Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Pyridinium-based symmetrical diamides as chemosensors in visual sensing of citrate through indicator displacement assay (IDA) and gel formation

Kumaresh Ghosh*, Avik Ranjan Sarkar

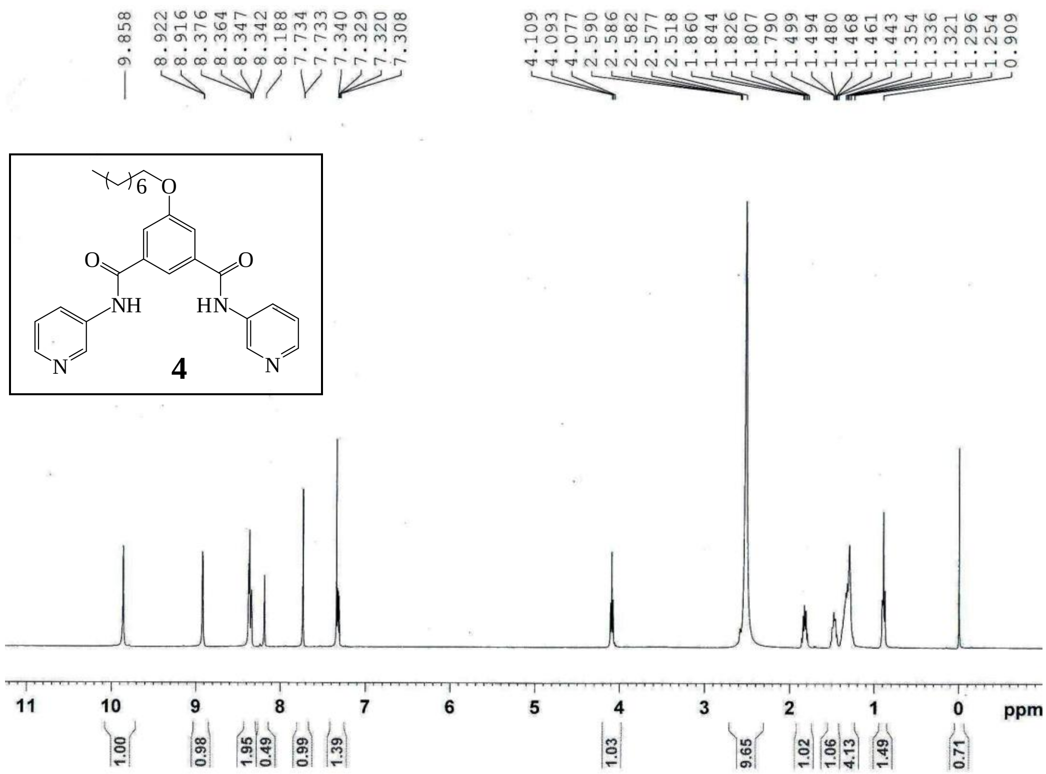
Department of Chemistry, University of Kalyani, Kalyani-741235, India.

E-mail : *ghosh_k2003@yahoo.co.in*

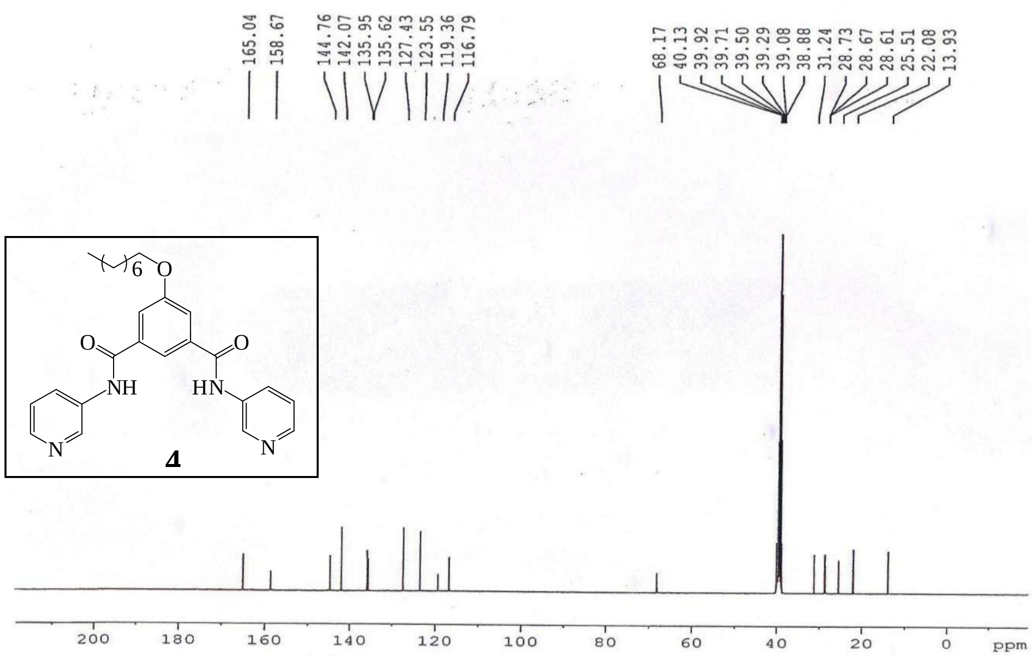
Contents

Spectral data of compounds:

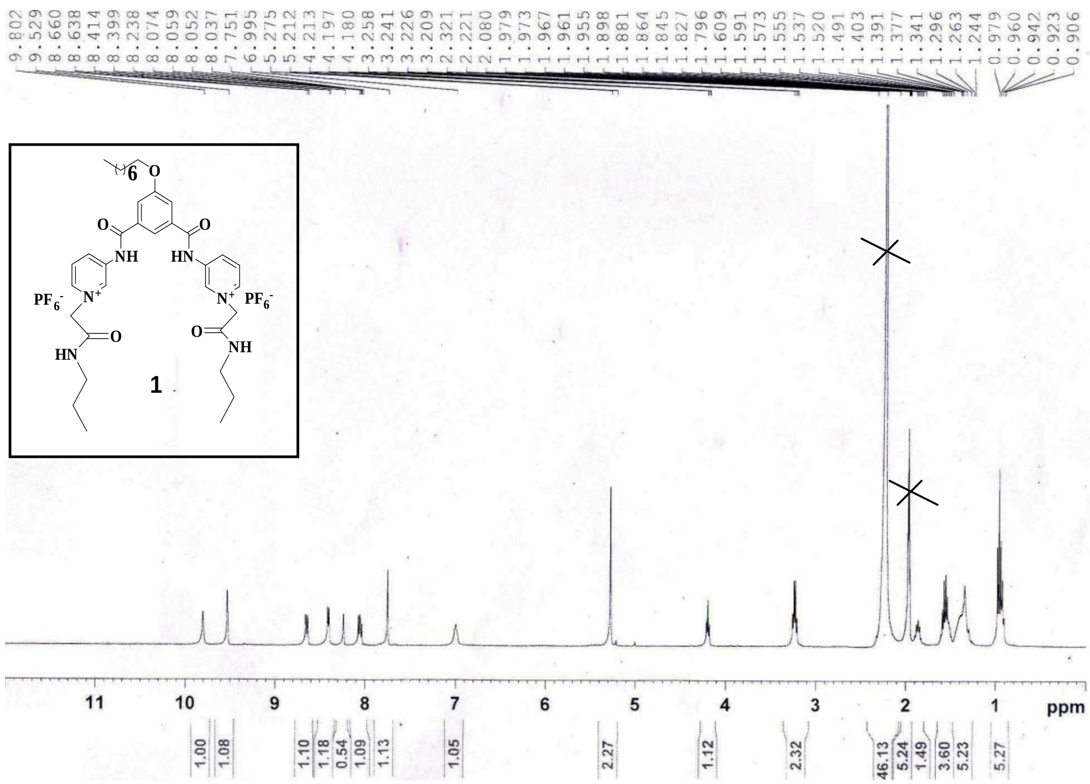
^{1}H NMR of 4(400 MHz, $CDCl_3$ containing few drops of d_6-DMSO):



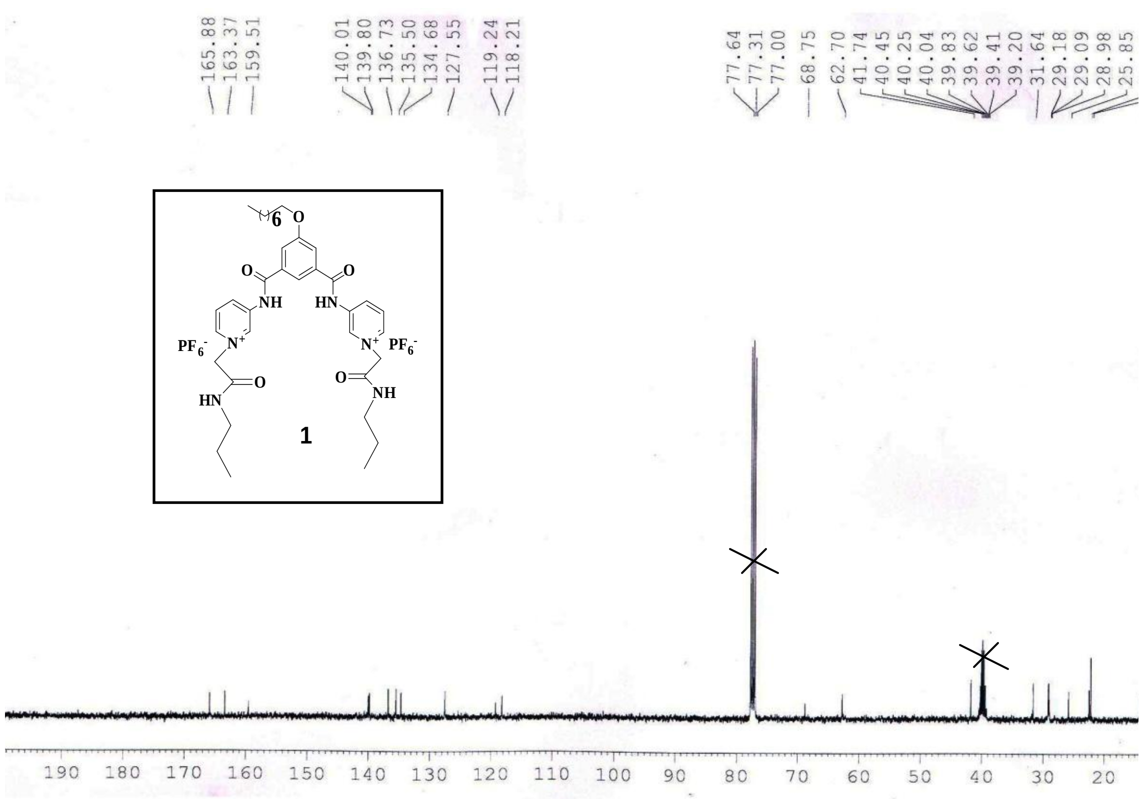
^{13}C NMR of 4 (100 MHz, d_6-DMSO):



