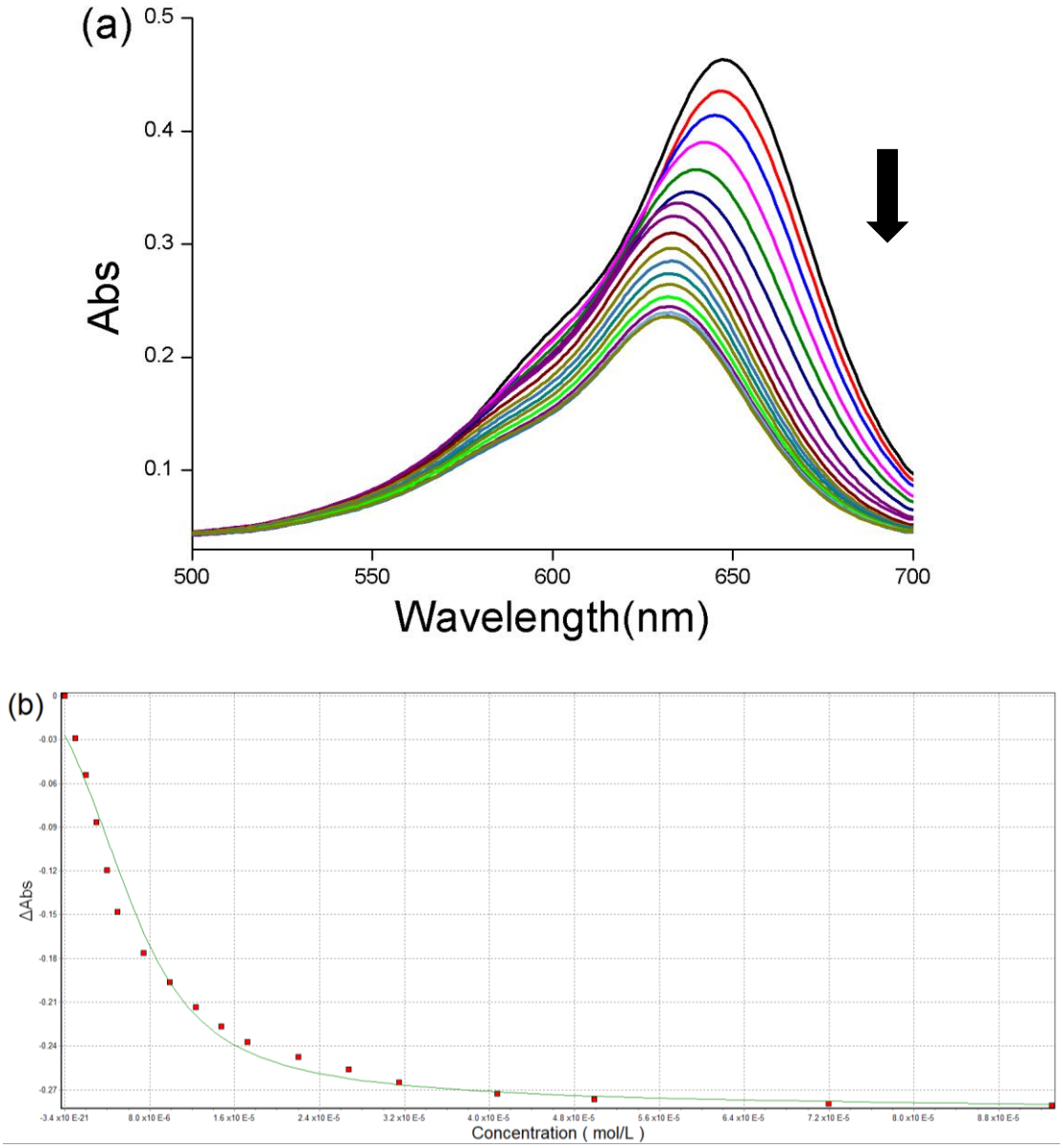

Figure S29. Displacement titration of a solution of dye **3** (10 μM) and **WP6** (10 μM) solution with guest **7** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **7** with Scientist™. K_a was calculated to be (8.4 ± 2.8) × 10^6 M^{-1}.

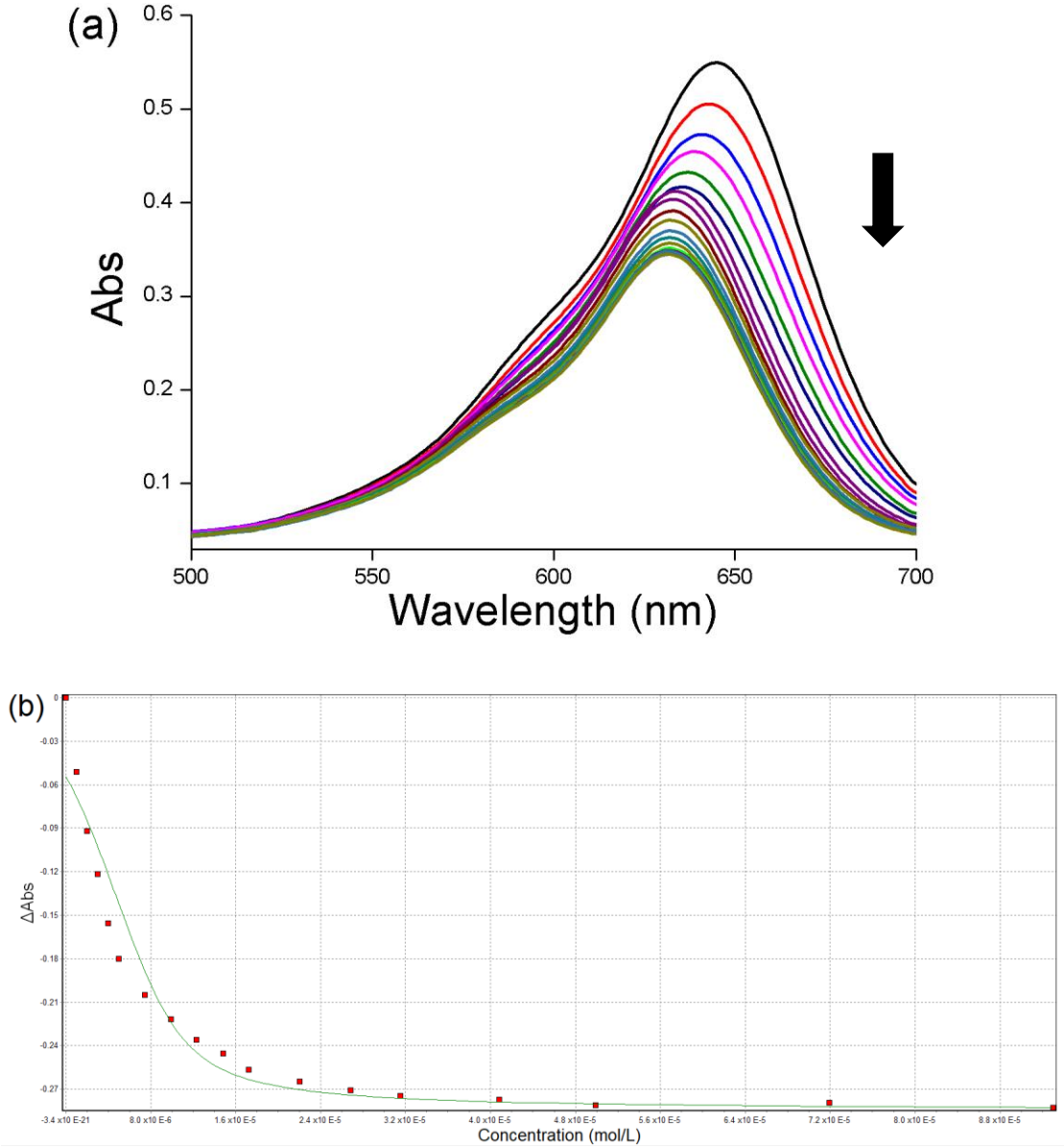

Figure S30. Displacement titration of a solution of dye **3** (10 μM) and **WP6** (10 μM) solution with guest **8** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **8** with Scientist^{TM}. K_a was calculated to be (1.7 ± 1.2) × 10^7 M^{-1}.

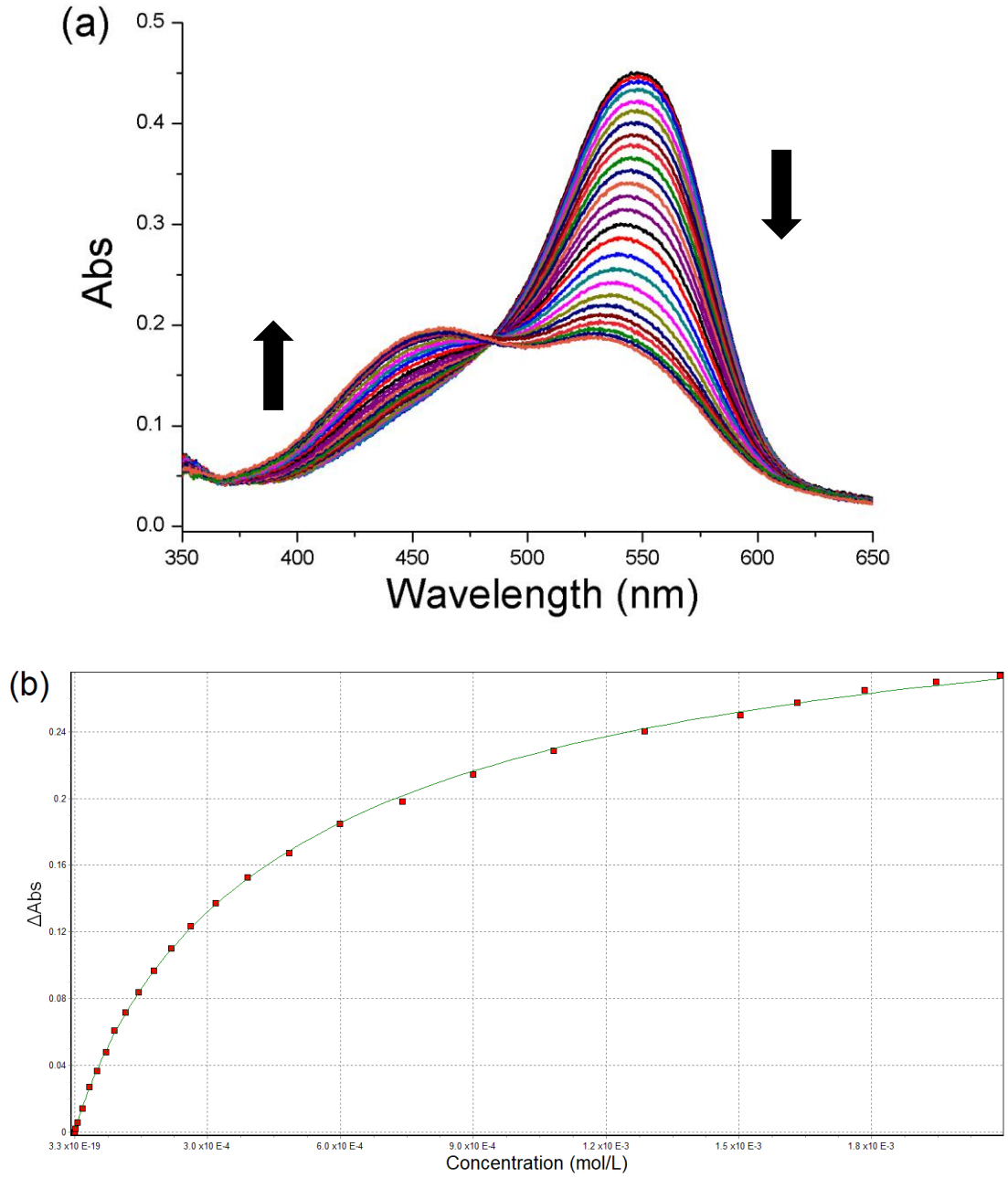

Figure S31. Displacement titration of a solution of dye **1** (30 μM) and **WP6** (40 μM) solution with guest **9** (0 – 2089 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 560 nm *versus* concentration for the displacement titration of guest **9** with Scientist™. K_a was calculated to be (1.4 ± 0.1) × 10^4 M^{-1}.

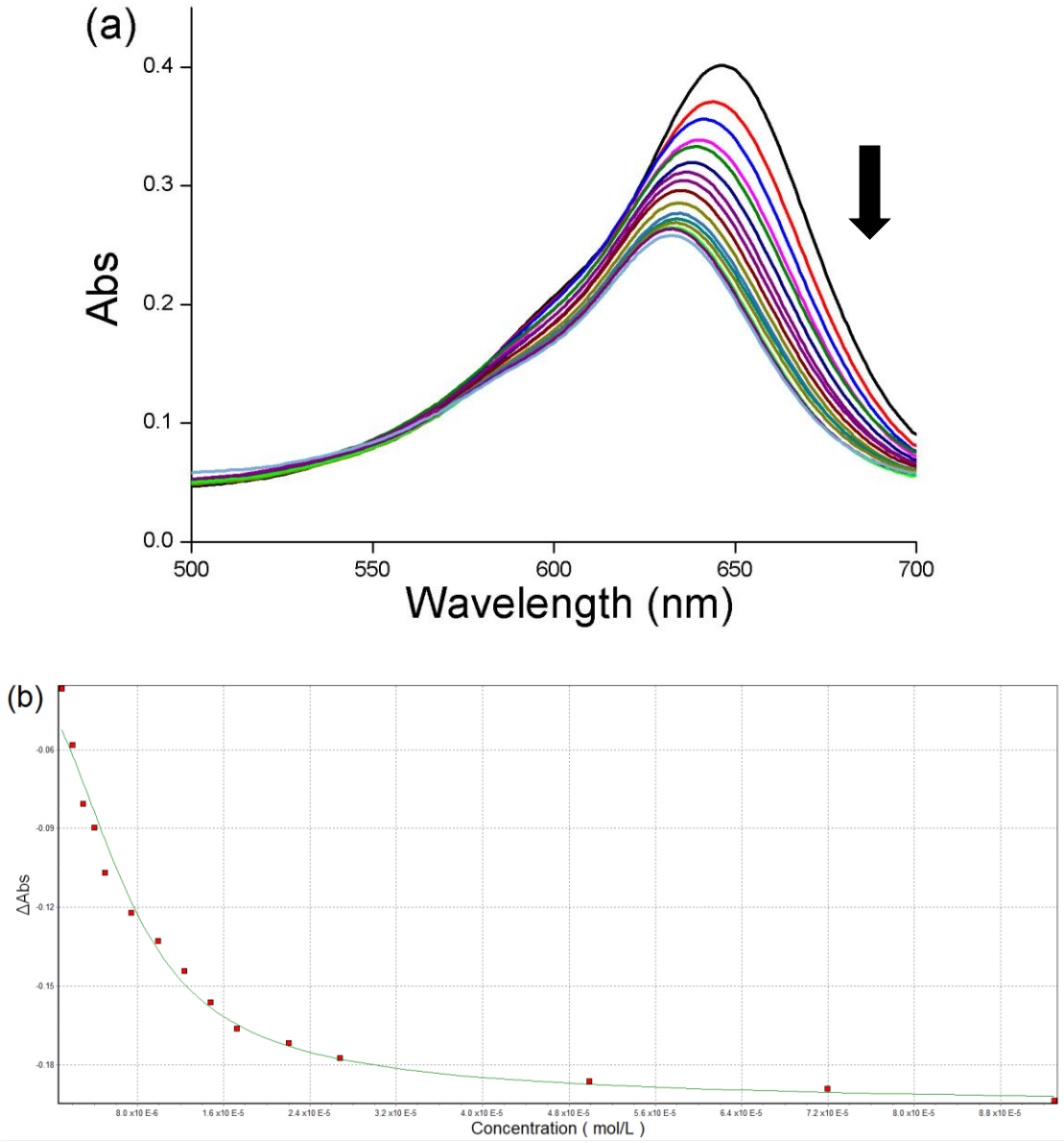

Figure S32. Displacement titration of a solution of dye **3** (10 μM) and **WP6** (10 μM) solution with guest **11** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A - A_0) at 650 nm *versus* concentration for the displacement titration of guest **11** with Scientist^{TM}. K_a was calculated to be (5.6 ±1.6) × 10^6 M^{-1}.

