Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Anthracene-based open and macrocyclic receptors in flurometric detection of urea

Kumaresh Ghosh*, Goutam Masanta

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Absorption study of 1 -2 in $CHCl_3$

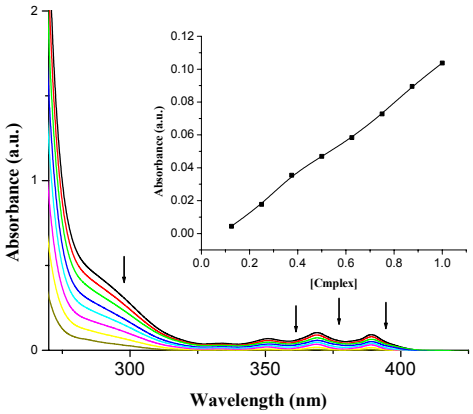


Fig. S1 UV spectra of the complex **1.thiourea** (c = 1 x 10^{-5} M) and its change of absorbance on dilution; (inset) plot of absorbance *vs*. concentration of the 1:1 complex of thiourea with **1**.

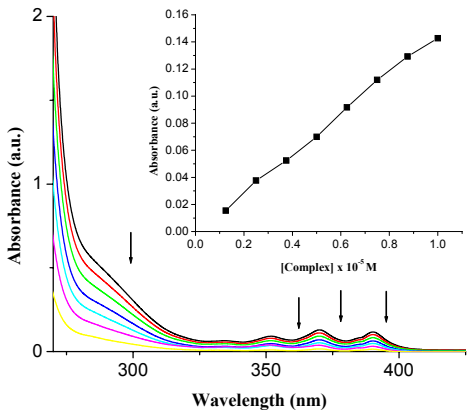


Fig. S2 UV spectra of the complex **2.thiourea** (c = 1 x 10^{-5} M) and its change of absorbance on dilution; (inset) plot of absorbance *vs*. concentration of the 1:1 complex of thiourea with **2**.

Absorption study of 1 -2 in CH_3CN

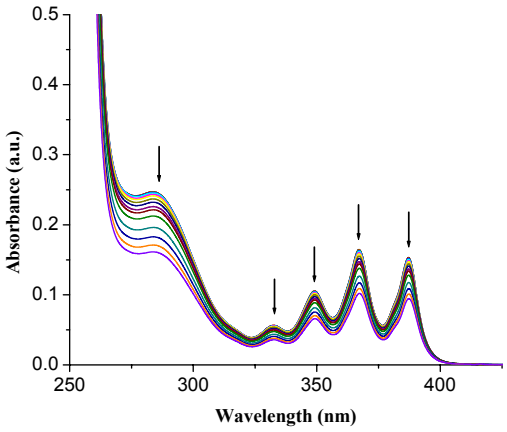


Fig. S3 Change in absorption of receptor **2** (c = 1 x 10^{-5} M) in CH_3CN in presence of urea.

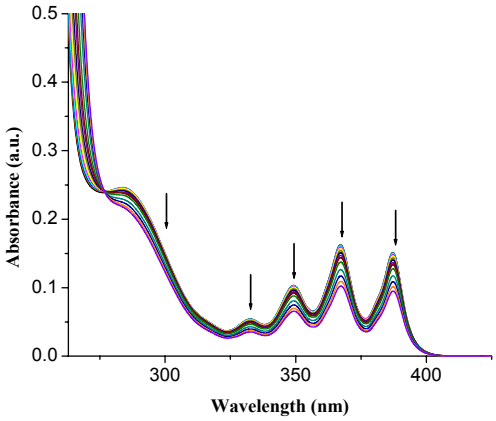


Fig. S4 Change in absorption of receptor **2** (c = 1 x 10^{-5} M) in CH_3CN in presence of thiourea.