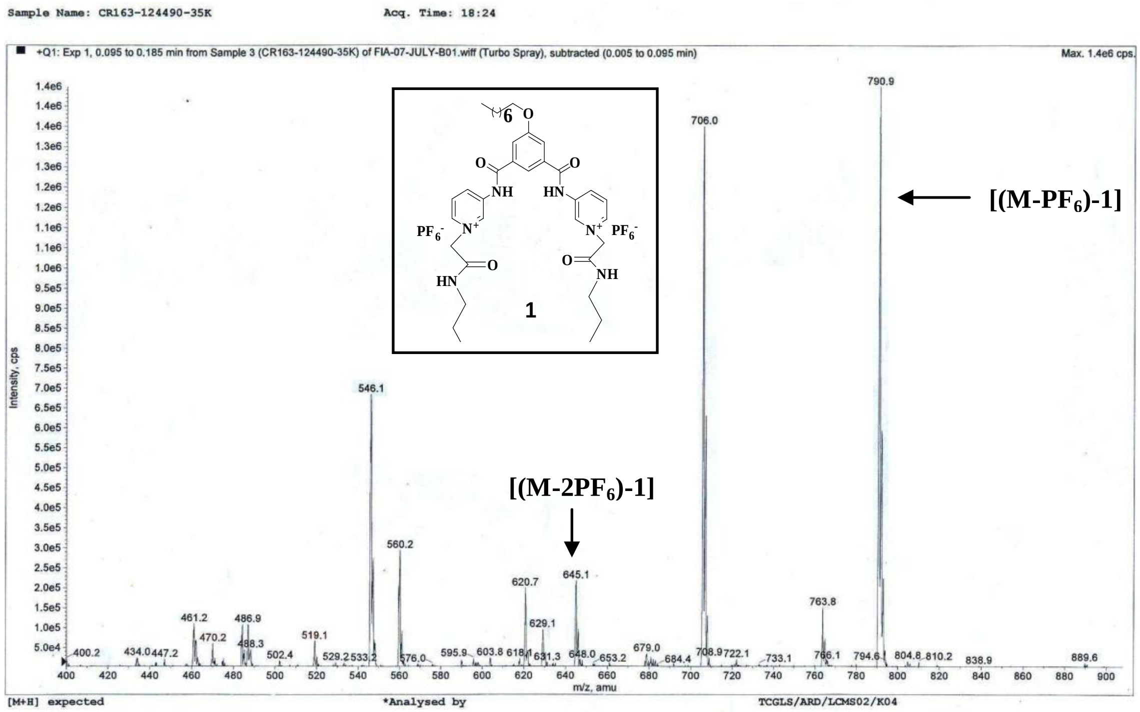
[1]H NMR of 1 (400 MHz, CD_3CN):



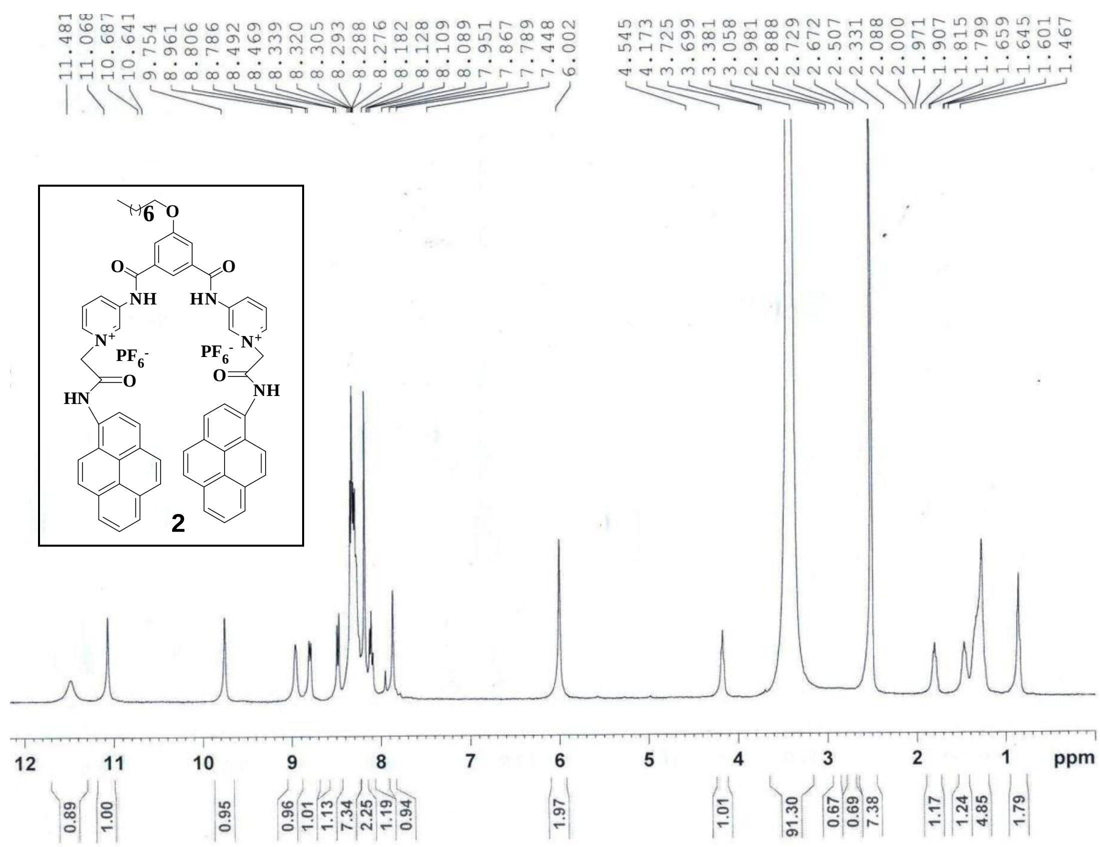
[13]C NMR of 1 (100 MHz, $CDCl_3$ containing few drops of d_6-DMSO):



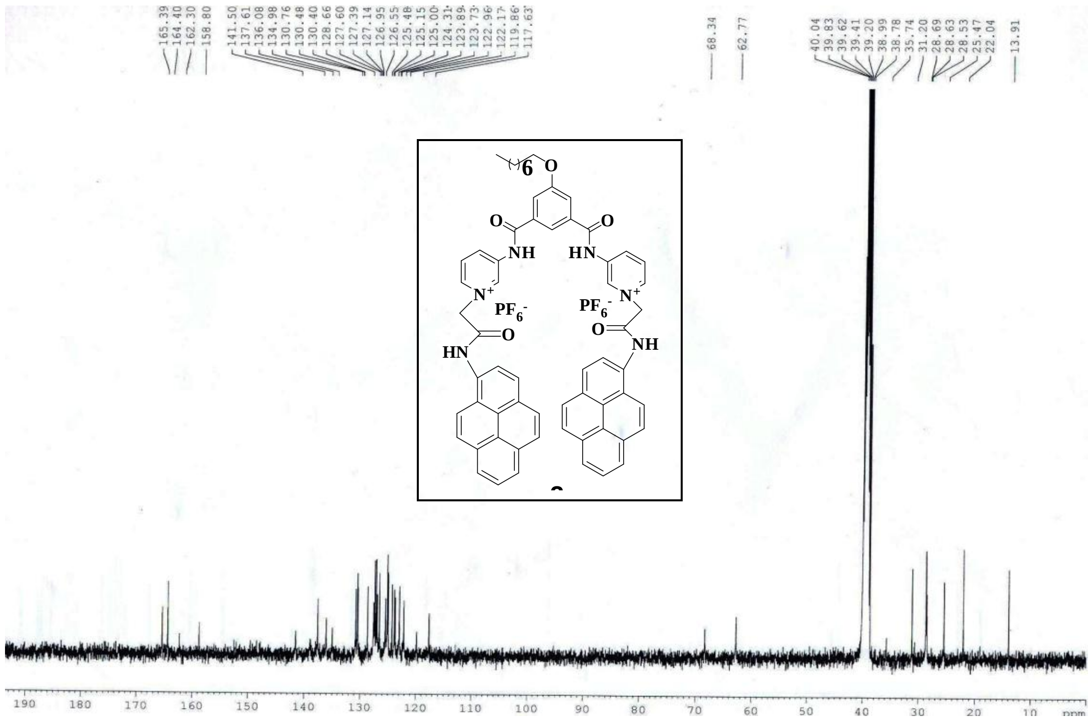
ESI mass of 1:



[1]H NMR of 2 (400 MHz, d_6-DMSO):



^{13}C NMR of 2 (100 MHz, d_6-DMSO):