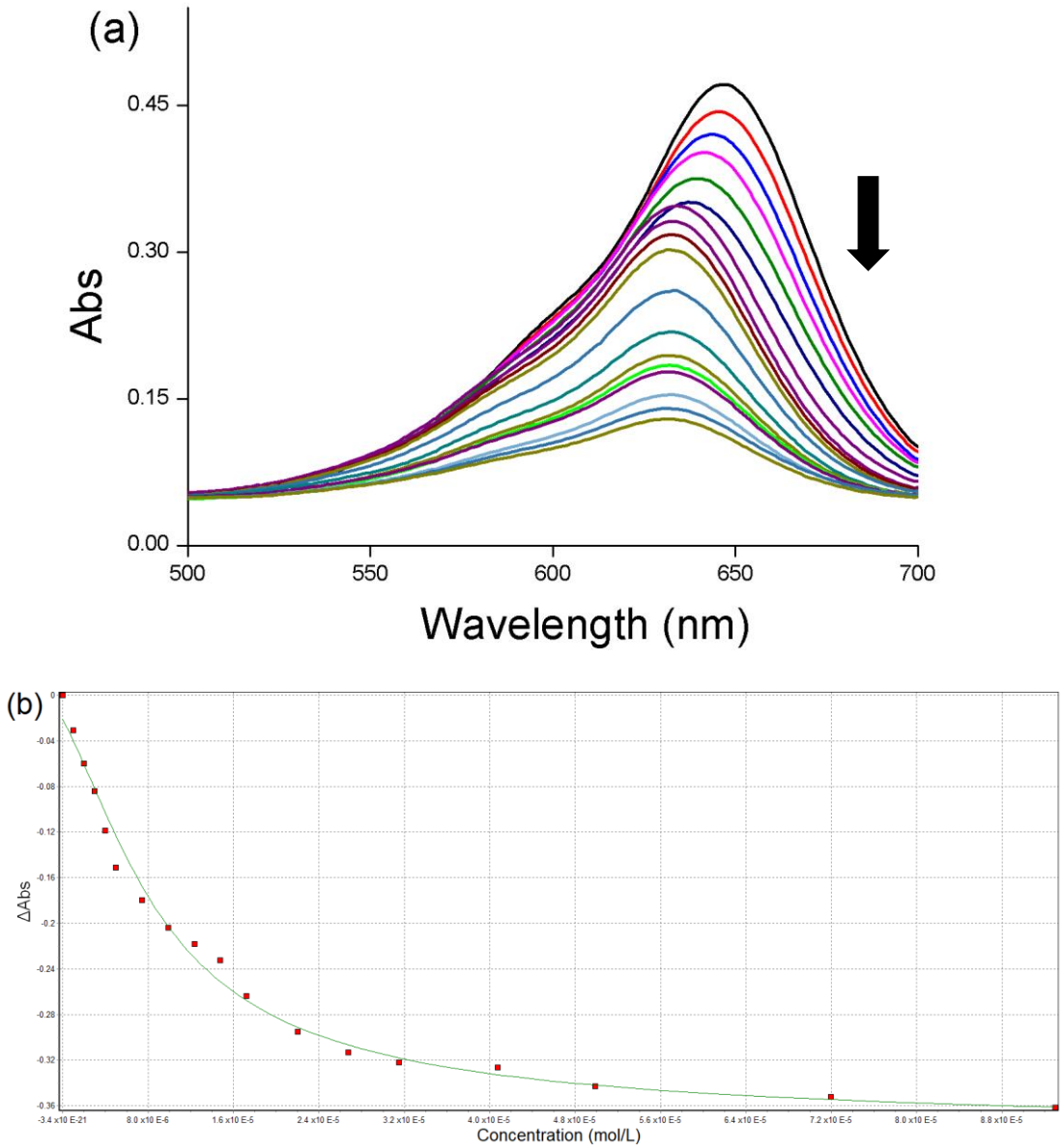

Figure S33. Displacement titration of a solution of dye **3** (10 μM) and **WP6** (10 μM) solution with guest **12** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A - A_0) at 650 nm *versus* concentration for the displacement titration of guest **12** with Scientist™. K_a was calculated to be (3.8 ± 0.5) × 10^6 M^{-1}.

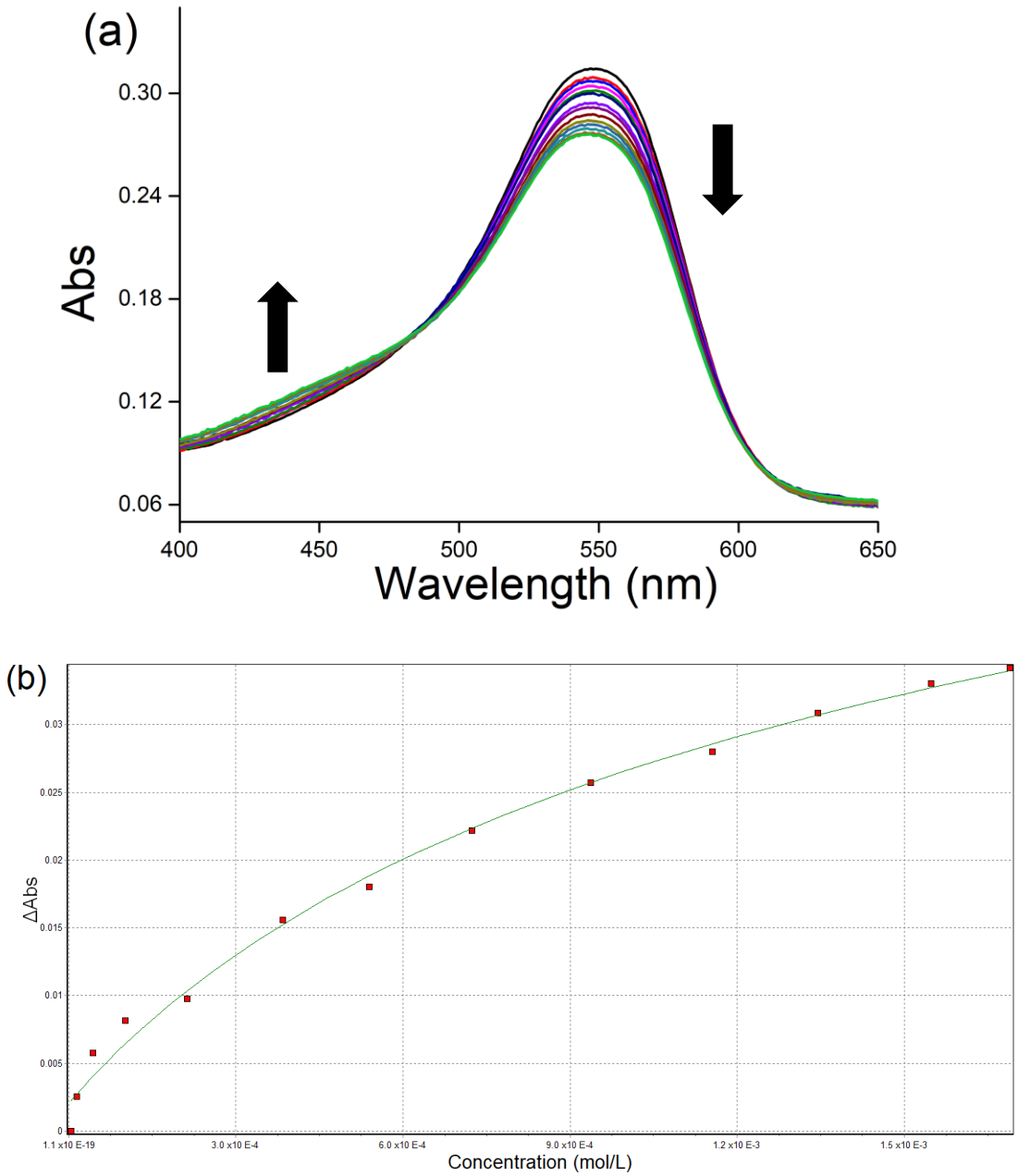

Figure S34. Displacement titration of a solution of dye **1** (30 μM) and **WP6** (30 μM) solution with guest **13** (0 – 1689 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 560 nm *versus* concentration for the displacement titration of guest **13** with Scientist^{TM}. K_a was calculated to be calculated to be $(3.2 \pm 0.8) \times 10^3$ M^{-1}.

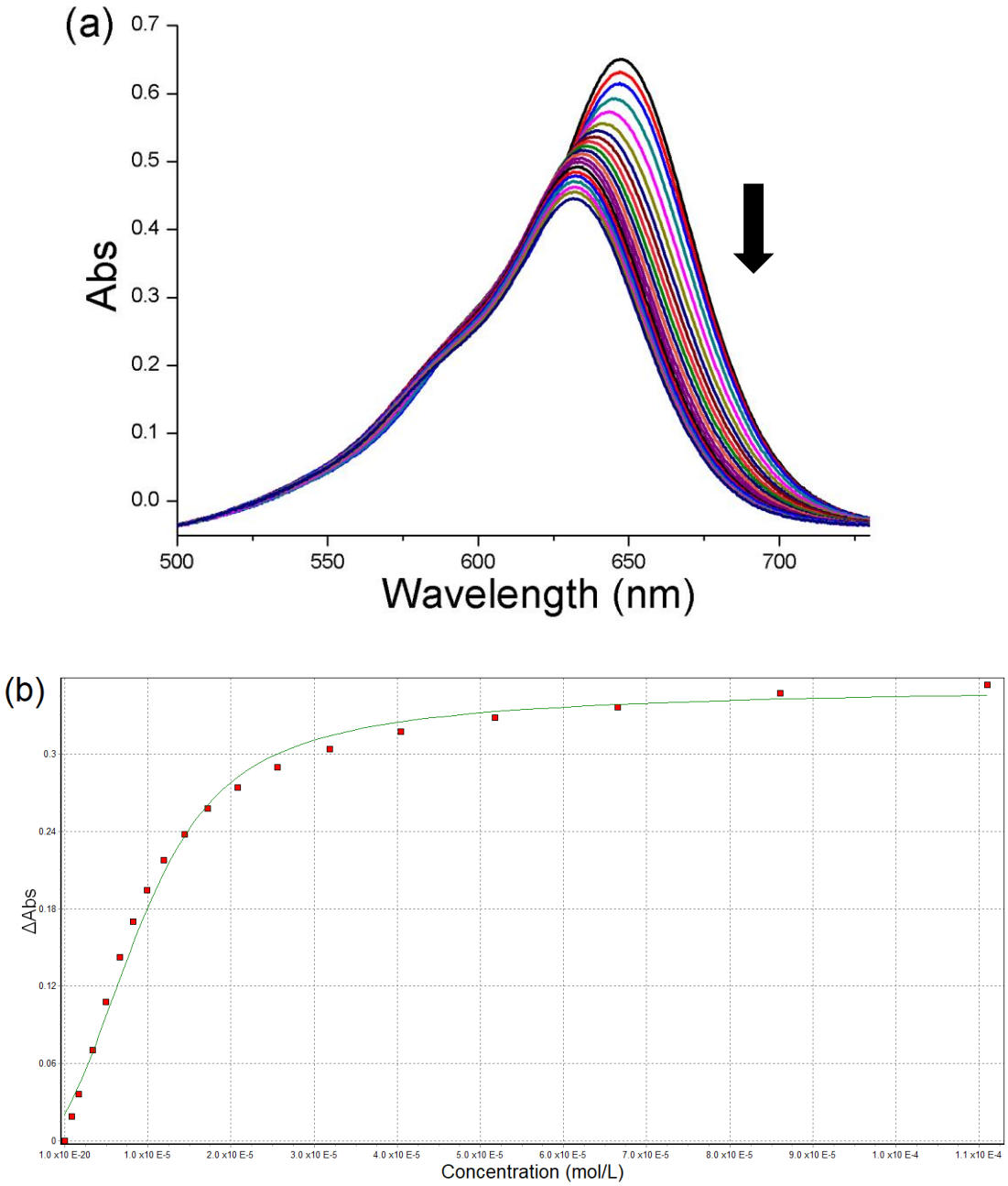

Figure S35. Displacement titration of a solution of dye **3** (15 μM) and **WP6** (15 μM) solution with guest **18** (0 – 181 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 660 nm *versus* concentration for the displacement titration of guest **18** with Scientist™. K_a was calculated to be (7.7 ± 1.7) × 10^6 M^{-1}.

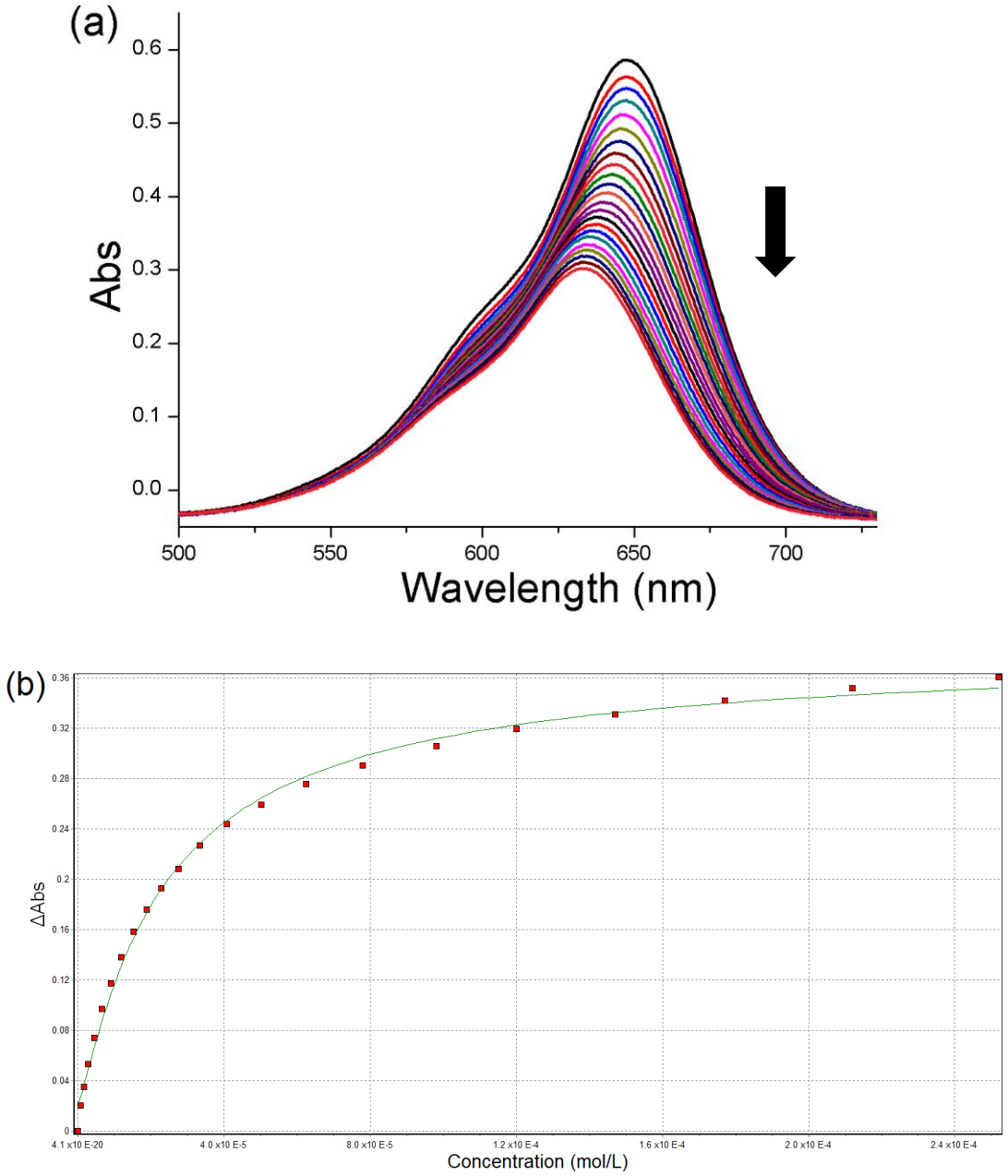

Figure S36. Displacement titration of a solution of dye **3** (15 μM) and **WP6** (15 μM) solution with guest **21** (0 – 252 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 660 nm *versus* concentration for the displacement titration of guest **21** with Scientist™. K_a was calculated to be (8.9 ± 0.8) × 10^5 M^{-1}.