Flourescence study of 1 -2 in $CHCl_3$

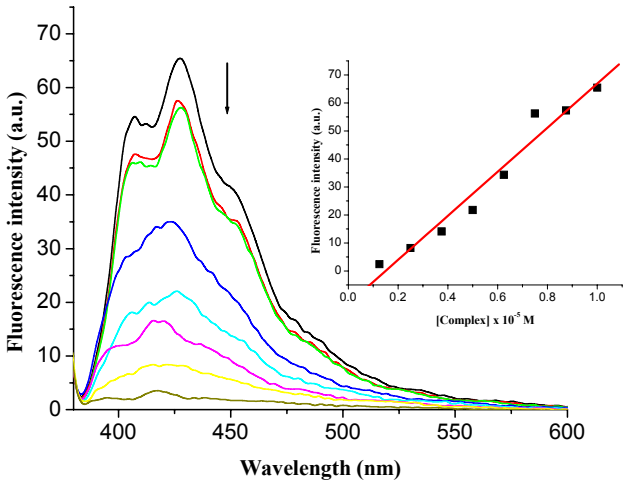


Fig. S5 Change in emission of **1** (c = 1 x 10^{-5} M) in $CHCl_3$ in presence of stoichiometric amounts of thiourea and the dilution spectra of the 1:1 complex (λ_{ex} = 368 nm). (inset) plot of fluorescence intensity *vs*. concentration of the 1:1 complex of thiourea with **1**

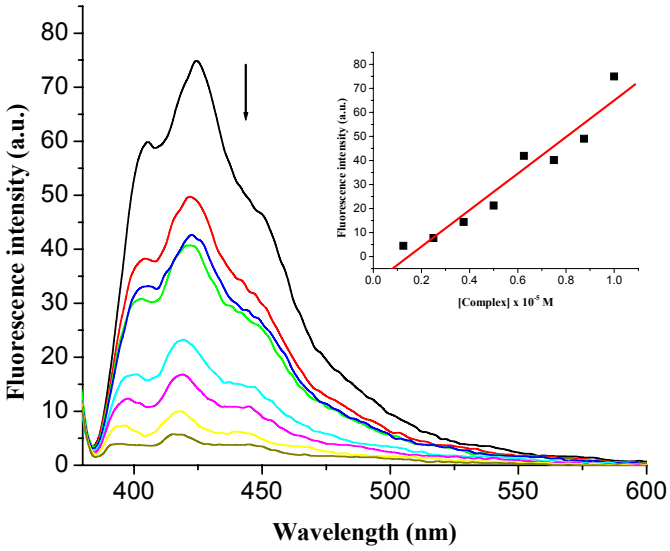


Fig. S6 Change in emission of **2** (c = 1 x 10^{-5} M) in $CHCl_3$ in presence of stoichiometric amounts of thiourea and the dilution spectra of the 1:1 complex (λ_{ex} = 368 nm). (inset) plot of fluorescence intensity *vs*. concentration of the 1:1 complex of thiourea with **2**

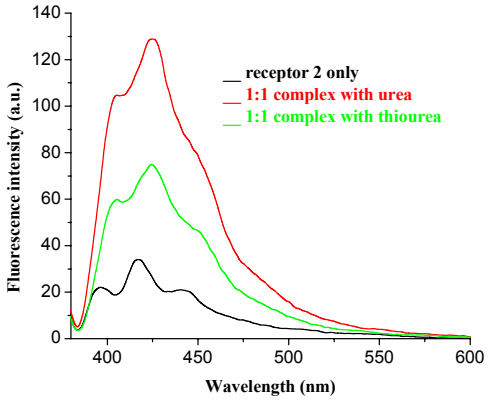


Fig. S7 Change in emission of receptor **2** (c = 1 x 10^{-5} M) and its 1:1 complexes with urea and thiourea in $CHCl_3$.

UV Job's Plot [1]

The stoichiometry was determined by the continuous variation method (Job Plot). In this method, solutions of host and guests of equal concentrations were prepared in dry CH_3CN. Then host and guest solutions were mixed in different proportions maintaining a total volume of 3 mL of the mixture. The related compositions for host:guest (*v/v*) were 3:0, 2.5:0.5, 2.2:0.8, 2:1, 1.8:1.2, 1.5:1.5, 1:2, 0.8:2.2, 0.5:2.5, 0.2:2.8. All the prepared solutions were kept for 1 h with occasional stirring at room temperature. Then absorption of the solutions of different compositions was recorded. The concentration of the complex i.e., [HG] was calculated by the equation [HG] = $\Delta A/A_0$ x [H] where $\Delta A/A_0$ indicates the relative absorbance and [H] corresponds the concentration of pure host. Mole fraction of the guest (X_G) was plotted against concentration of the complex [HG]. In the plot, the mole fraction of the guest at which the concentration of the host-guest complex concentration [HG] is maximum, gives the stoichiometry of the complex.