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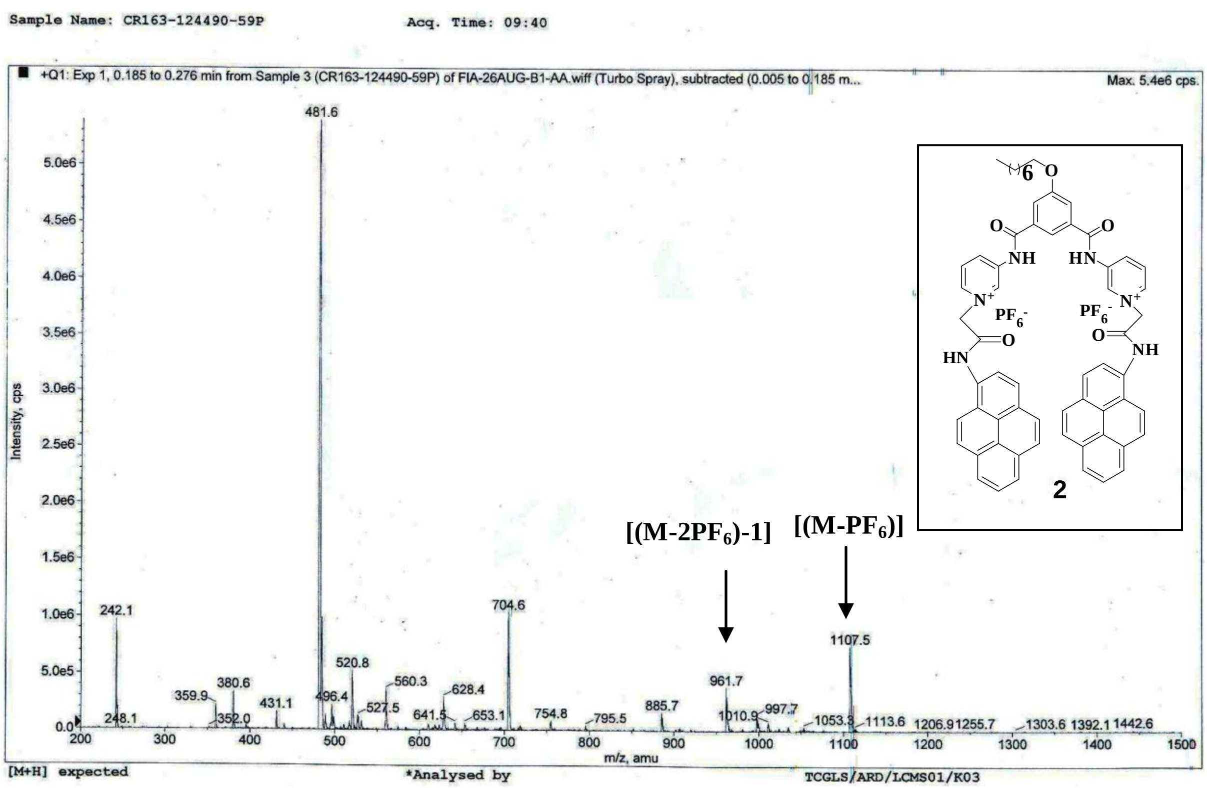
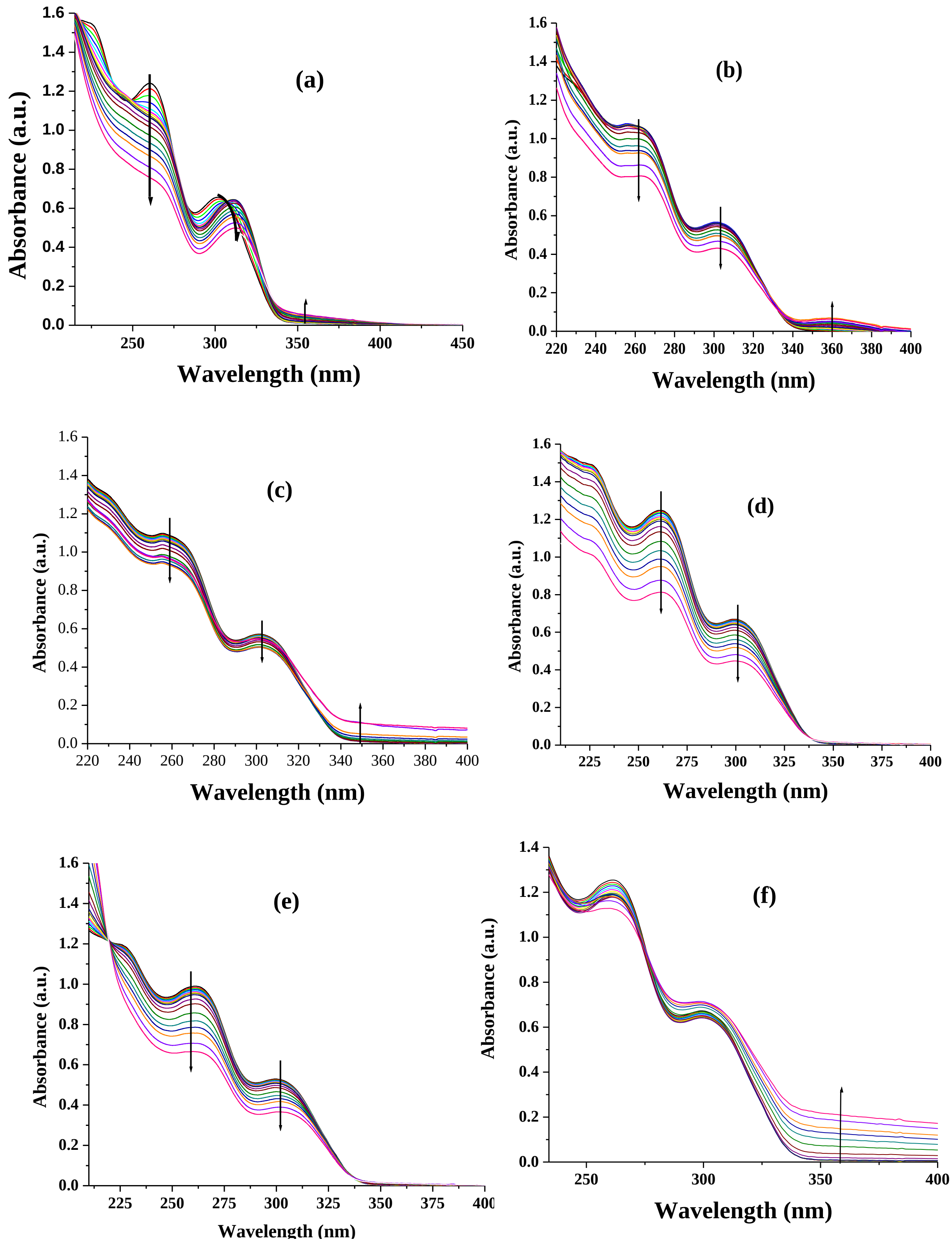


Selected UV-vis titration curves for receptor 1 in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer)



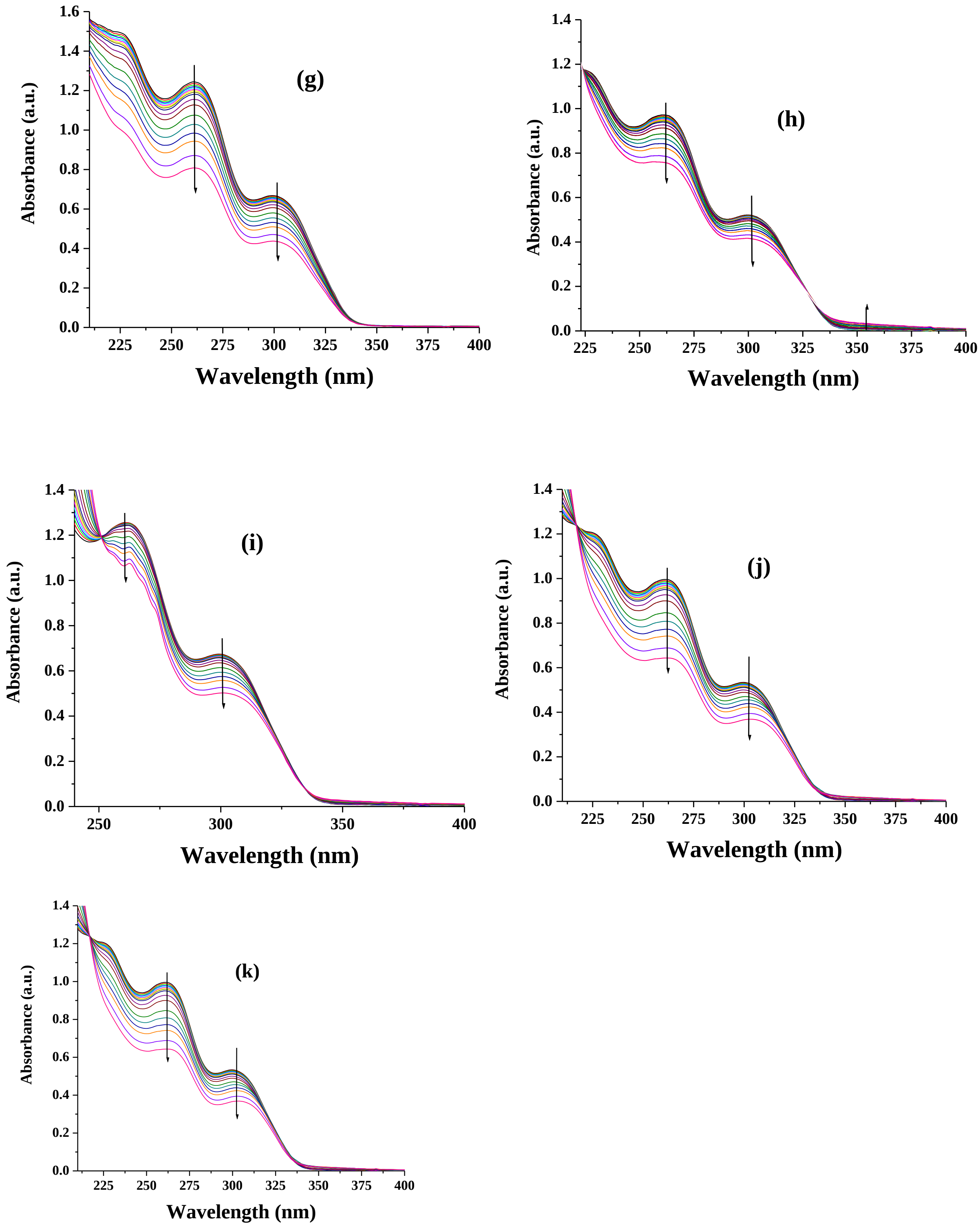


Figure 1S: UV-vis titration curves of receptor **1** (c = 4.8 x 10^{-5} M) with the tetrabutylammonium (a) Citrate, (b) tartarate, (c) malate, (d) acetate, (e) adipate, (f) dihydrogenphosphate, (g) fluoride, (h) glutarate, (i) malonate, (j) N-Ts glutamate (k) pimelate in 4:1 CH_3CN:H_2O (v/v) 10 mM Tris/HCl buffer pH = 6.3, where the concentration of all guests (c = 9.6 x 10^{-4} M).