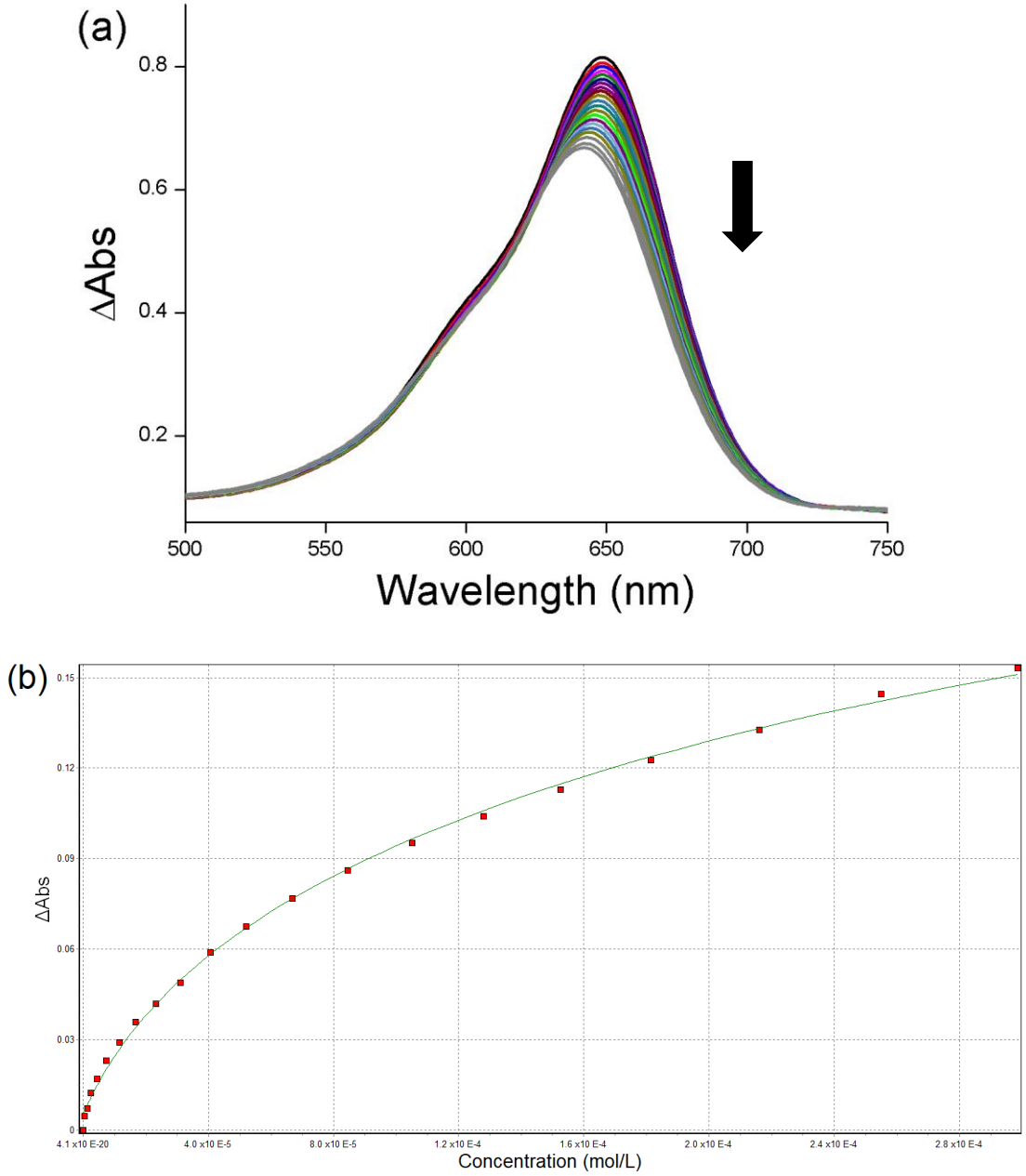

Figure S37. Displacement titration of a solution of dye **3** (15 μM) and **WP7** (15 μM) solution with guest **4** (0 – 299 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **4** with Scientist™. K_a was calculated to be (2.1 ± 0.2) × 10^5 M^{-1}.

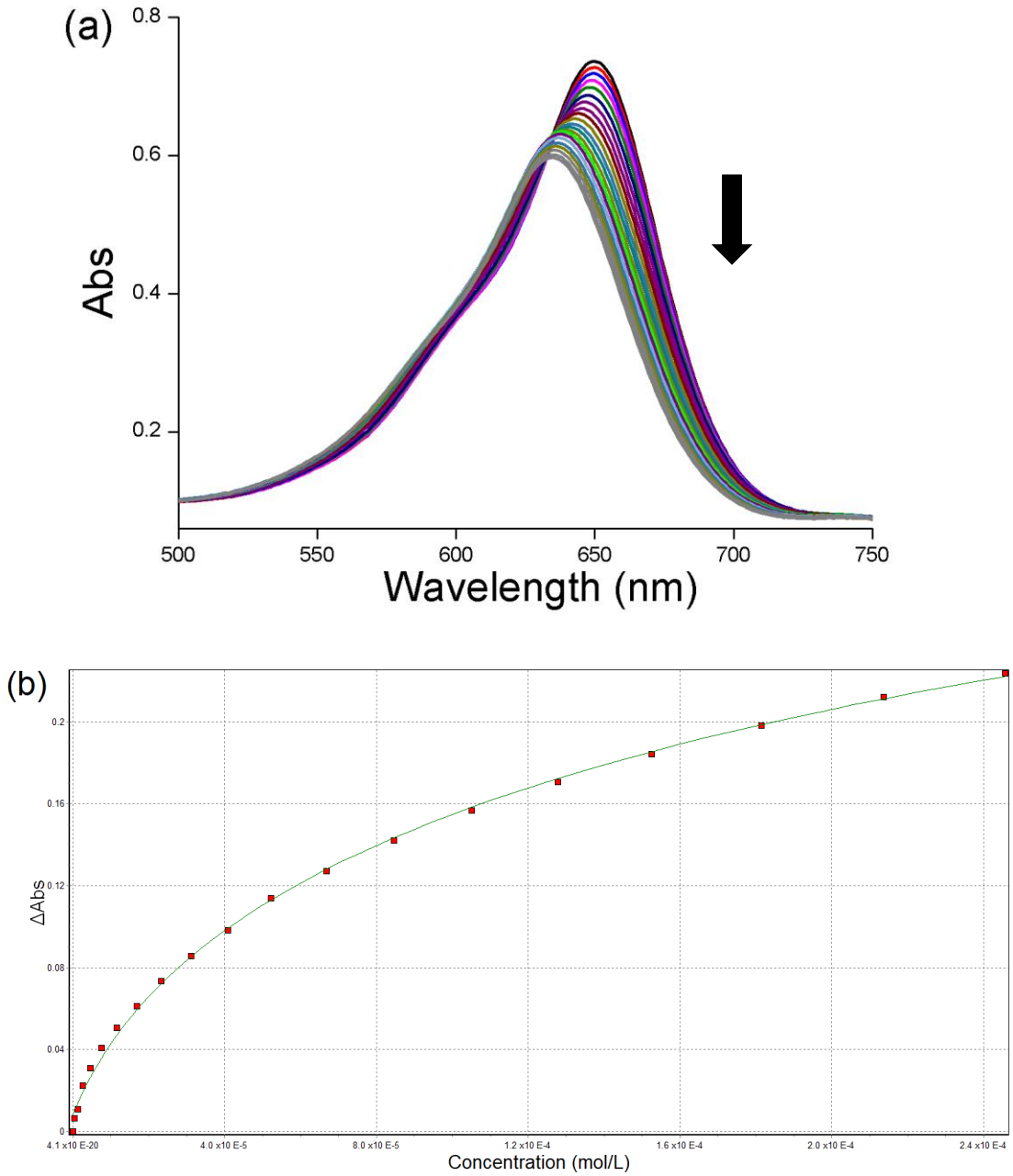

Figure S38. Displacement titration of a solution of dye **3** (15 μM) and **WP7** (15 μM) solution with guest **5** (0 – 299 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **5** with Scientist™. K_a was calculated to be (1.2 ± 0.1) × 10^6 M^{-1}.

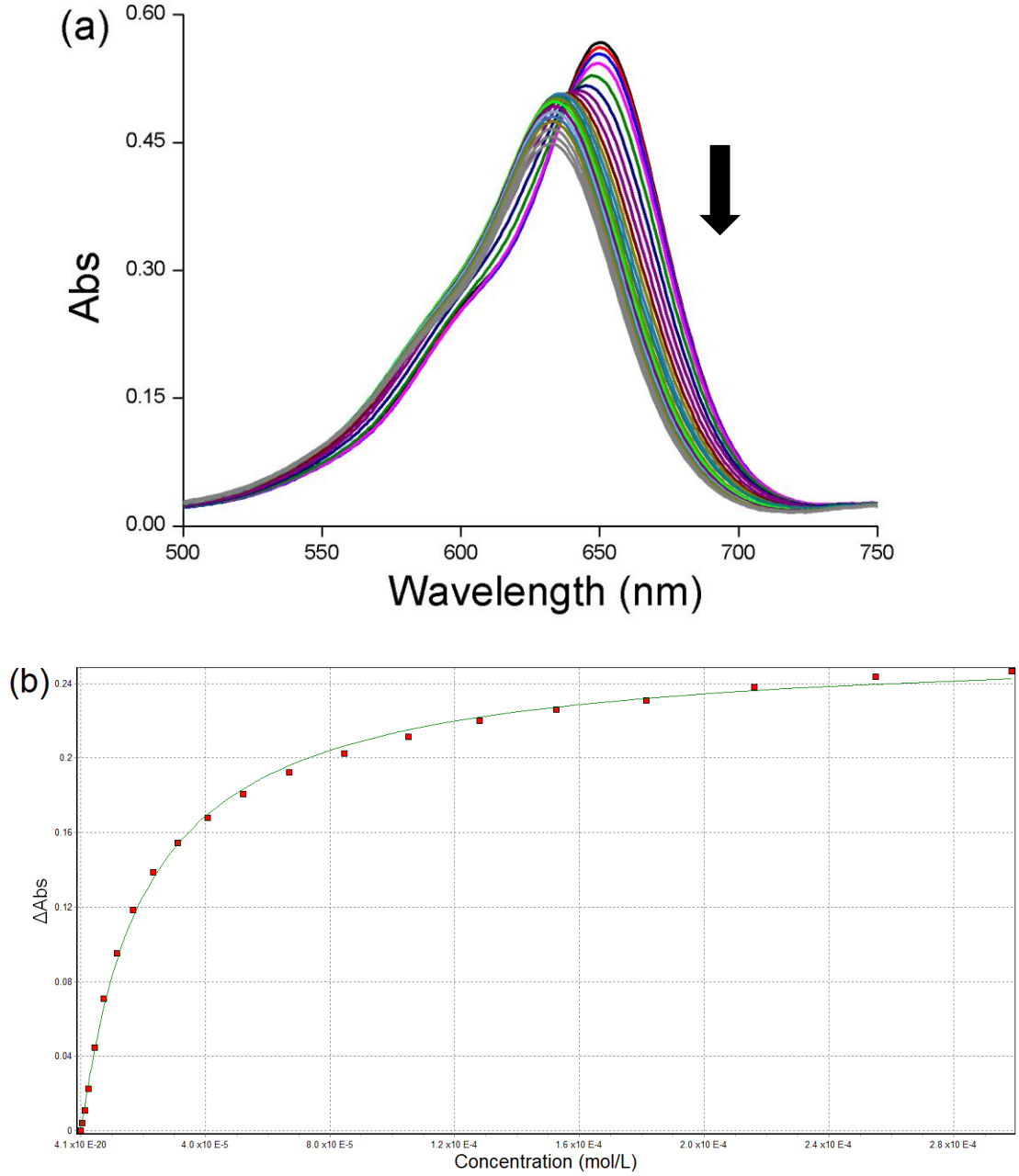

Figure S39. Displacement titration of a solution of dye **3** (15 μM) and **WP7** (15 μM) solution with guest **6** (0 – 299 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **6** with Scientist^{TM}. K_a was calculated to be (4.7 ± 0.3) × 10^6 M^{-1}.

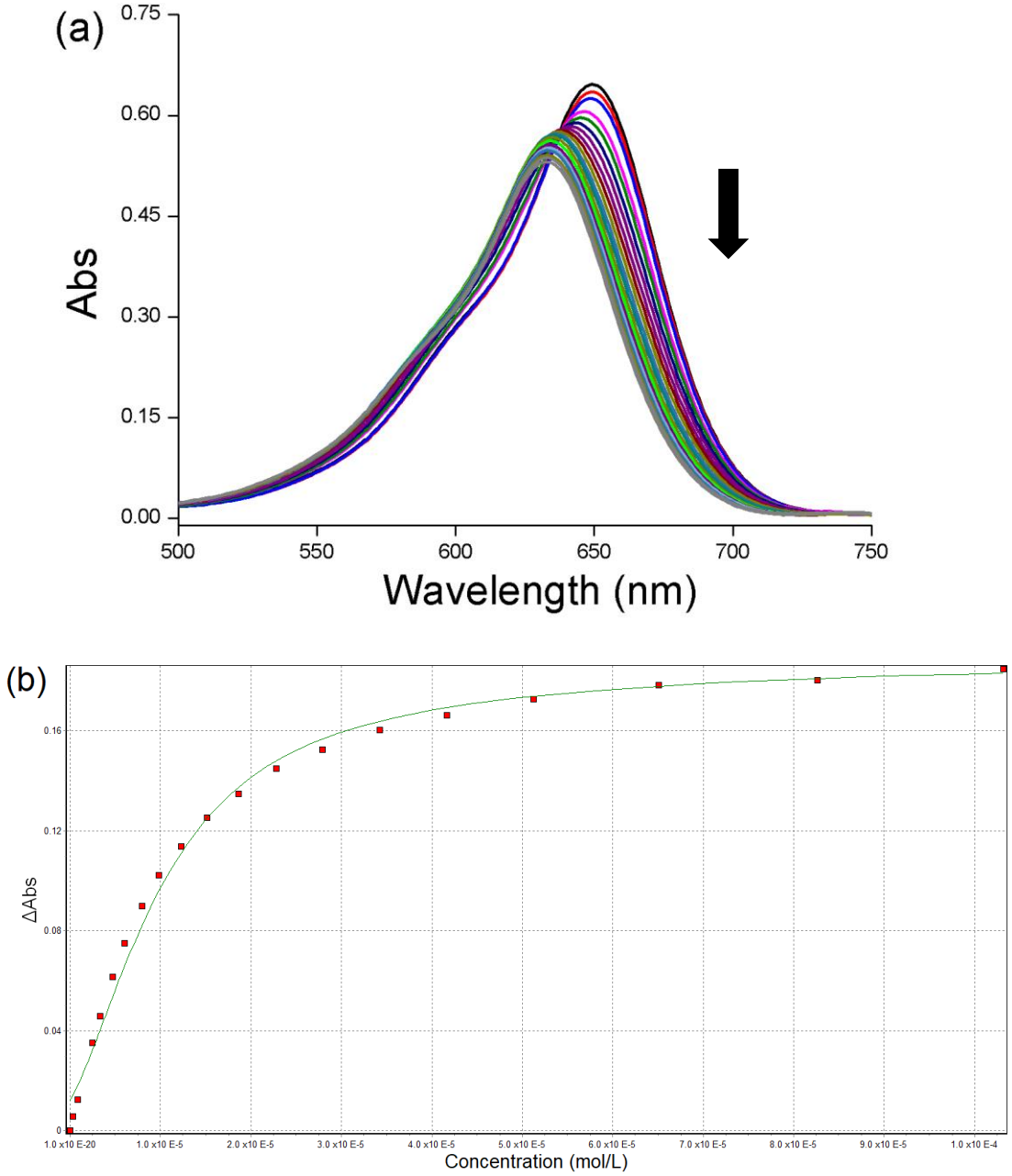

Figure S40. Displacement titration of a solution of dye **3** (15 μM) and **WP7** (15 μM) solution with guest **7** (0 – 103 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **7** with Scientist™. K_a was calculated to be (2.5 ± 0.6) × 10^7 M^{-1}.