Determination of binding constants

Calculation for approximate binding constant (K_a) determination from dilution method for the urea complex of 1 in $CHCl_3$ by fluorescence method[2]

Working formula[3]: $d/A_c = (1/K_c\varepsilon_c l)^{1/2} \cdot 1/(A_c)^{1/2} + 1/\varepsilon_c l$……(1)

Here K_a calculation is based on the assumptions:

1:1 complex formation between urea and receptor **1**.

Complex with other stoichiometries are absent.

Here the concentration term (d) and the absorbance term (A_c) are considered only for the urea-complex (assuming complete complexation with the help of excess urea which does not effect concerned spectra)

But here the absorbance term (A_c) is replaced by using the equation[4]

$F = 2.3I_0\Phi\varepsilon bc$……(2)

Where F = Fluorescence intensity, I_0 = Intensity of the excitation source

ε = molar absorptivity at the excitation wavelength

b = path length

Φ = Fluorescence quantum yield

Evidently $\varepsilon bc = A_c$ (absorbance or optical density)

Now from (2), $F = 2.3I_0\,\Phi\varepsilon bc = 2.3I_0\,\Phi A_c$

$A_c = (F/2.3I_0\,\Phi)$…….(3)

From (1), $d/(F/2.3I_0\,\Phi) = (1/K_a\,\varepsilon_c l)^{1/2} \cdot 1/(F/2.3I_0\,\Phi)^{1/2} + 1/\varepsilon_c l$

or, $d \times 2.3I_0/(F/\Phi) = (1/K_a\,\varepsilon_c l)^{1/2} \cdot (2.3I_0)^{1/2}/(F/\Phi)^{1/2} + 1/\varepsilon_c l$

$(d/Z) = [(1/K_a\,\varepsilon_c l)^{1/2}]\,[(2.3I_0)^{1/2}/Z^{1/2}]\,[1/2.3I_0] + 1/[2.3I_0\,\varepsilon_c l]$

$= (1/2.3I_0\,K_a\,\varepsilon_c l)^{1/2}\,(1/Z^{1/2}) + 1/(2.3I_0\,\varepsilon_c l)$ [where, $Z = F/\Phi$]

From a linear plot of (d/Z) *vs* $1/Z^{1/2}$, we get an equation of the type $Y = BX + A$

Where, $Y = (d/Z)$, $B = (1/2.\,3I_0\,K_a\,\varepsilon_c l)^{1/2}$, $X = 1/Z^{1/2}$, $A = 1/2.3I_0\,\varepsilon_c l$

From this $A/B^2 = (1/2.\,3I_0\,K_a\,\varepsilon_c l)/[(\,1/2.\,3I_0\,K_a\,\varepsilon_c l)^{1/2}]^2 = K_a$ (binding constant)

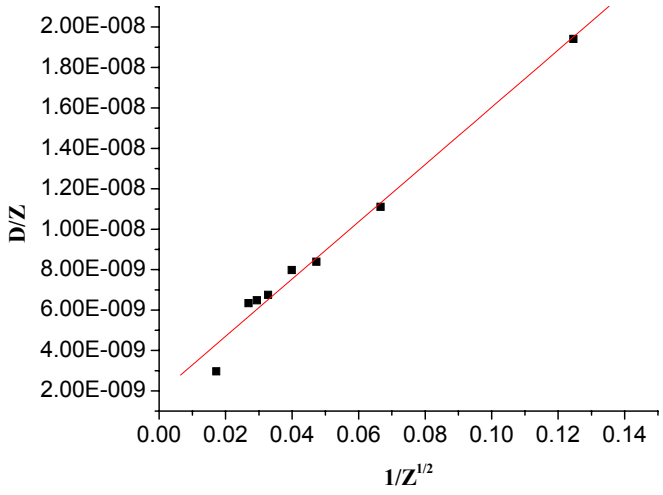
Here, in the calculation of quantum yield Φ is measured by busing the equation[5],

$$\Phi_u = \Phi_s (F_u/F_s) (A_s/A_u) (\lambda_{exc(s)}/ \lambda_{exc(u)}) (\eta_u/\eta_s)$$

Where, u and s indicate the unknown and standard solution, respectively. Φ = quantum yield, F = area under the emission curve, A = absorbance at excitation wavelength, λ = excitation wavelength, η = refractive index of the solvent.