Binding constant curve for receptor 1 with tetrabutylammonium citrate from UV-vis in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer)

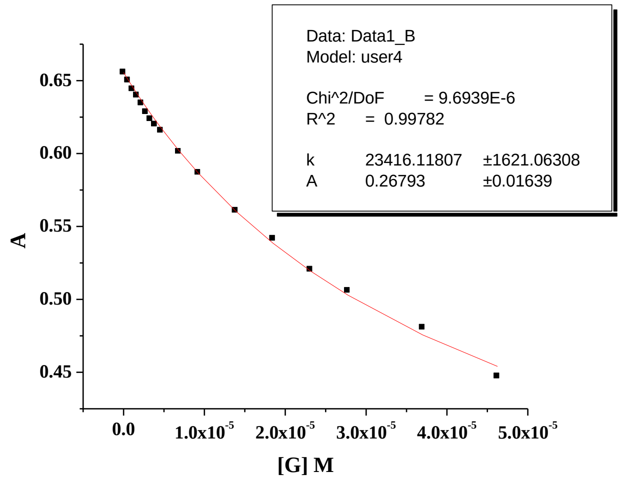
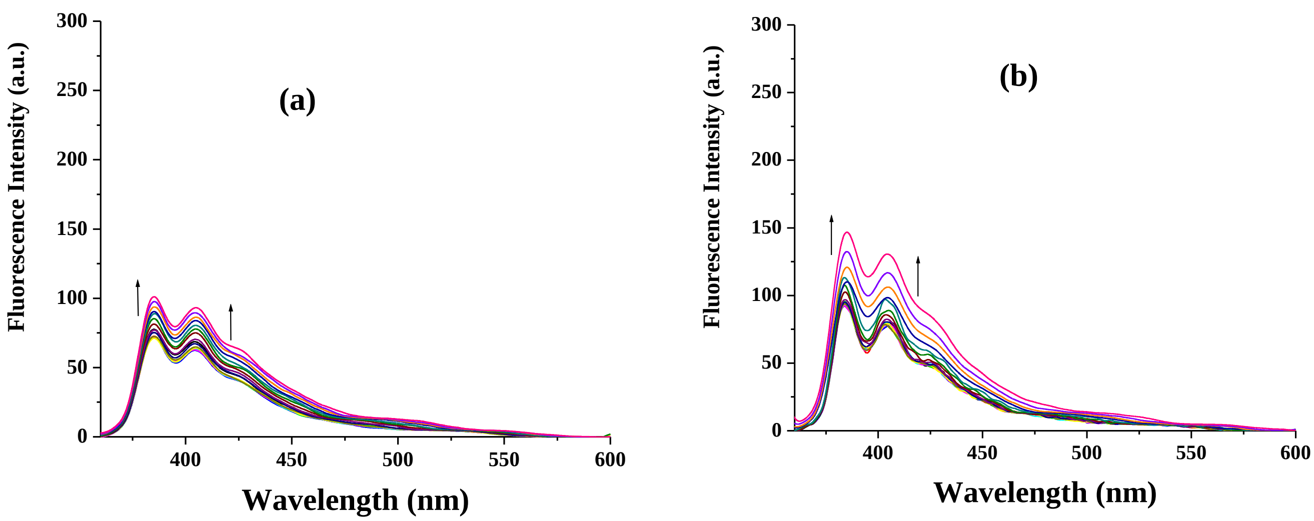


Figure 2S: Binding constant curve for **1** (c = 4.80 x 10^{-5} M) with citrate (c = 4.2 x 10^{-4} M) [Determined using non-linear curve fitting y= (A_0+A*K*x)/ (1+K*x). x = [G], y= absorbance in CH_3CN: H_2O (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) at λ_{max} = 295 nm].

Selected fluorescence titration curves for receptor 2 in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer)



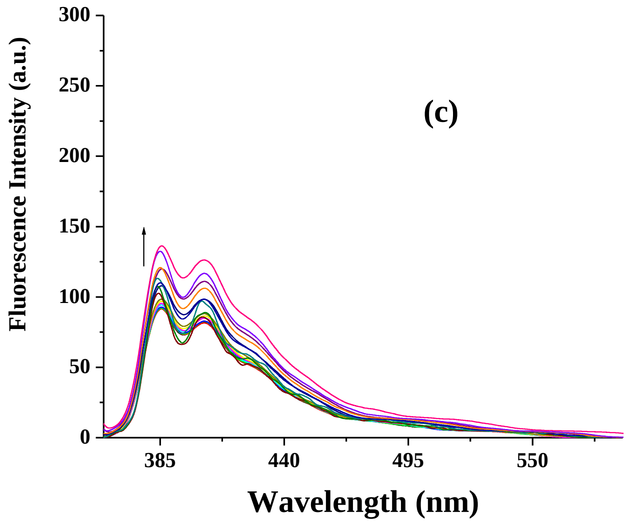
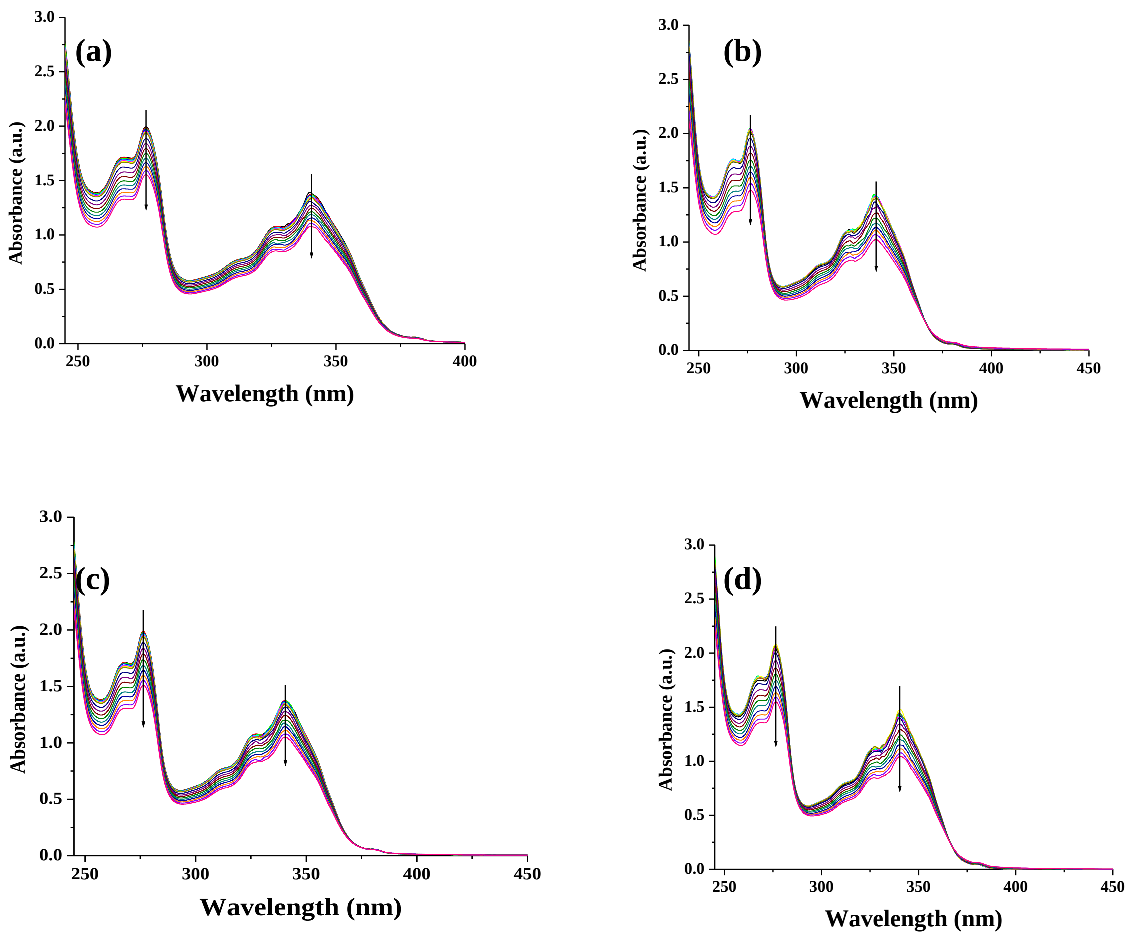


Figure 3S: Fluorescence titration curves of receptor **2** (c = 2.5 x 10^{-5} M) with the tetrabutylammonium (a) Glutarate, (b) Dihydrogenphosphate (c) Pimelate in 4:1 $CH_3CN{:}H_2O$ (v/v) 10 mM TrisHCl buffer pH = 6.3 [Concentration of all guests were 9.6 x 10^{-4} M].