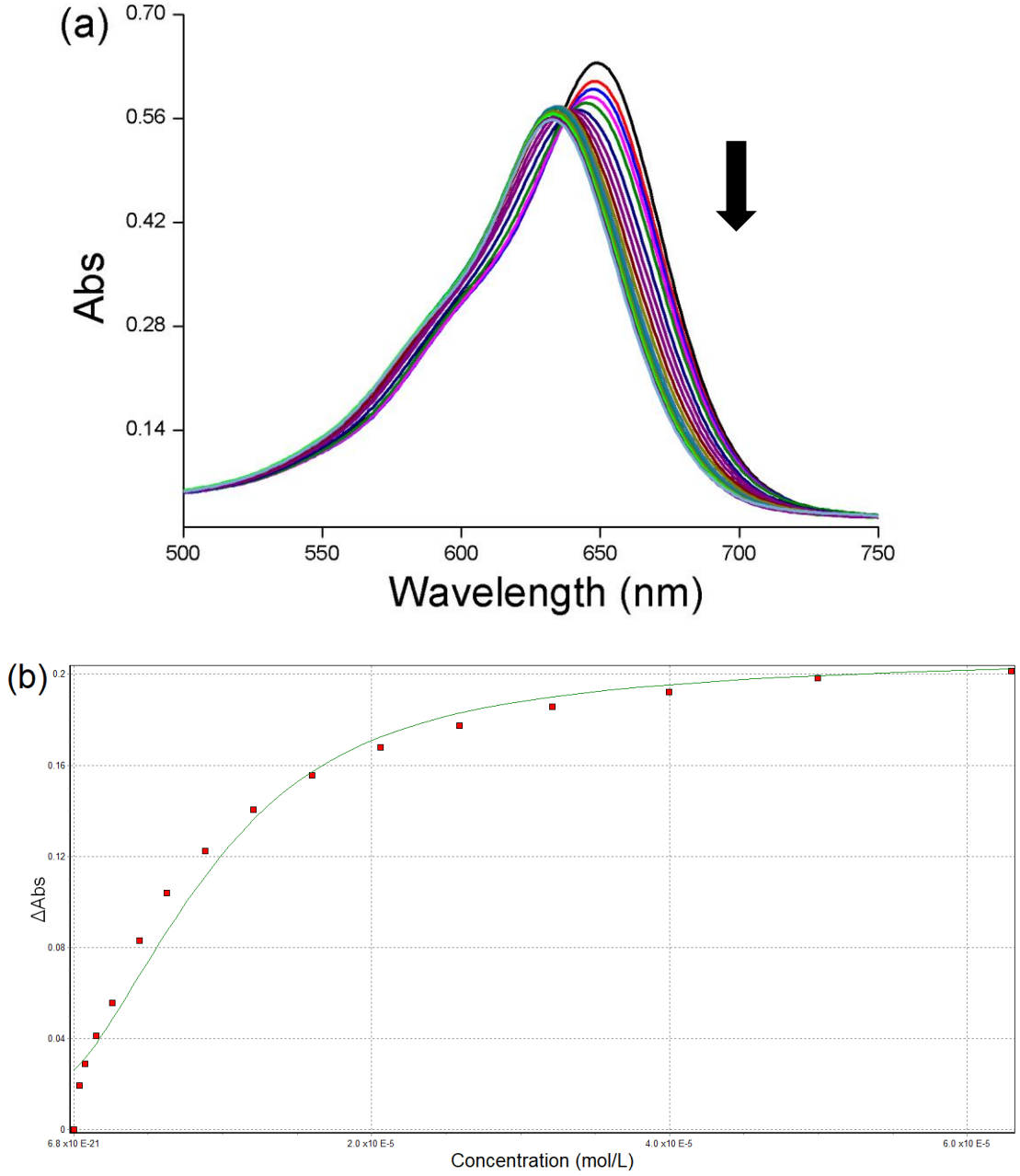

Figure S41. Displacement titration of a solution of dye **3** (15 μM) and **WP7** (15 μM) solution with guest **8** (0 – 63 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **8** with Scientist™. K_a was calculated to be (4.0 ± 2.4) × 10^7 M^{-1}.

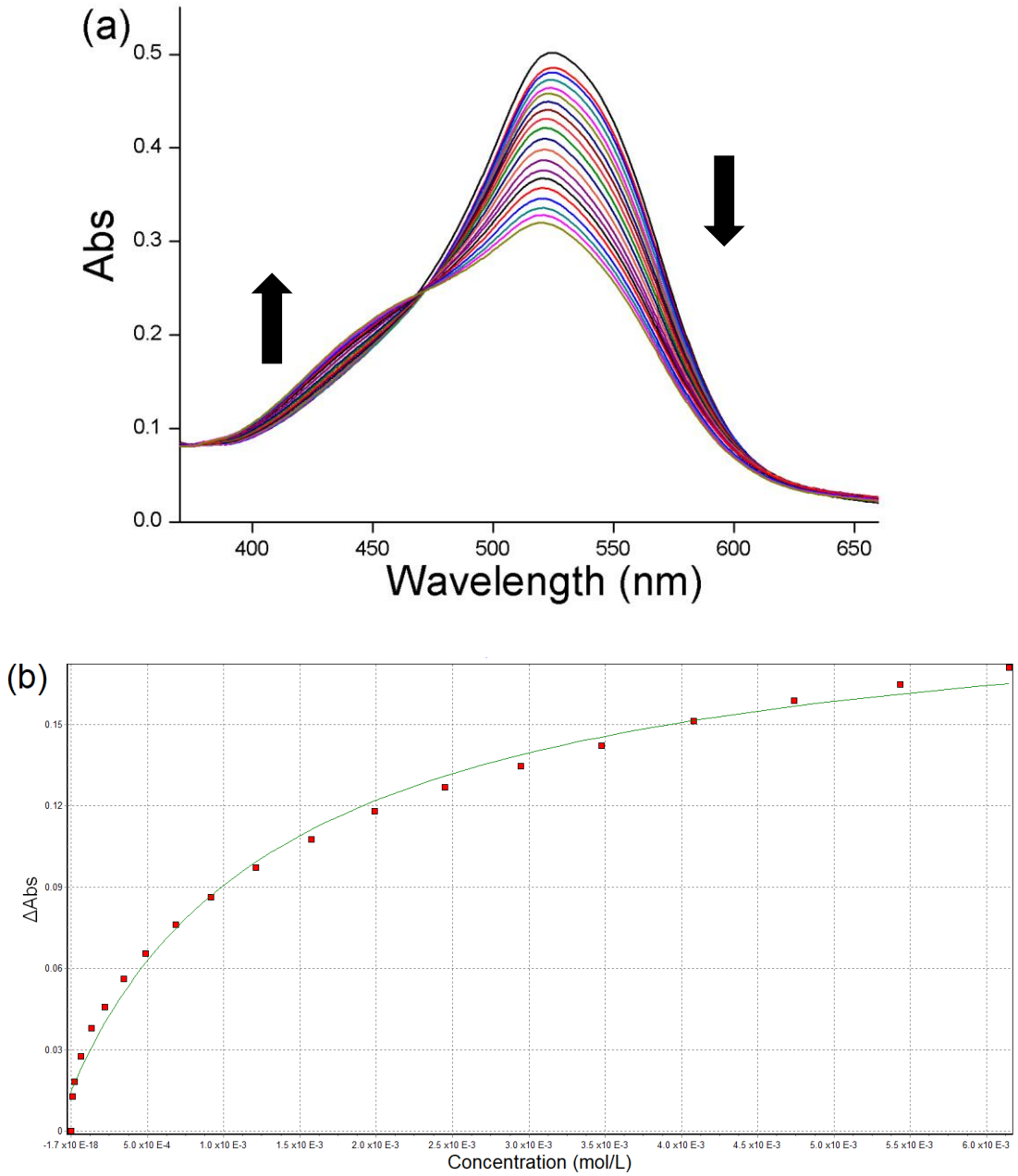

Figure S42. Displacement titration of a solution of dye **1** (40 μM) and **WP7** (40 μM) solution with guest **9** (0 –6147 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 550 nm *versus* concentration for the displacement titration of guest **9** with Scientist™. K_a was calculated to be (1.7 ± 0.2) × 10^3 M^{-1}.

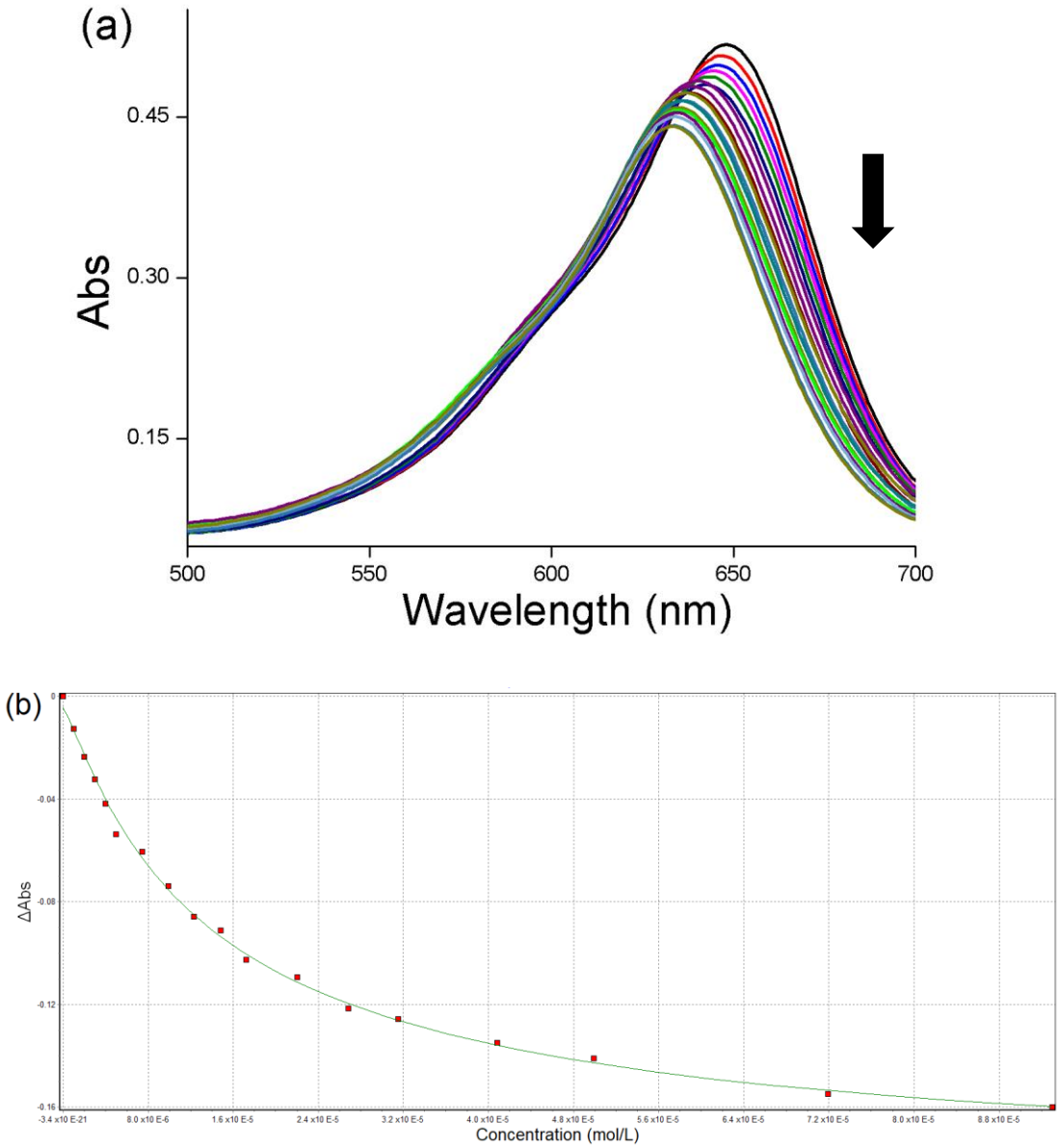

Figure S43. Displacement titration of a solution of dye **3** (10 μM) and **WP7** (10 μM) solution with guest **11** (0 – 93 μM) in sodium phosphate buffer (pH 7.4, 20 mM) : (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A - A_0) at 650 nm *versus* concentration for the displacement titration of guest **11** with Scientist^{TM}. K_a was calculated to be (4.5 ± 0.4) × 10^6 M^{-1}.