Here Φ measurements were performed using anthracene in ethanol as standard [Φ = 0.27][6].

System	Concentration (d) M	Fluorescence Intensity (F) At 426 nm	Ouantum Yield (Φ)	F/ Φ = Z	(d/Z) = Y	$1/Z^{1/2}$ = X
Urea complex of receptor **1** (UCR **1**)	1×10^{-5}	85.42	0.0551	3365.15	2.97×10^{-9}	0.0172
UCR **1** : $CHCl_3$ (3.5:0.5) by vol.	0.875×10^{-5}	58.89	0.0427	1379.15	6.34×10^{-9}	0.0269
UCR **1** : $CHCl_3$ (3:1) by vol.	0.75×10^{-5}	51.41	0.0444	1157.88	6.48×10^{-9}	0.0294
UCR **1** : $CHCl_3$ (2.5:1.5) by vol.	0.625×10^{-5}	34.36	0.0371	926.14	6.75×10^{-9}	0.0328
UCR **1** : $CHCl_3$ (2:2) by vol.	0.50×10^{-5}	13.53	0.0216	626.39	7.98×10^{-9}	0.0399
UCR **1** : $CHCl_3$ (1.5:2.5) by vol.	0.375×10^{-5}	14.08	0.0315	446.98	8.39×10^{-9}	0.0473
UCR **1** : $CHCl_3$ (1:3) by vol.	0.25×10^{-5}	6.10	0.0271	225.09	11.107×10^{-9}	0.0666
UCR **1** : $CHCl_3$ (0.5:3.5) by vol.	0.125×10^{-5}	3.60	0.0559	64.4	19.41×10^{-9}	0.1246



Y = A + B * X

Parameter	Value	Error
A	1.86817E-9	4.32334E-10
B	1.41621E-7	7.47662E-9

R	SD	N	P
0.99174	6.79115E-10	8	<0.0001

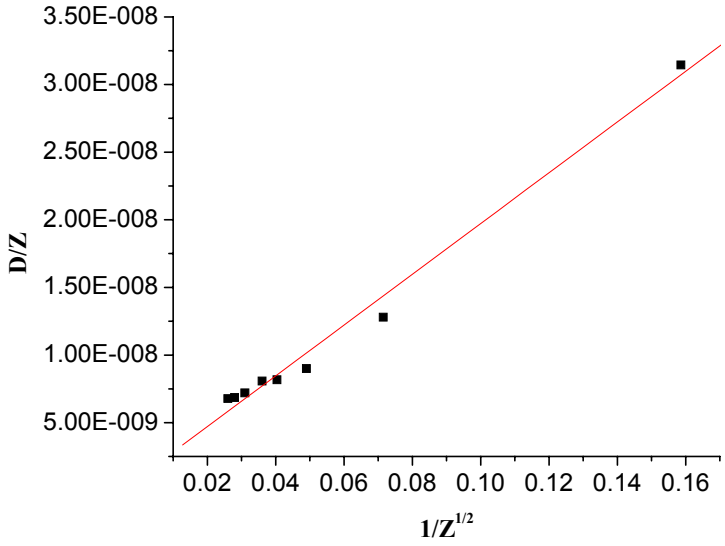
From the equation, $K_a = A/B^2$ i.e. K_a = (intercept)/(slope)^2 = 1.14 x 10^5 M^{-1}

Quantum yield (Φ) of receptor **1** = 0.0058

Calculation for approximate binding constant (K_a) determination from dilution method for the thiourea complex of 1 in $CHCl_3$ by fluorescence method

In a similar way as described above, K_a for **1**-thiourea complex can be determined by following way,