Selected UV-vis titration curves for receptor 2 in $CH_3CN{:}H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer)



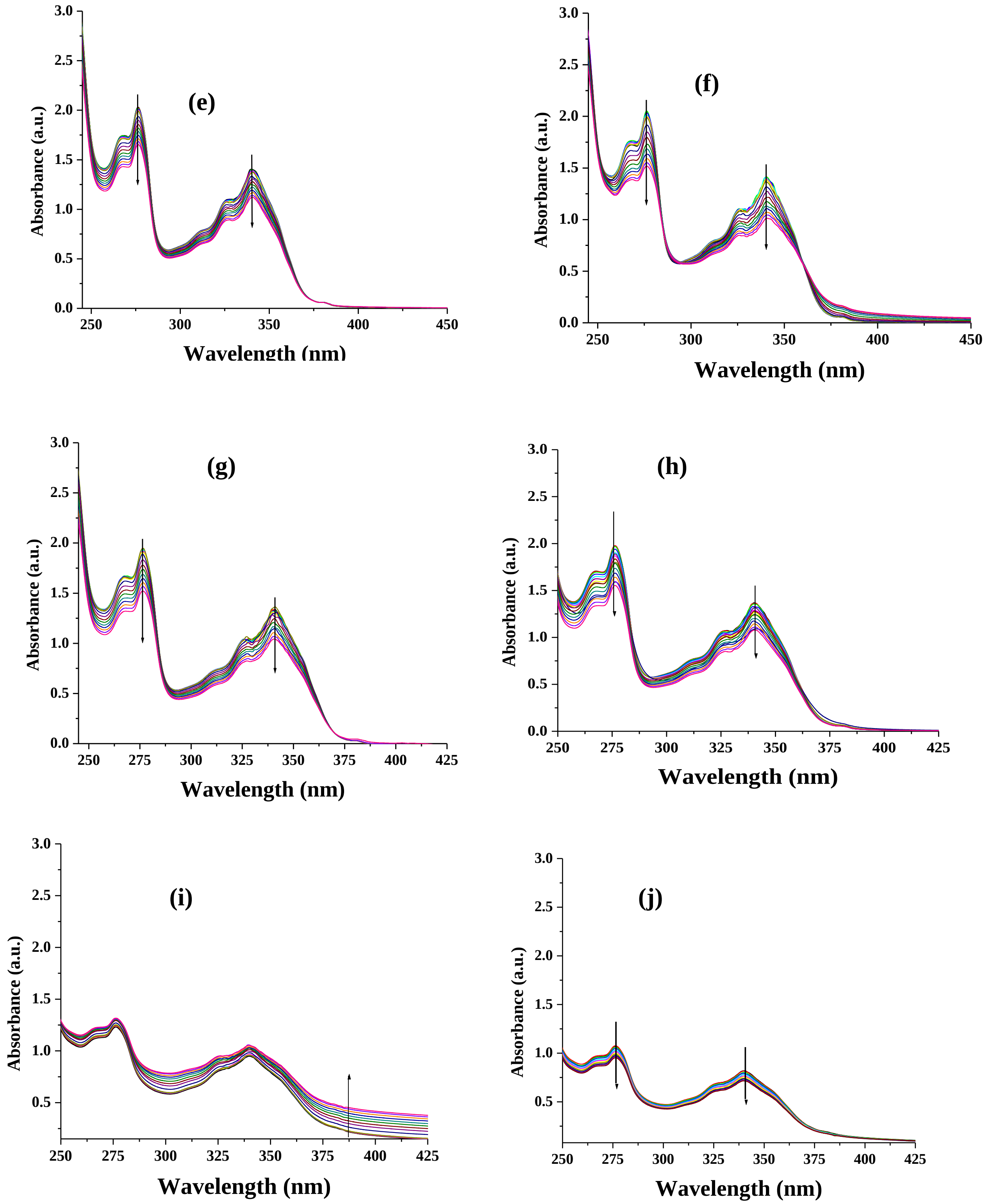


Figure 4S: UV-vis titration curves of receptor **2** (c = 2.5 x 10^{-5} M) with the tetrabutylammonium (a) acetate, (b) adipate, (c) fluoride, (d) glutarate, (e) malonate, (f) N-Ts glutamate, (g) pimelate, (h) dihydrogenphosphate, (i) tartarate, (j) malate in 4:1 CH_3CN:H_2O (v/v) 10 mM Tris/HCl buffer pH = 6.3 [concentration of all guests (c = 9.6 x 10^{-4} M)].

Job plots of 2 with some selected guests from UV-vis and fluorescence.

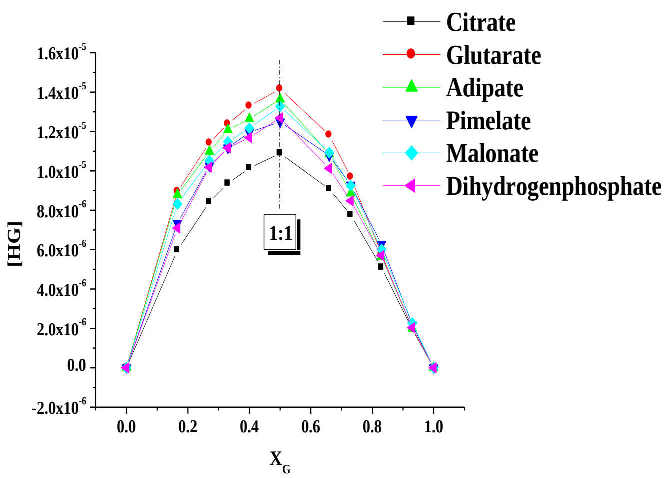


Figure 5S: UV-vis Job plots for **2** with tetrabutylammonium salts of (a) Citrate, (b) Glutarate, (c) Adipate, (d) Pimelate, (e) Malonate and (f) Dihydrogenphosphate at 340 nm in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) where [G] = [H] = 8.5 x 10^{-5} M at 25 ^{0}C.

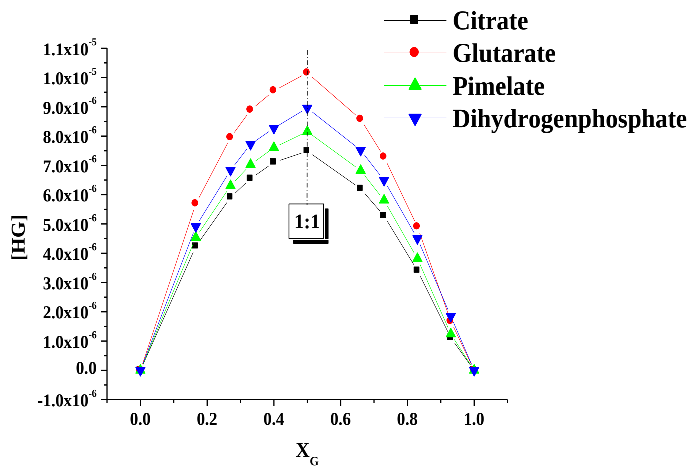


Figure 6S: Fluorescence Job plots of **2** with tetrabutylammonium salts of (a) Citrate, (b) Glutarate, (c) Pimelate and (d) Dihydrogenphosphate at 385 nm in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) where [G] = [H] = 8.5 x 10^{-5} M at 25 ^{0}C.

Binding constant curve for receptor 2 with citrate from fluorescence in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) at 25^{0}C, λ_{max} = 385 nm:

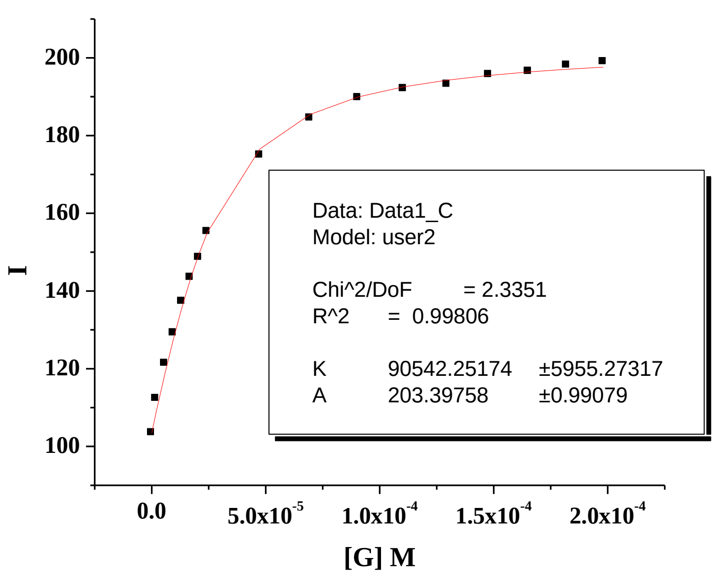


Figure 7S: Binding constant curve of **2** (c = 2.5 x 10^{-5} M) with the tetrabutylammonium citrate (c = 9.6 x 10^{-4} M) from fluorescence titration in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer). Working formula y=I_0+((I-I_0)/(2*x_2))*(x_1+x_2+1/K-((x_1+x_2+1/K)^2-4*x_1*x_2)^.5), x_1= [G], x_2 = [H], y = intensity.