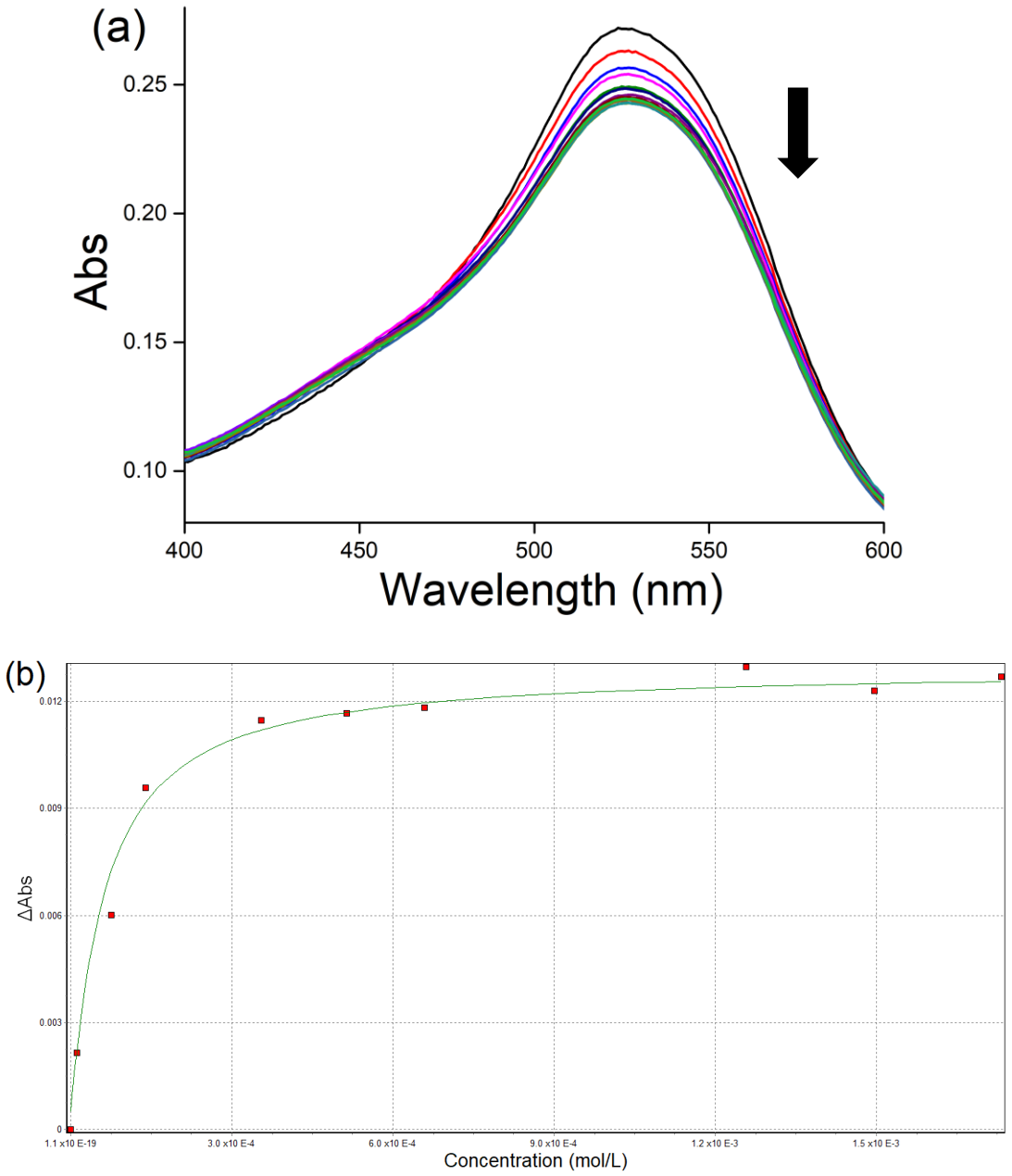

Figure S44. Displacement titration of a solution of dye **1** (20 μM) and **WP7** (20 μM) solution with guest **13** (0 – 1732 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 490 nm *versus* concentration for the displacement titration of guest **13** with Scientist^{TM}. K_a was calculated to be calculated to be $(3.4 \pm 0.8) \times 10^4$ M^{-1}.

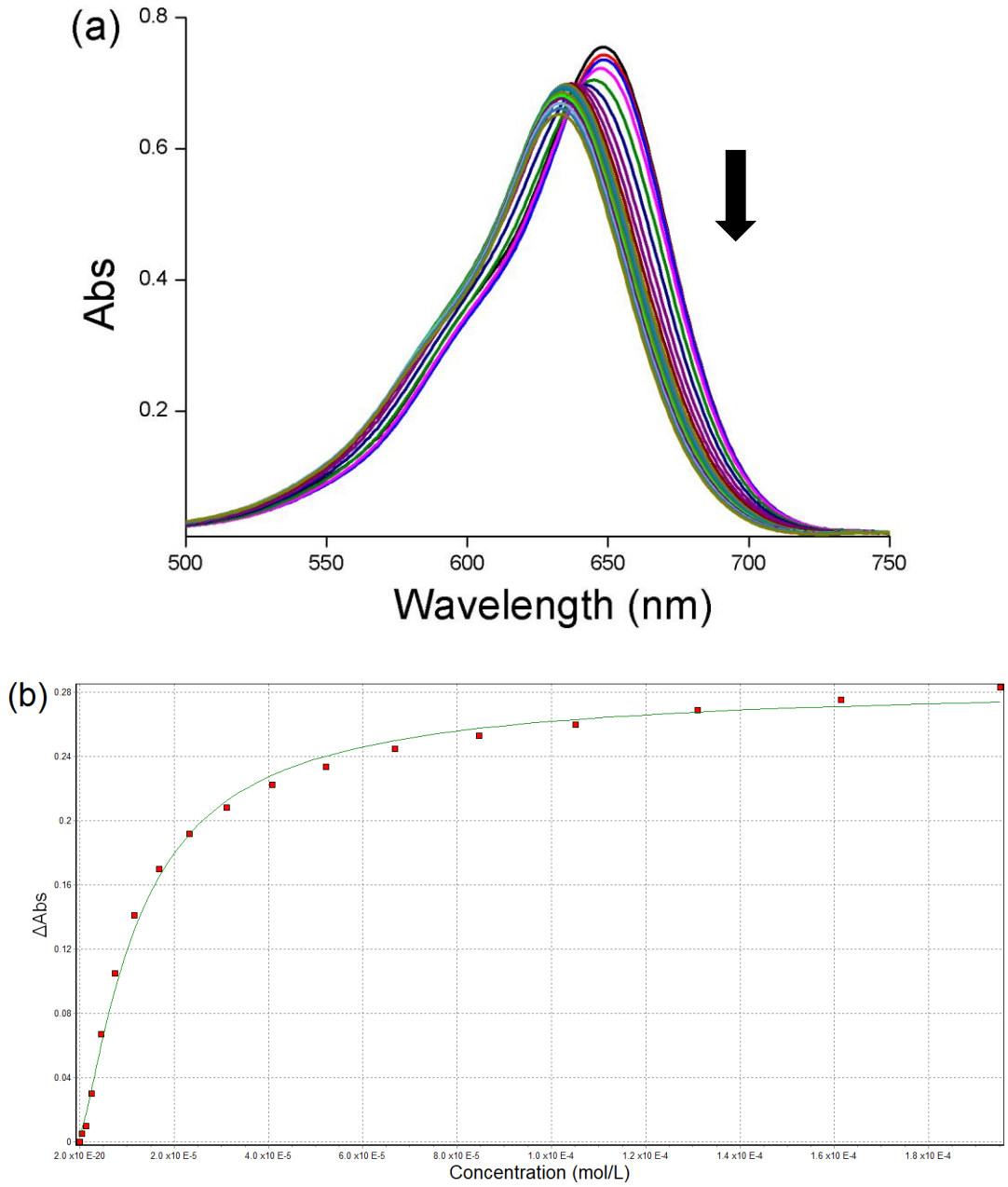

Figure S45. Displacement titration of a solution of dye **3** (15 μM) and **WP7** (15 μM) solution with guest **18** (0 – 195 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of normalized ΔAbs (A_0 - A) at 675 nm *versus* concentration for the displacement titration of guest **18** with Scientist™. K_a was calculated to be (1.2 ± 0.2) × 10^7 M^{-1}.

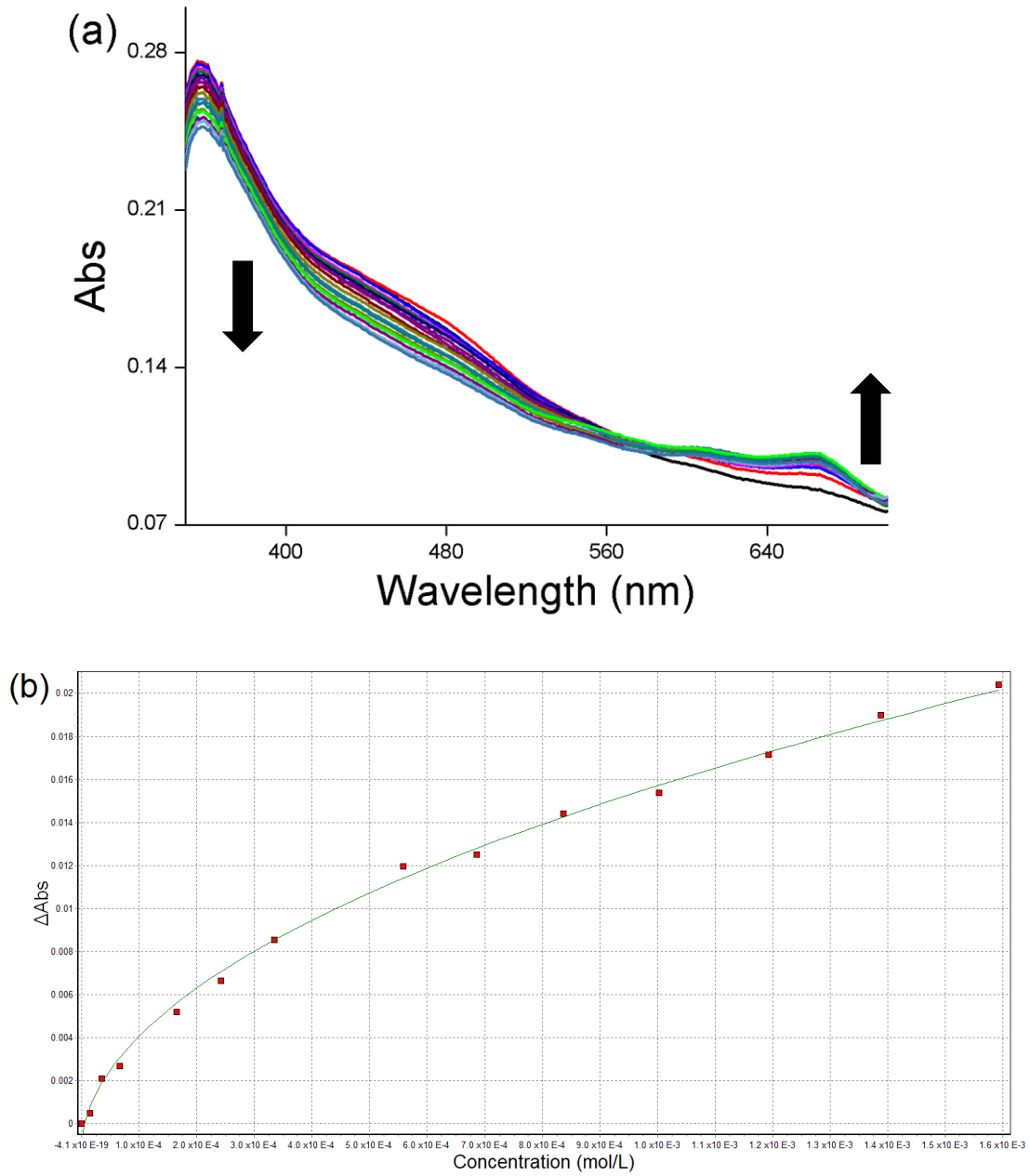

Figure S46. Displacement titration of a solution of guest **19** (200 μM) and **WP7** (200 μM) solution with guest **5** (0 – 1593 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0- A) at 475 nm *versus* concentration for the displacement titration of guest **5** with Scientist™. K_a was calculated to be $(8.9 \pm 1.2) \times 10^{10}\ M^{-1}$.

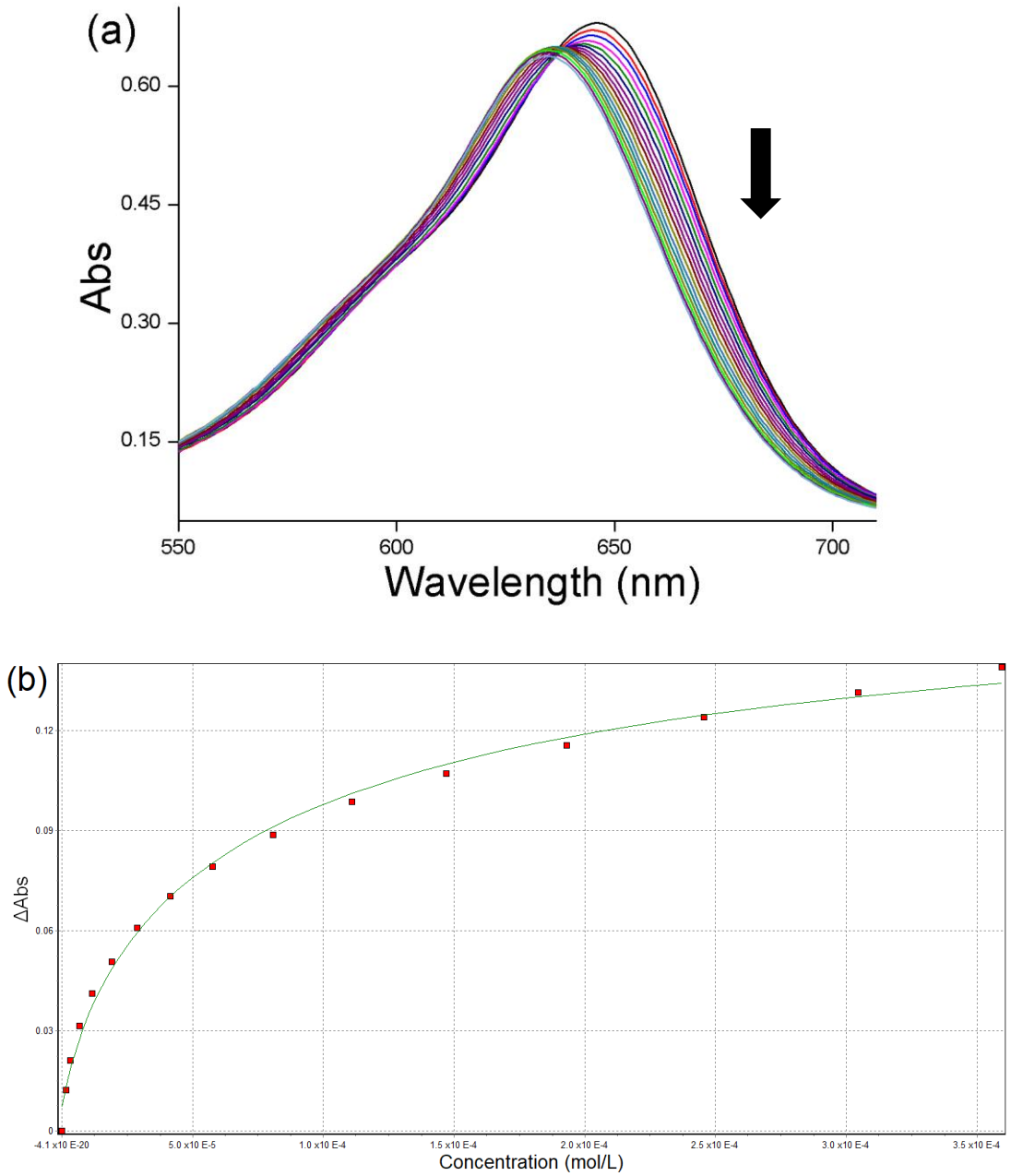

Figure S47. Displacement titration of a solution of dye **3** (10 μM) and **WP7** (10 μM) solution with guest **20** (0 – 360 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 650 nm *versus* concentration for the displacement titration of guest **20** with Scientist^{TM}. K_a was calculated to be (6.9 ± 1.0) × 10^5 M^{-1}.

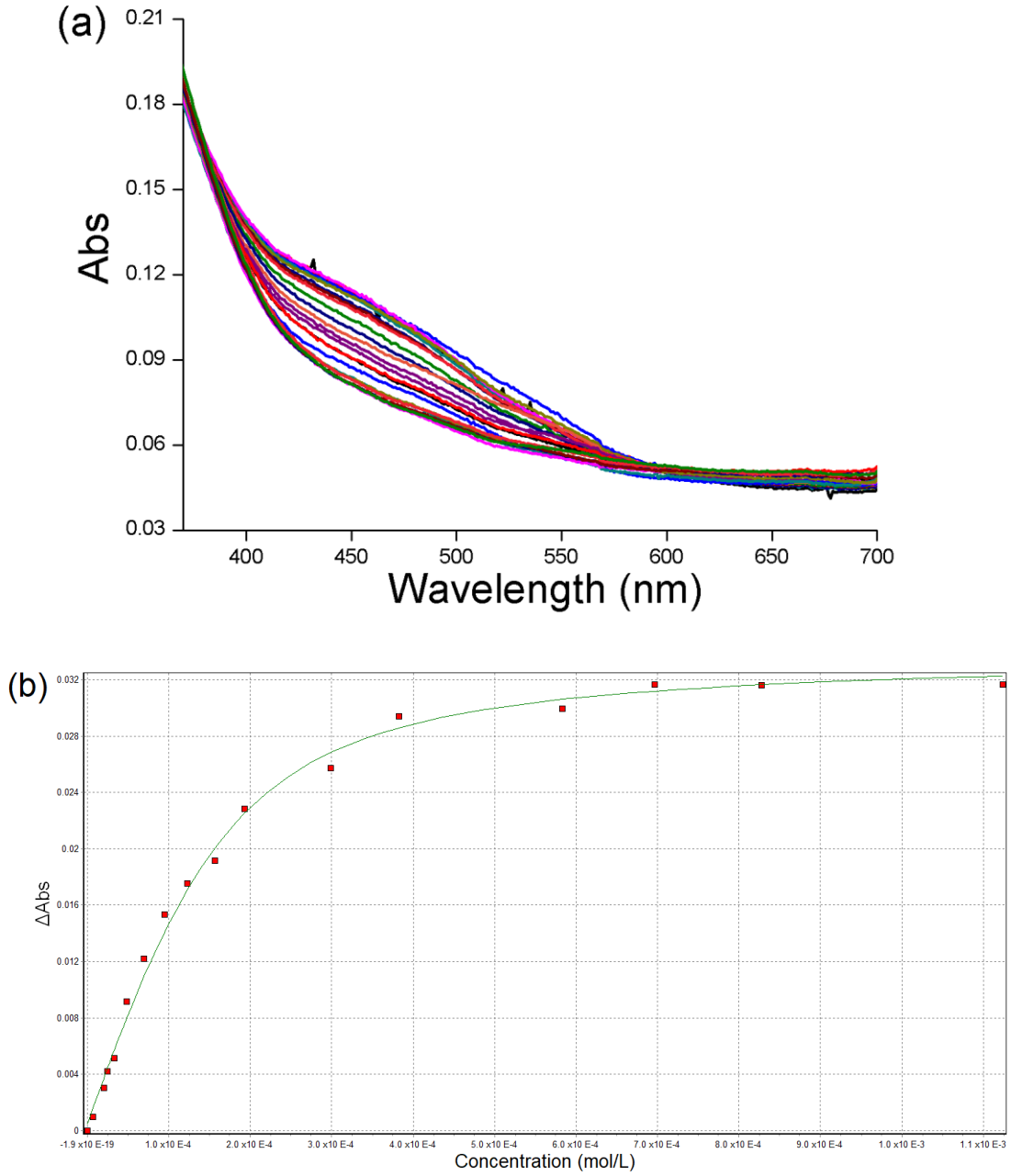

Figure S48. Displacement titration of a solution of guest **19** (200 μM) and **WP7** (200 μM) solution with guest **21** (0 – 1124 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0- A) at 450 nm *versus* concentration for the displacement titration of guest **5** with Scientist™. K_a was calculated to be (3.8 ± 0.9) × 10^{11} M^{-1}.

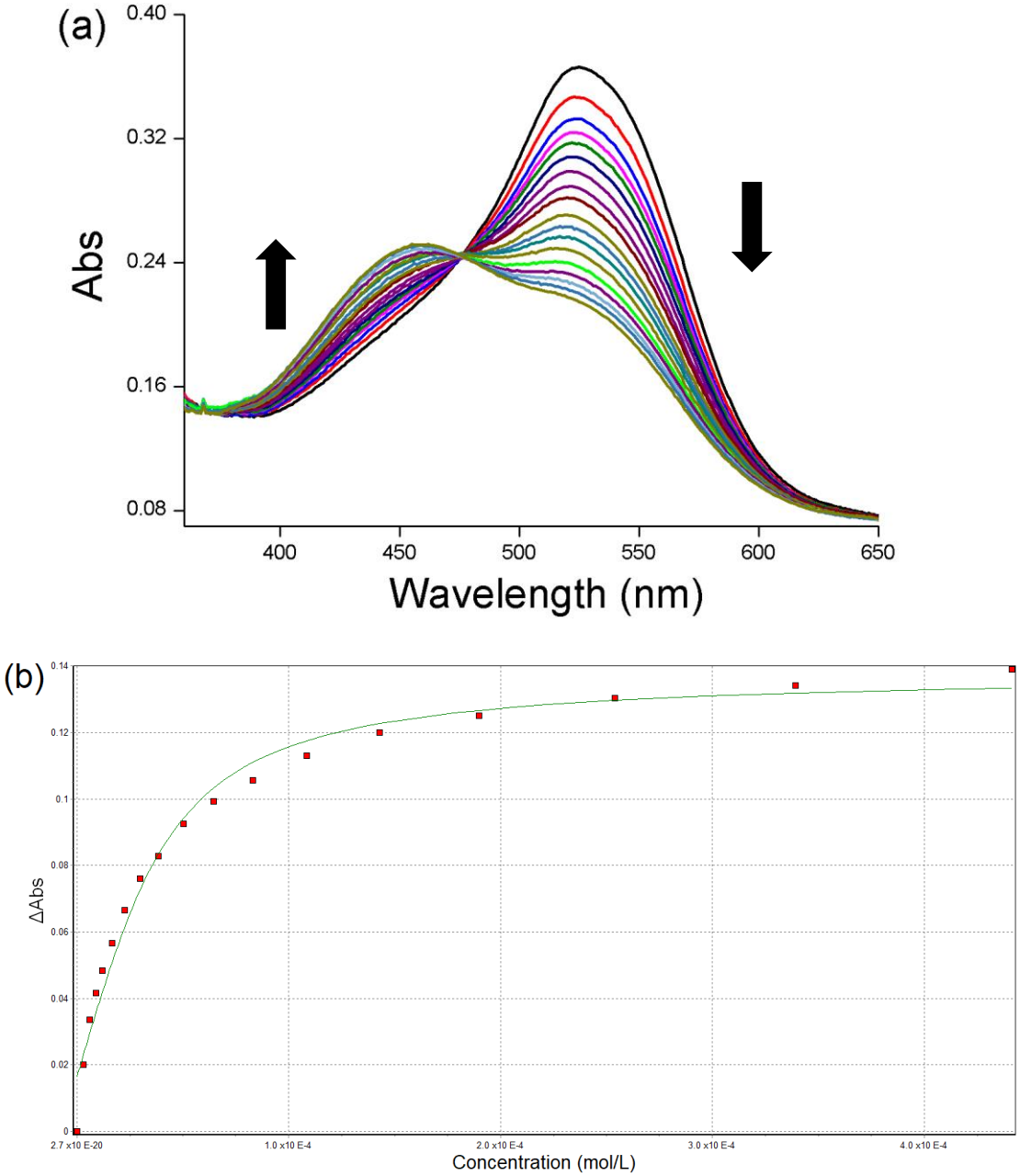

Figure S49. Displacement titration of a solution of dye **1** (30 μM) and **WP7** (30 μM) solution with guest **21** (0 – 441 μM) in sodium phosphate buffer (pH 7.4, 20 mM): (a) UV-Vis spectral change, (b) Nonlinear fitting plot of ΔAbs (A_0 - A) at 550 nm *versus* concentration for the displacement titration of guest **21** with Scientist^{TM}. K_a was calculated to be (1.3 ± 0.3) × 10^5 M^{-1}.

Association constant determination for guest 6, 12 and WP*n* by isothermal titration calorimetry (ITC) measurement.

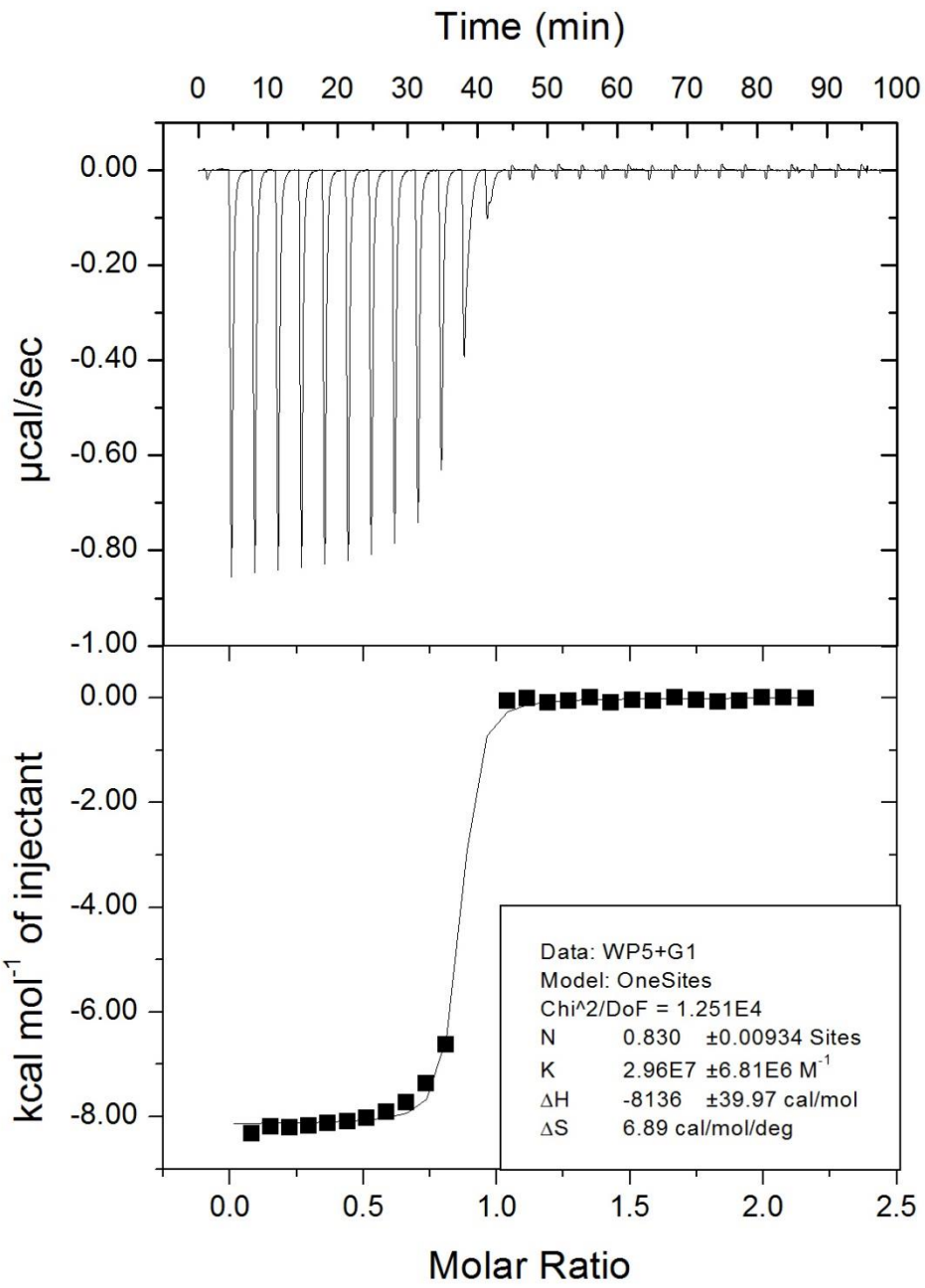

Figure S50. Microcalorimetric titration of guest **6** with **WP5** in sodium phosphate buffer (pH 7.4, 20 mM) at 298.15 K. (Top) Raw ITC data for guest **6** solution (300 µM) into a **WP5** solution (30 µM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

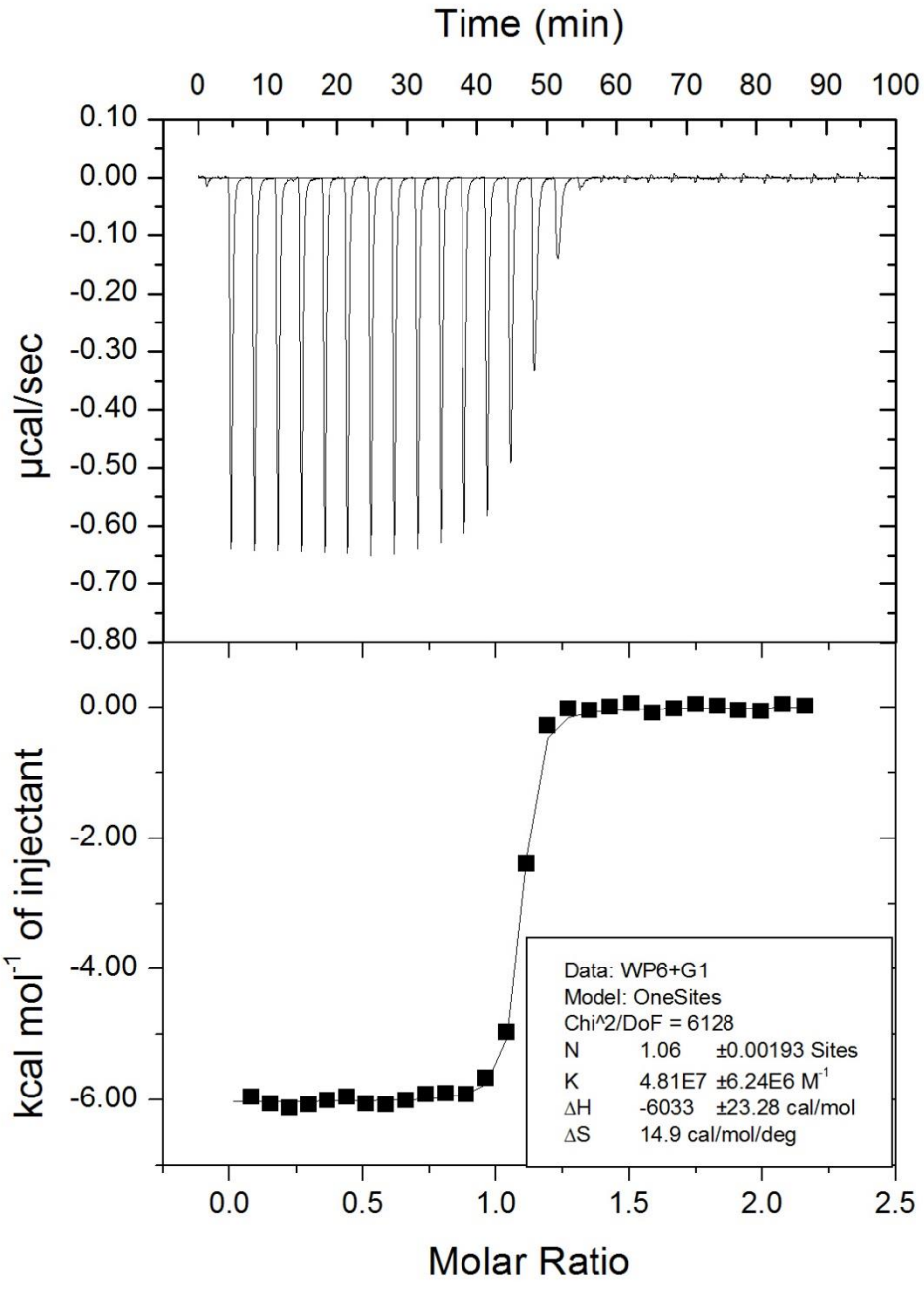

Figure S51. Microcalorimetric titration of guest **6** with **WP6** in sodium phosphate buffer (pH 7.4, 20 mM) at 298.15 K. (Top) Raw ITC data for guest **6** solution (300 µM) into a **WP6** solution (30 µM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