Binding constant curve for receptor 2 with citrate in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) at 25 ^{0}C λ_{max} = 340 nm:

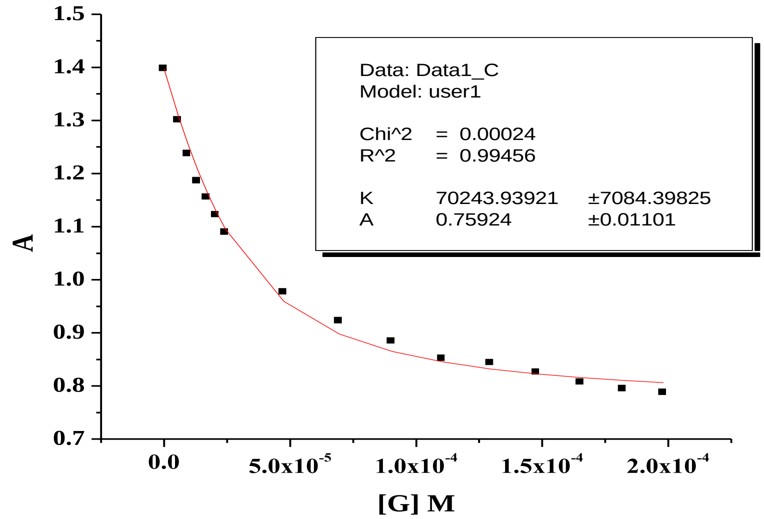


Figure 8S: Binding constant curve for receptor **2** (c = 2.5 x 10^{-5} M) with the tetrabutylammonium citrate (c = 9.6 x 10^{-4} M) from UV-vis titration in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer). Working formula: $y=A_0+((A-A_0)/(2*x\_2))*(x\_1+x\_2+1/K-((x\_1+x\_2+1/K)^2-4*x\_1*x\_2)^{.5})$, x_1= [G], x_2 = [H], y = intensity, Y= absorbance.

Indicator displacement experiments on 1 and 2 with Uranine dye 3:

From UV-vis study

Change in absorption upon gradual addition of 1 and 2 individually to the solution of 3:

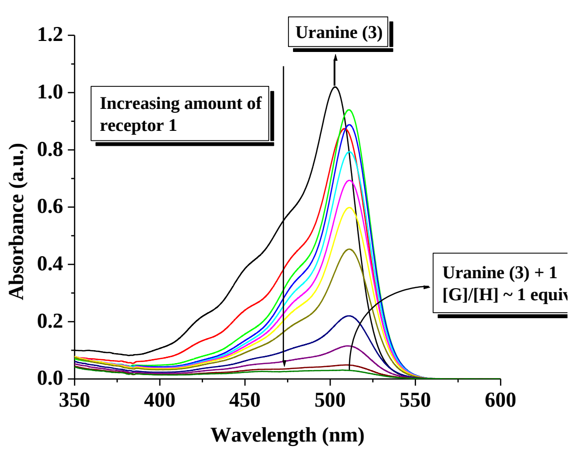


Figure 9S: Addition of **1** (c = 4.2 x 10^{-4} M) into the solution of **3** (c = 8.0 x 10^{-5} M) causes a decrease in the absorption intensity of **3** at 502 nm in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) at 25 ^{0}C.

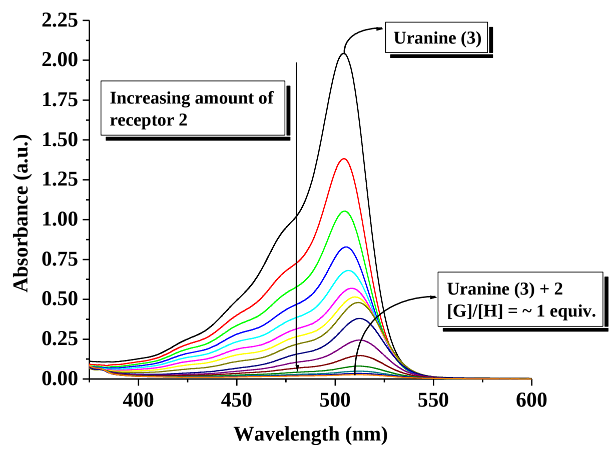


Figure 10S: Addition of **2** (c = 4.2 x 10^{-4} M) into the solution of **3** (c = 8.5 x 10^{-5} M) causes a decrease in the absorption intensity of **3** at 502 nm in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) at 25 ^{0}C.

Binding constant for receptor 1 with Uranine dye 3 in CH_3CN:H_2O (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer) from UV-vis.

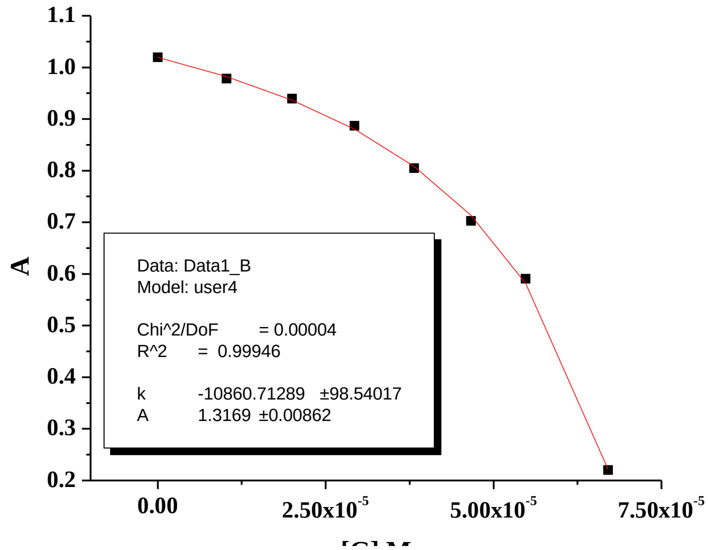


Figure 11S: Binding constant curve for **1** (c = 4.2 x 10^{-4} M) with Uranine dye **3** (c = 8.0 x 10^{-5} M) at λ_{max} = 502 nm. at 25 ^{0}C. [Working formula: y= (A_0+A*K*x)/ (1+K*x). x = [G], y= absorbance].

Binding constant for receptor 2 with Uranine dye 3 in CH_3CN:H_2O (4:1 v/v, pH = 6.3, 10 mM Tris/HCl buffer)

- **From UV-vis:**

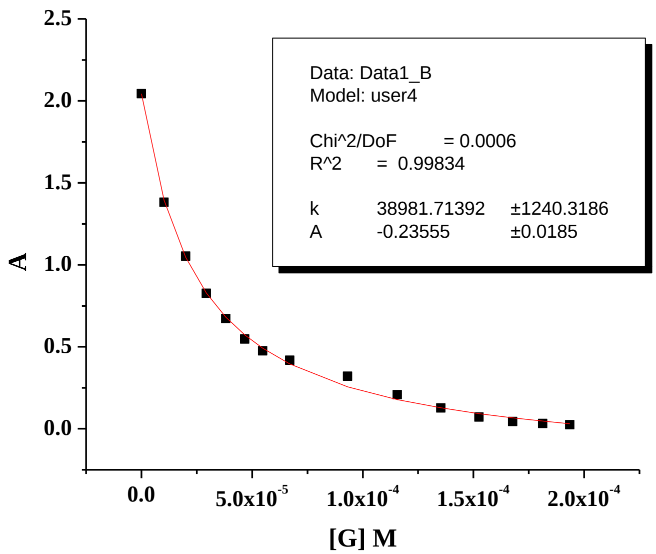


Figure 12S: Binding constant at λ_{max} = 502 nm. of Uranine **3** (c = 8.5 x 10^{-5} M) with **1** (c = 4.2 x 10^{-3} M) at 25 ^{0}C [working formula: y=A_0+((A-A_0)/(2*x_2))*(x_1+x_2+1/K-((x_1+x_2+1/K)^2-4*x_1*x_2)^.5), x_1= [G], x_2 = [H], y = absorbance].

Dye displacement from the ensemble of 1/3 using citrate and the corresponding changes in absorbance

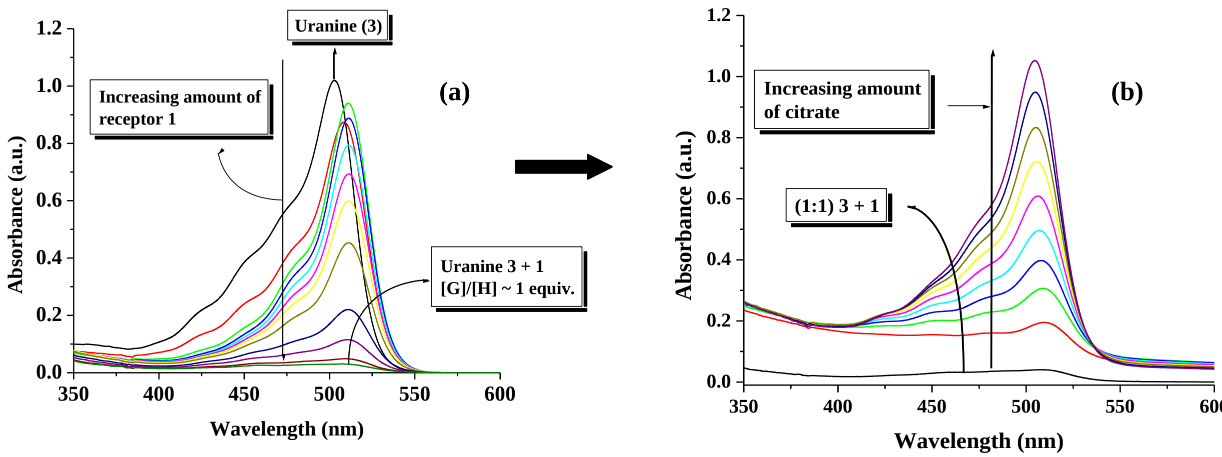


Figure 13S: (a) change in absorbance of dye **3** (c = 8.0 x 10^{-5} M) upon the addition of increasing amount of **1** (c = 4.2 x 10^{-4} M), (b) gradual addition of citrate (c = 4.62 x 10^{-3} M) to the ensemble of dye **3**/**1** (1:1). All titration are performed at 25 ^{0}C in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM TrisHCl buffer).

Dye displacement from the ensemble of 2/3 using citrate and the corresponding changes in absorbance

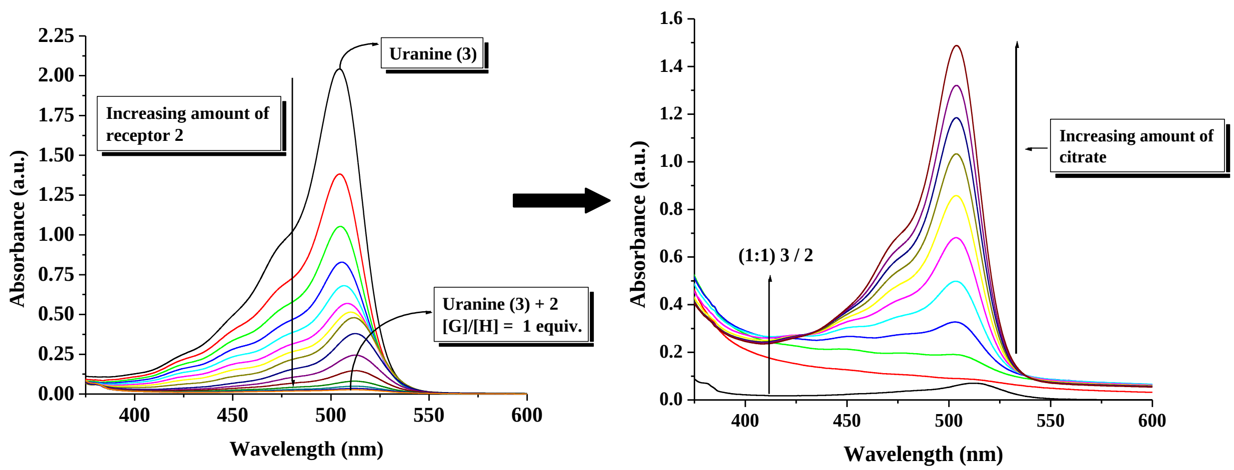


Figure 14S: (a) change in absorbance of dye **3** (c = 8.5 x 10^{-5} M) upon the addition of increasing amount of **2** (c = 4.2 x 10^{-4} M), (b) gradual addition of citrate (c = 4.62 x 10^{-3} M) to the ensemble of dye **3**/**2** (1:1). All titration are performed at 25 ^{0}C in $CH_3CN:H_2O$ (4:1 v/v, pH = 6.3, 10 mM TrisHCl buffer).

Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Dye displacement from the ensemble of 1/3 using of tetrabutylammonium salt of various anions and the corresponding changes in absorbance

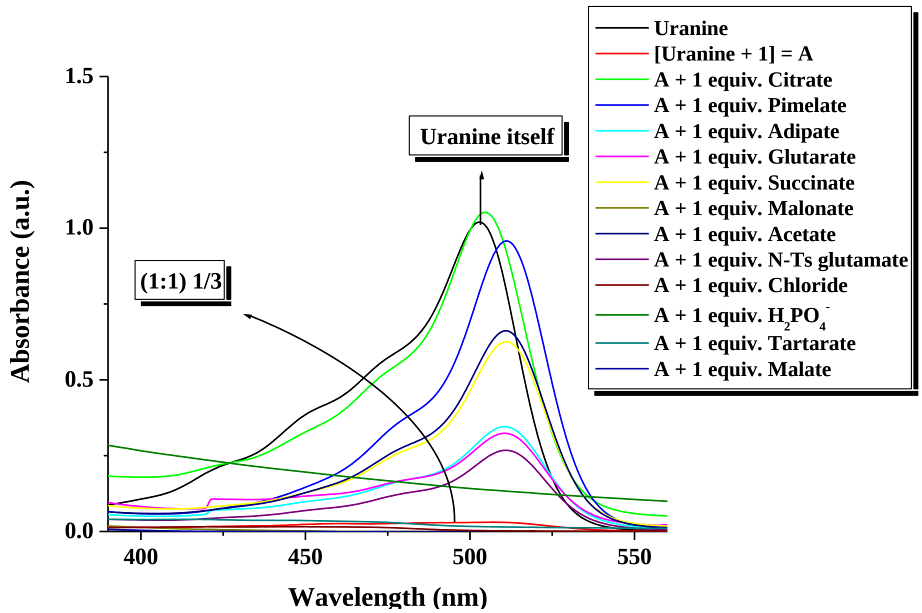


Figure 15S: Change in absorption after addition of 1 equiv. amount of different tetrabutylammonium salts (G) to the ensemble of **1**/**3** (1:1) ([G] = 4.62 x 10^{-3} M, [**3**] = 8.0 x 10^{-5} M). All titration are performed at 25 ^{0}C in CH_3CN:H_2O (4:1 v/v, pH = 6.3, 10 mM TrisHCl buffer).

Dye displacement from the ensemble of 2/3 using of tetrabutylammonium salt of various anions and the corresponding changes in absorbance

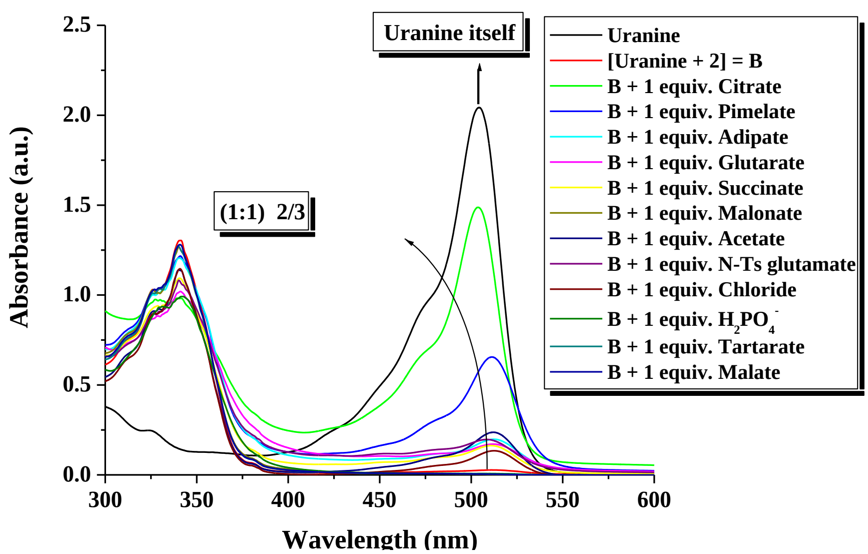


Figure 16S: Change in absorption after addition of 1 equiv. amount of different tetrabutylammonium salts (G) to the ensemble of **2**/**3** (1:1) ([G] = 4.62 x 10^{-3} M, [**3**] = 8.0 x 10^{-5} M). All titration are performed at 25 ^{0}C in CH_3CN:H_2O (4:1 v/v, pH = 6.3, 10 mM TrisHCl buffer).

Dye displacement from the ensemble of 2/3 using citrate and the corresponding changes in fluorescence intensity.

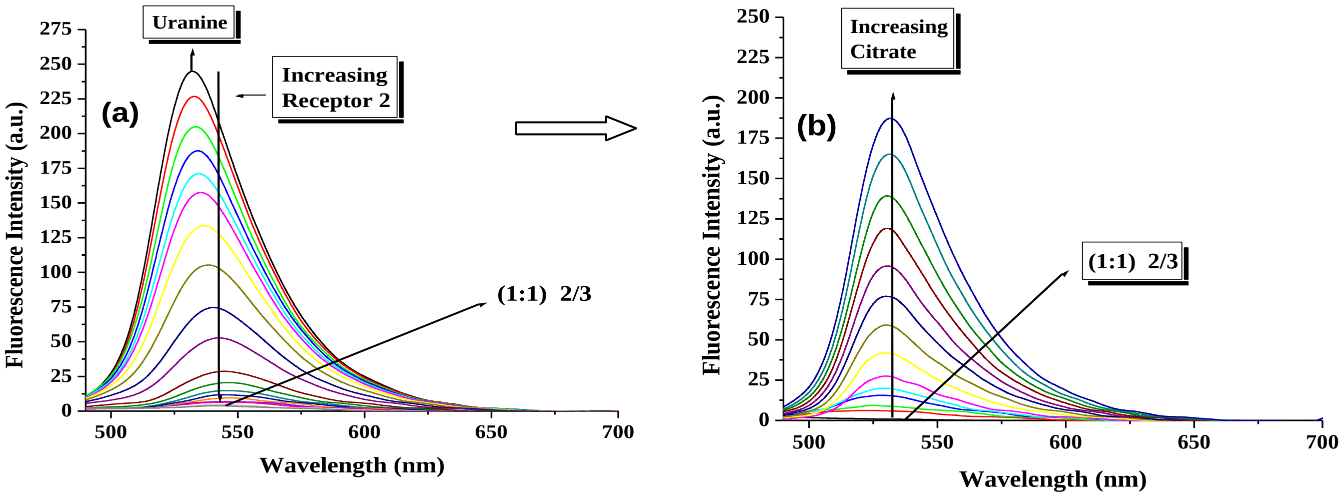


Figure 17S. (a) Change in emission of dye **3** (c = 8.0 x 10^{-5} M) upon increasing addition of **2** (c = 4.2 x 10^{-4} M) and (b) retrieval of emission upon increasing addition of citrate (c = 4.62 x 10^{-3} M) to the ensemble **2**/**3** in CH_3CN:H_2O (4:1, v/v, pH 6.3, 10 mM Tris/HCl buffer).

Dye displacement from the ensemble of 1/3 using various tetrabutylammonium salts and the corresponding changes in fluorescence intensity.