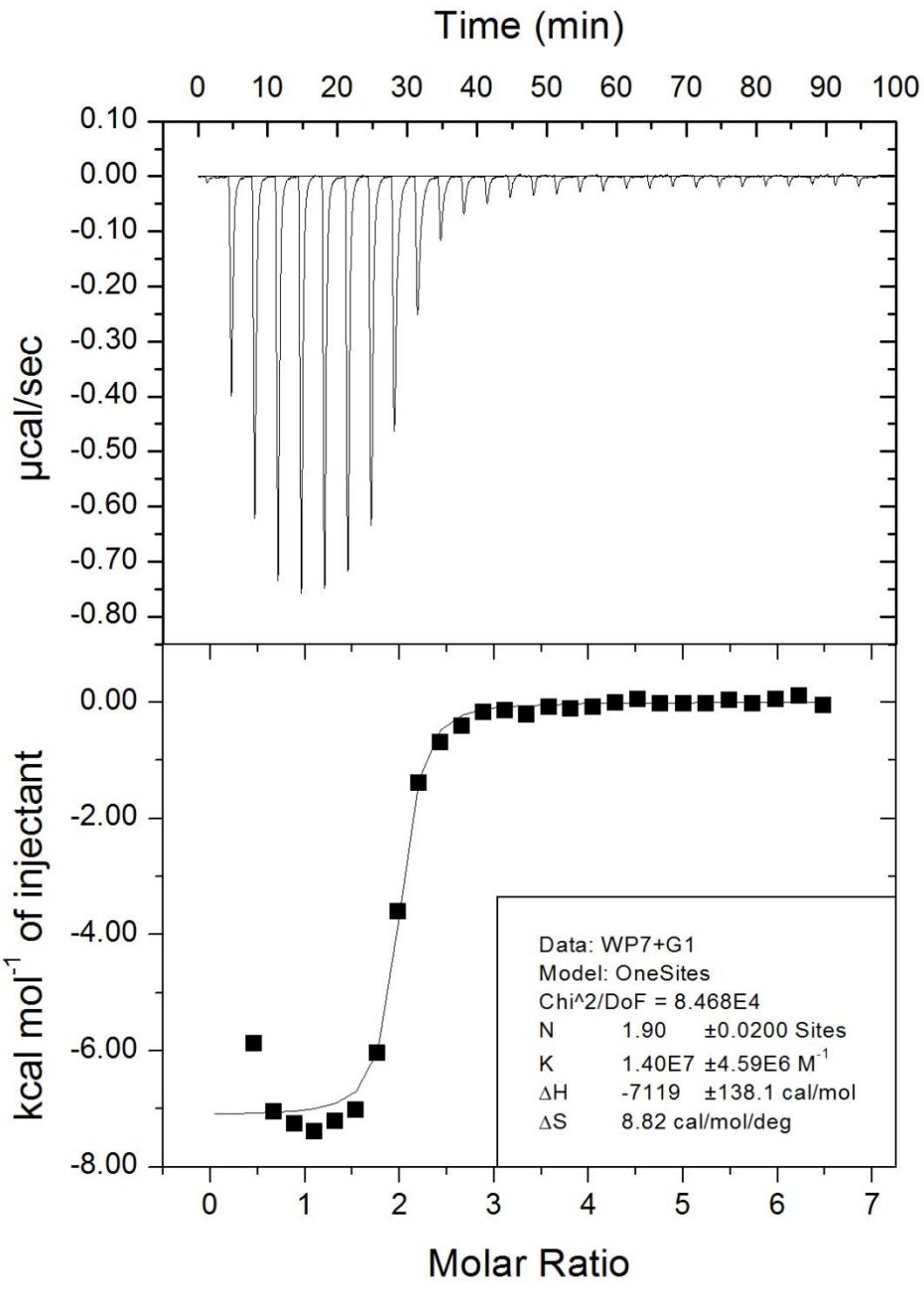

Figure S52. Microcalorimetric titration of guest **6** with **WP7** in sodium phosphate buffer (pH 7.4, 20 mM) at 298.15 K. (Top) Raw ITC data for guest **6** solution (300 µM) into a **WP7** solution (10 µM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

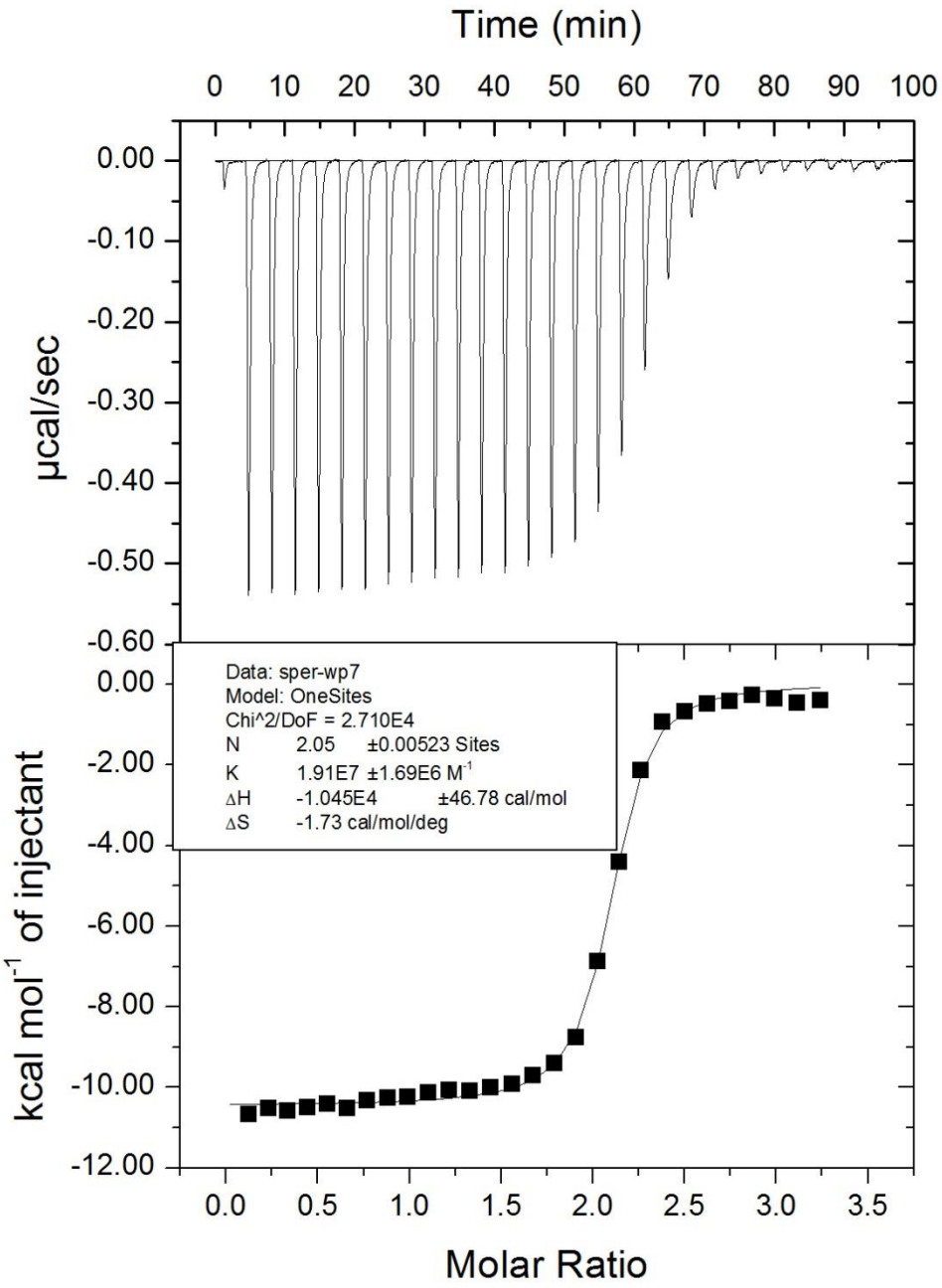

Figure S53. Microcalorimetric titration of guest **12** with **WP7** in sodium phosphate buffer (pH 7.4, 20 mM) at 298.15 K. (Top) Raw ITC data for guest **12** solution (150 µM) into a **WP7** solution (10 µM). (Bottom) Net reaction heat obtained from the integration of the calorimetric traces.

Job Plot for WP*n* and dyes

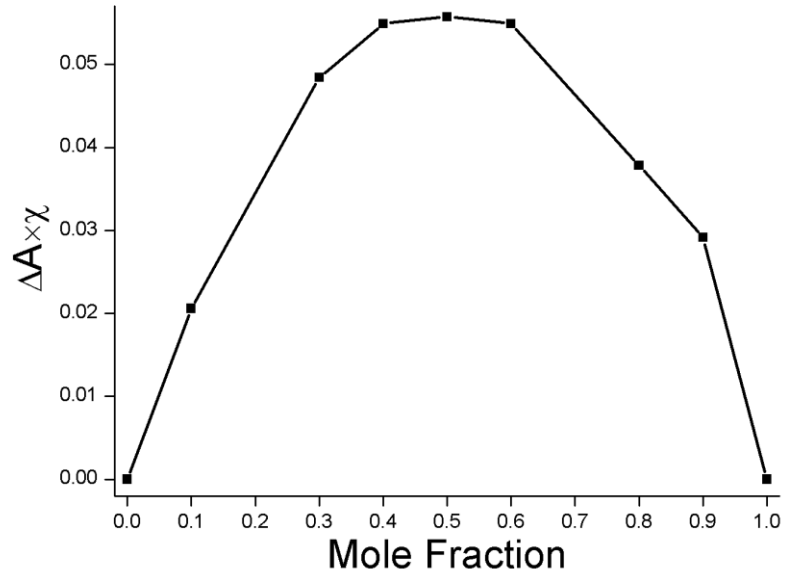

Figure S54. Job plot for **WP5** and dye **1** derived from UV-Vis absorbance in sodium phosphate buffer (pH 7.4, 20 mM) ([dye **1**] + [**WP5**] = 30 μM). χ: neutral red mole fraction; ΔA: absorbance change at 450 nm.

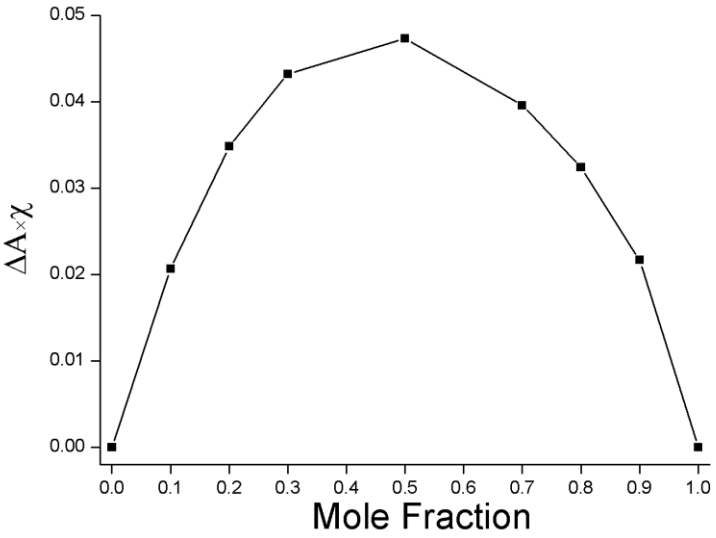

Figure S55. Job plot for **WP6** and dye **1** derived from UV-Vis absorbance in sodium phosphate buffer (pH 7.4, 20 mM) ([dye **1**] + [**WP6**] = 30 μM). χ: neutral red mole fraction; ΔA: absorbance change at 450 nm.

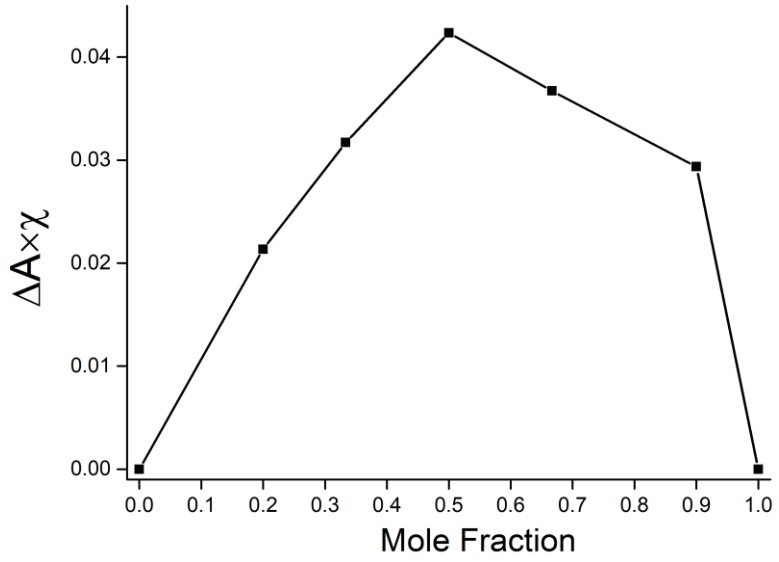

Figure S56. Job plot for **WP7** and dye **1** derived from UV-Vis absorbance in sodium phosphate buffer (pH 7.4, 20 mM) ([dye **1**] + [**WP7**] = 20 μM). χ: neutral red mole fraction; ΔA: absorbance change at 450 nm.

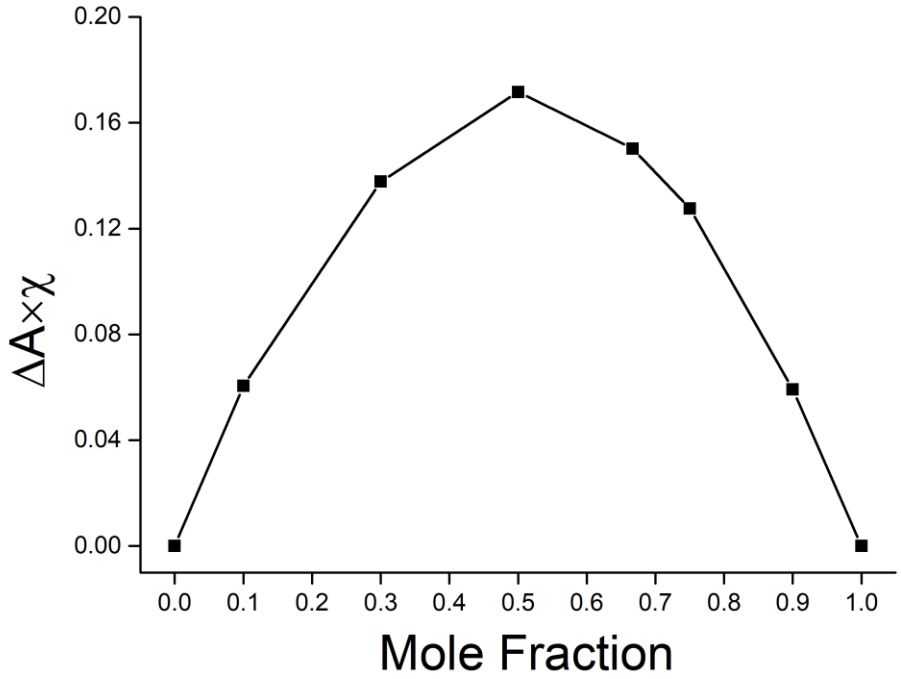

Figure S57. Job plot for **WP5** and dye **3** derived from UV-Vis absorbance in sodium phosphate buffer (pH 7.4, 20 mM) ([dye **3**] + [**WP5**] = 10 μM). χ: methyl green mole fraction; ΔA: absorbance change at 630 nm.

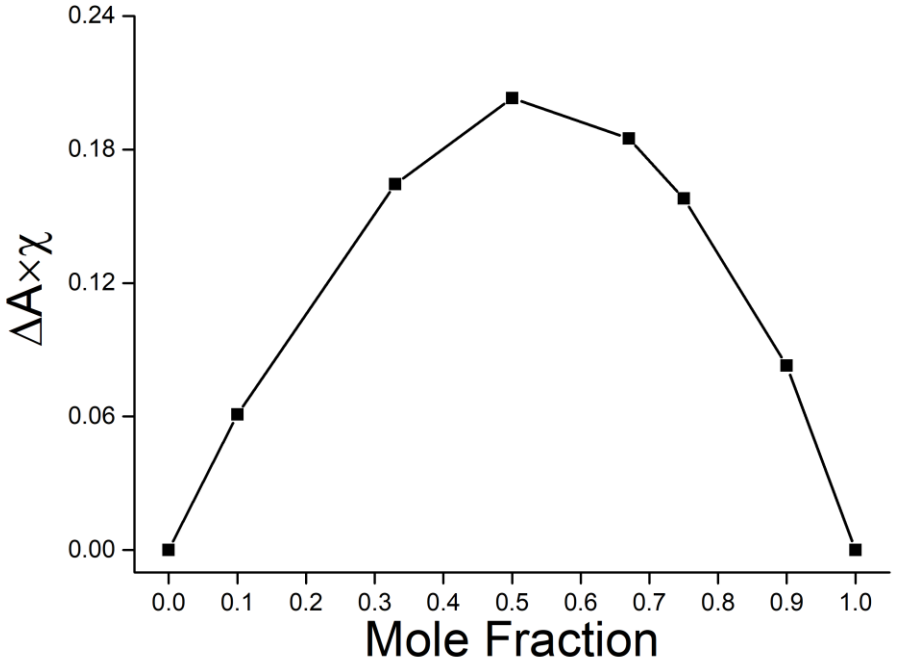

Figure S58. Job plot for **WP6** and dye **3** derived from UV-Vis absorbance in sodium phosphate buffer (pH 7.4, 20 mM) ([dye **3**] + [**WP6**] = 10 μM). χ: methyl green mole fraction; ΔA: absorbance change at 630 nm.

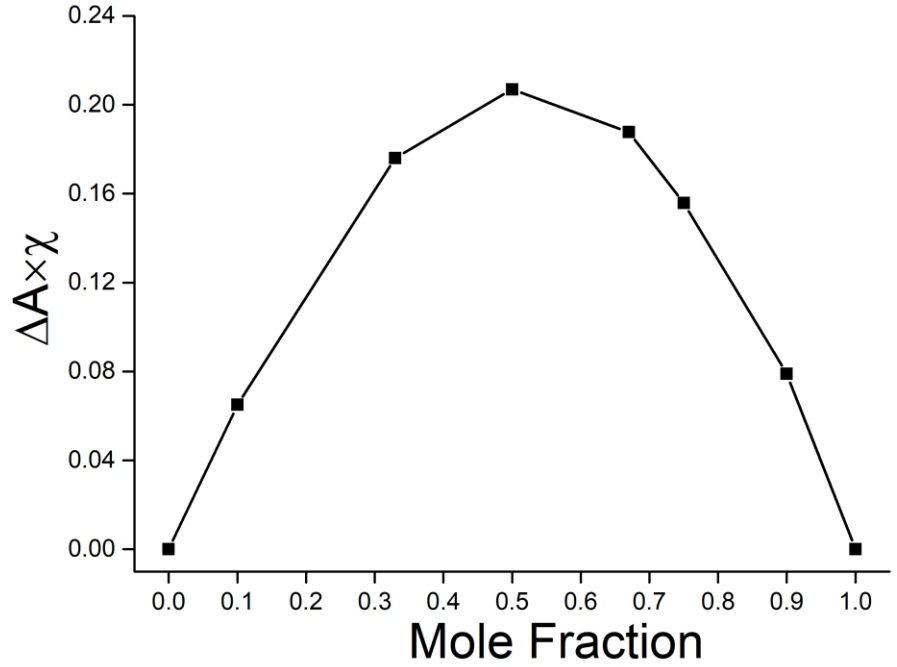

Figure S59. Job plot for **WP7** and dye **3** derived from UV-Vis absorbance in sodium phosphate buffer (pH 7.4, 20 mM) ([dye **3**] + [**WP7**] = 10 μM). χ: methyl green mole fraction; ΔA: absorbance change at 630 nm.

^{1}H NMR Spectra

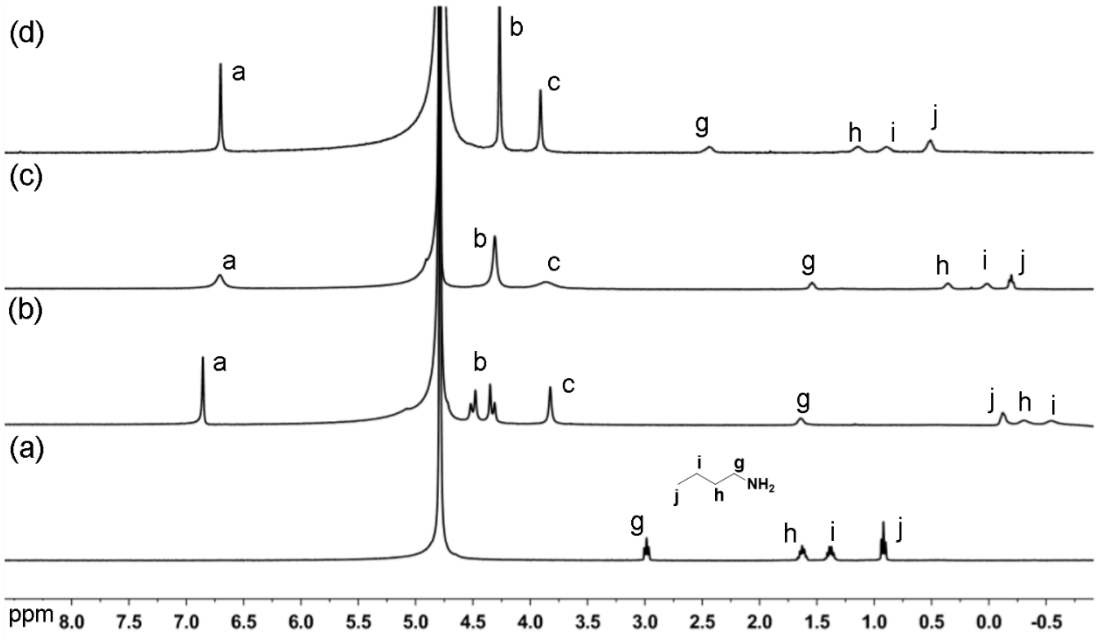

Figure S60. ^{1}H NMR spectra record for (a) guest **9**; (b) 1:1 **WP5·9**; (c) 1:1 1-butylamine and **WP6·9**; (d) 1:1 **WP7·9** ([**9**] = [**WP5**] = [**WP6**] = [**WP7**] = 1 mM, 400 MHz, 20 mM NaD_2PO_4).

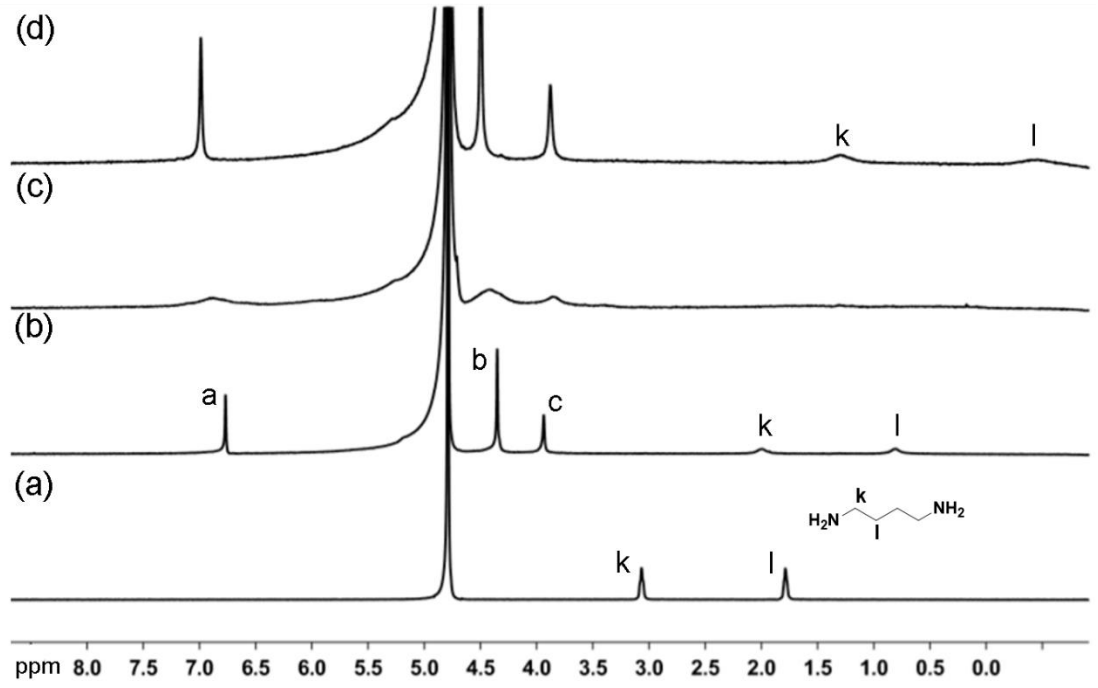

Figure S61. ^{1}H NMR spectra record for (a) guest **4**; (b) 1:1 **WP7·4**; (c) 1:1 **WP6·4**; (d) 1:1 **WP5·4** ([**4**] = [**WP5**] = [**WP6**] = [**WP7**] = 1 mM, 400 MHz, 20 mM NaD_2PO_4).

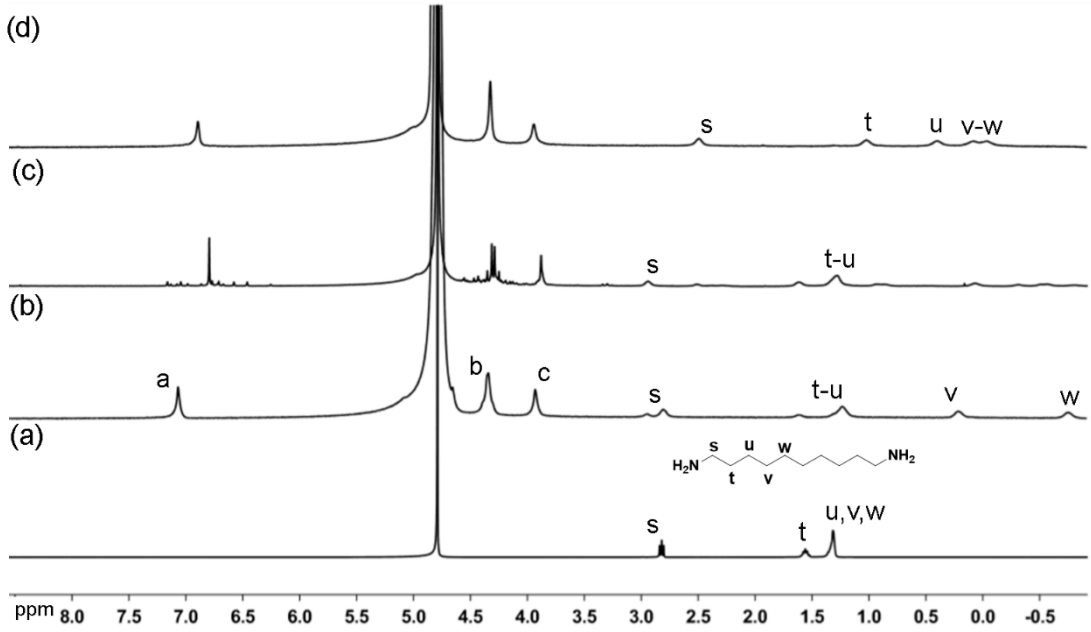

Figure S62. ^{1}H NMR spectra record for (a) guest **7**; (b) 1:1 **WP5·7**; (c) 1:1 **WP6·7**; (d) 1:1 **WP7·7** ([**7**] = [**WP5**] = [**WP6]** = [**WP7**] = 1 mM, 400 MHz, 20 mM NaD_2PO_4).

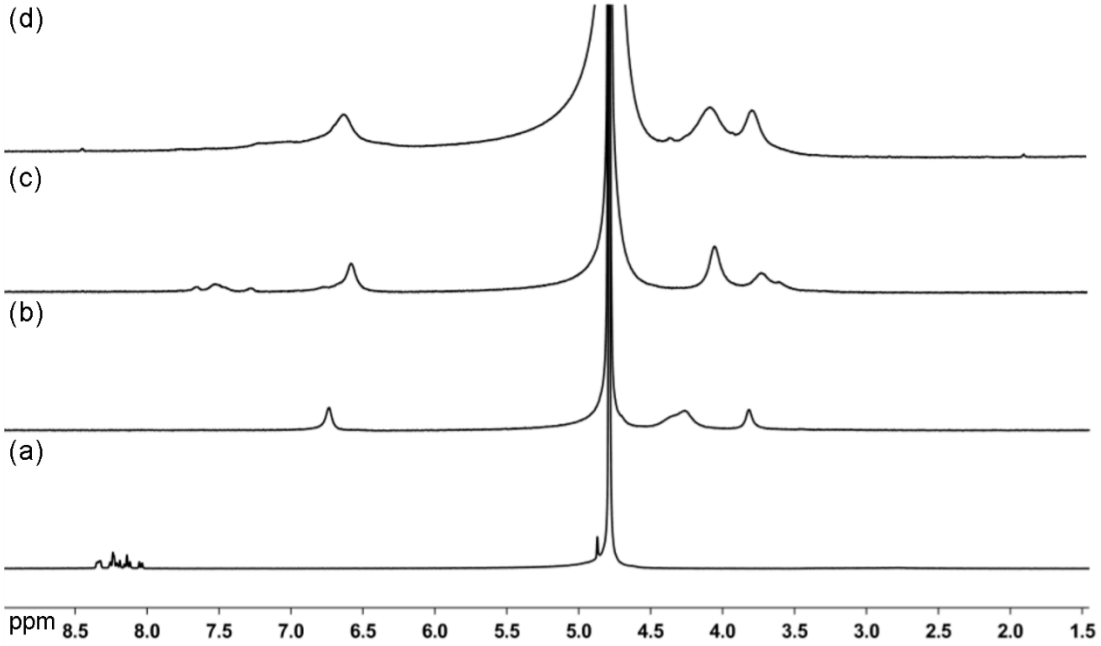

Figure S63. ^{1}H NMR spectra record for (a) guest **16**; (b) 1:1 **WP5·16**; (c) 1:1 **WP6·16**; (d) 1:1 **WP7·16** ([**16**] = [**WP5**] = [**WP6**] = [**WP7**] = 1 mM, 400 MHz, 20 mM NaD_2PO_4).

Self-assembly

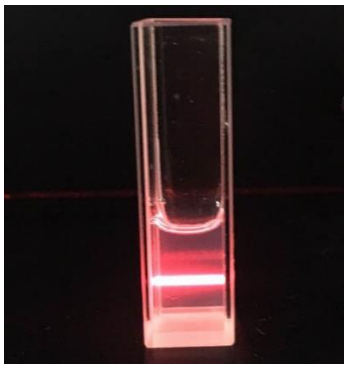

Figure S64. Tyndall effect for **WP5·16** in sodium phosphate buffer (20 mM, pH 7.4).