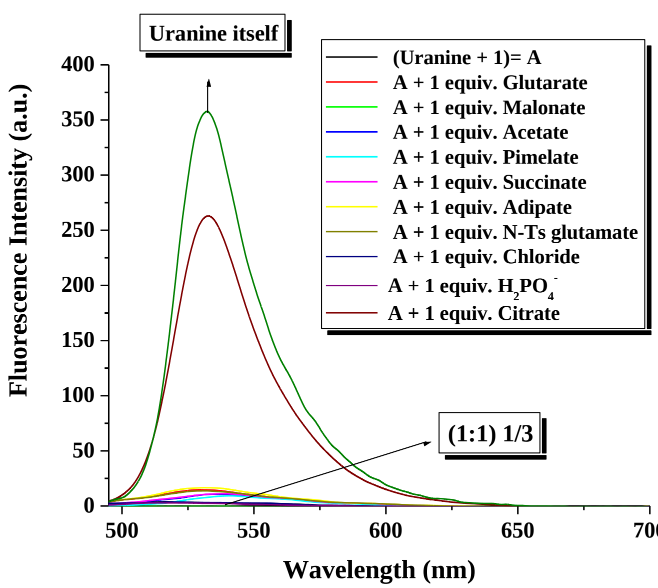


Figure 18S: Change in emission after addition of 1 equiv. amount of different tetrabutylammonium salts (G) to the ensemble of **1**/**3** (1:1) ([G] = 4.62 x 10^{-3} M, [**3**] = 8.0 x 10^{-5} M). All titration are performed at 25 ^{0}C in CH_3CN:H_2O (4:1 v/v, pH = 6.3, 10 mM TrisHCl buffer).

Dye displacement from the ensemble of 2/3 using different tetrabutylammonium salts the corresponding changes in fluorescence intensity

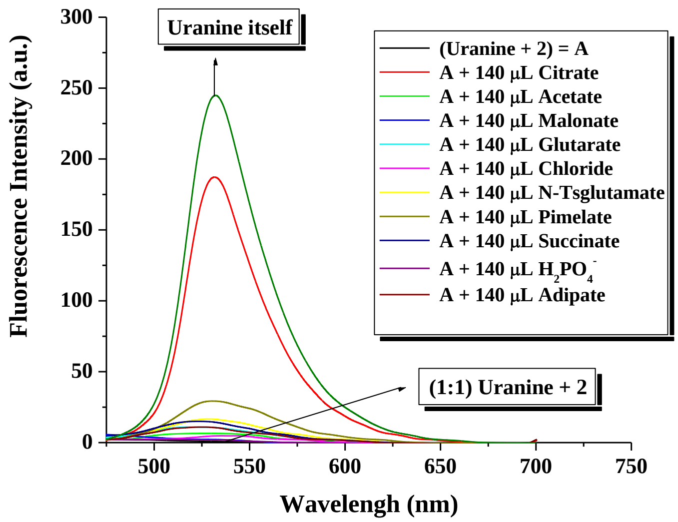


Figure 19S: Change in emission after addition of 1 equiv. amount of different tetrabutylammonium salts (G) to the ensemble of **2**/**3** (1:1) ([G] = 4.62 x 10^{-3} M, [**3**] = 8.0 x 10^{-5} M). All titration are performed at 25 ^{0}C in CH_3CN:H_2O (4:1 v/v, pH = 6.3, 10 mM TrisHCl buffer).

- **Binding constant curve for 3 with 2 from Fluorescence titration:**

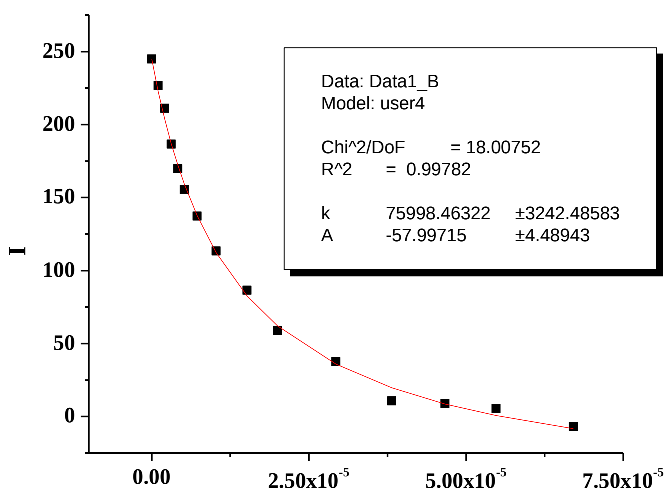


Figure 20S: Binding constant at λ = 532 nm for dye **3** (c = 8.5 x 10^{-5} M) with receptor **1** (c = 4.2 x 10^{-3} M) from fluorescence titration in CH_3CN:H_2O (4:1 v/v, pH = 6.3, 10 mM TrisHCl buffer). Working formula: y= I_0 + ((I-I_0)/(2*x_2))*(x_1+x_2+1/K-((x_1+x_2+1/K)^2-4*x_1*x_2)^.5), x_1= [G], x_2 = [H], y = intensity.

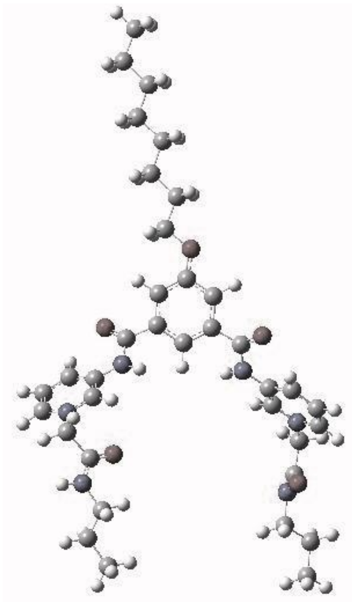


Figure 21S: DFT optimized geometry of **1** (E = -2106.1779 a.u.). Gaussian 03[3] was used for DFT calculation using 6-31G* basis set and the popular b3LYP functional on the structure **1**.

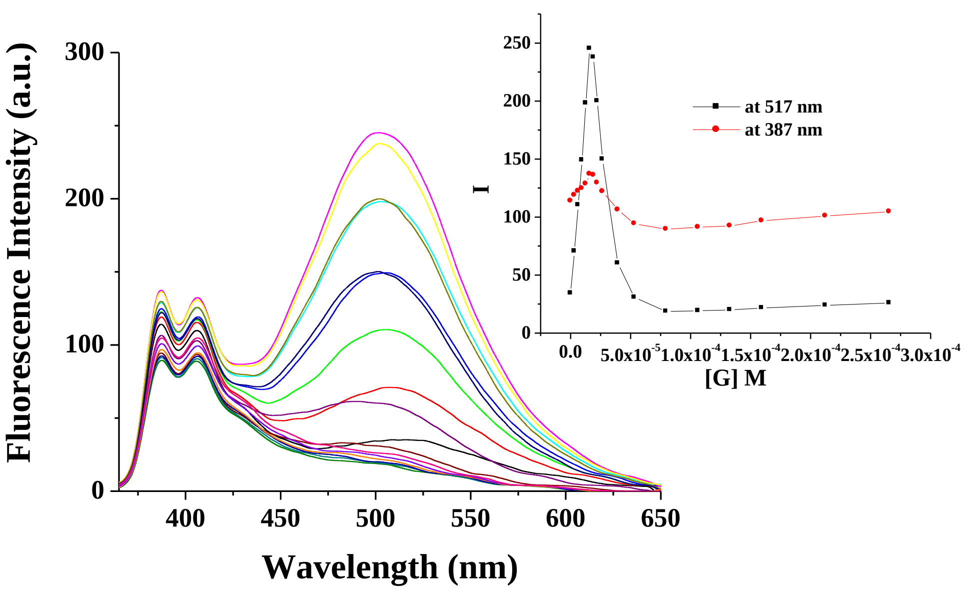


Figure 22S: Fluorescence titration spectra of **2** (*c* = 2.5 x 10^{-5} M) in 5% CH_3CN in $CHCl_3$ with the addition of citrate; Inset: change in emission intensity of **2** (*c* = 2.5 x 10^{-5} M) at 387 and 517 nm in 5% CH_3CN in $CHCl_3$ with the addition of citrate.

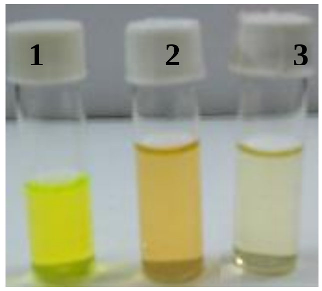


Figure23S: (1) dye **3**, (2) receptor **1** + dye **3** (1:1) = **A**, (3) **A** with 1 equiv. amount of citrate, [**3**] = 8.0 x 10^{-5} M, [**1**] = 4.2 x 10^{-4}, [G] = 4.62 x 10^{-3} M. In CH_3CN:H_2O (4:1 v/v , 10 mM Tris HCl buffer at pH = 7.3).

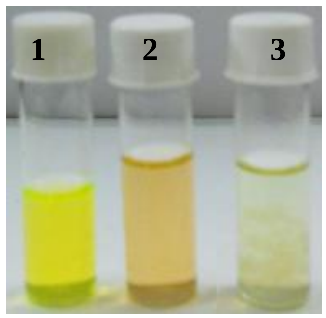


Figure24S: (1) dye **3**, (2) receptor **2** + dye **3** (1:1) = **B**, (3) **B** with 1 equiv. amount of citrate, [**3**] = 8.5 x 10^{-5} M, [**2**] = 4.2 x 10^{-4}, [G] = 2.0 x 10^{-3} M. In CH_3CN:H_2O (4:1 v/v, 10 mM Tris HCl buffer at pH = 7.3).

References

1. P. Job, *Ann. Chim*. 1928, **9**, 113.
2. B. Valeur, J. Pouget, J. Bourson, M. Kaschke, N. P. Eensting, *J. Phys. Chem.* 1992, **96**, 6545.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S.Iyengar, J. Tomasi,V. Barone, B. Mennucci, M. Cossi, G.Scalmani, N. Rega, G. A.Petersson, H. Nakatsuji, M. Hada, M.Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E.Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K.Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe,; P.M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision C.01; Gaussian, Inc.Wallingford, CT, 2004.