System	Concentration (d) M	Fluorescence Intensity (F) At 426 nm	Ouantum Yield (Φ)	F/ Φ = Z	(d/Z) = Y	$1/Z^{1/2}$ = X
Thiourea complex of receptor **1** (TUCR **1**)	1×10^{-5}	65.45	0.0444	1474.1	6.78×10^{-9}	0.026
TUCR **1** : $CHCl_3$ (3.5:0.5) by vol.	0.875×10^{-5}	57.30	0.0449	1276.17	6.85×10^{-9}	0.028
TUCR **1** : $CHCl_3$ (3:1) by vol.	0.75×10^{-5}	56.24	0.054	1041.48	7.2×10^{-9}	0.031
TUCR **1** : $CHCl_3$ (2.5:1.5) by vol.	0.625×10^{-5}	34.36	0.0444	773.87	8.07×10^{-9}	0.036
TUCR **1** : $CHCl_3$ (2:2) by vol.	0.50×10^{-5}	21.78	0.0356	611.79	8.17×10^{-9}	0.0404
TUCR **1** : $CHCl_3$ (1.5:2.5) by vol.	0.375×10^{-5}	14.08	0.0338	416.57	9×10^{-9}	0.049
TUCR **1** : $CHCl_3$ (1:3) by vol.	0.25×10^{-5}	8.20	0.042	195.24	12.8×10^{-9}	0.0715
TUCR **1** : $CHCl_3$ (0.5:3.5) by vol.	0.125×10^{-5}	2.44	0.0614	39.74	31.45×10^{-9}	0.1586



Y = A + B * X

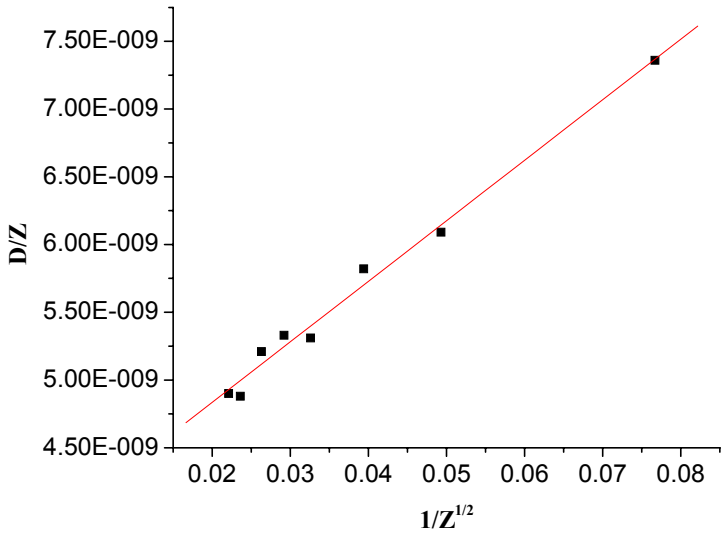
Parameter	Value	Error
A	9.5561E-10	5.91719E-10
B	1.87685E-7	8.58371E-9

R	SD	N	P
0.99378	1.00694E-9	8	<0.0001

K_a for **1**-thiourea complex = 2.71 x 10^4 M^{-1}

Calculation for approximate binding constant (K_a) determination from dilution method for the urea complex of 2 in $CHCl_3$ by fluorescence method

System	Concentration (d) M	Fluorescence Intensity (F) At 425 nm	Ouantum Yield (Φ)	F/ Φ = Z	(d/Z) = Y	$1/Z^{1/2}$ = X
Urea complex of receptor **2** (UCR **2**)	1×10^{-5}	128.85	0.0632	2038.76	4.90×10^{-9}	0.0221
UCR **2** : $CHCl_3$ (3.5:0.5) by vol.	0.875×10^{-5}	91.51	0.0511	1790.80	4.88×10^{-9}	0.0236
UCR **2** : $CHCl_3$ (3:1) by vol.	0.75×10^{-5}	65.06	0.0452	1439.38	5.21×10^{-9}	0.0263
UCR **2** : $CHCl_3$ (2.5:1.5) by vol.	0.625×10^{-5}	54.24	0.0463	1171.49	5.33×10^{-9}	0.0292
UCR **2** : $CHCl_3$ (2:2) by vol.	0.50×10^{-5}	48.07	0.0511	940.70	5.31×10^{-9}	0.0326
UCR **2** : $CHCl_3$ (1.5:2.5) by vol.	0.375×10^{-5}	23.47	0.0364	644.78	5.82×10^{-9}	0.0394
UCR **2**: $CHCl_3$ (1:3) by vol.	0.25×10^{-5}	15.31	0.0373	410.45	6.09×10^{-9}	0.0493
UCR **2** : $CHCl_3$ (0.5:3.5) by vol.	0.125×10^{-5}	8.86	0.0522	169.73	7.36×10^{-9}	0.0767



Y = A + B * X

Parameter	Value	Error
A	3.94147E-9	8.13852E-11
B	4.46798E-8	1.97984E-9

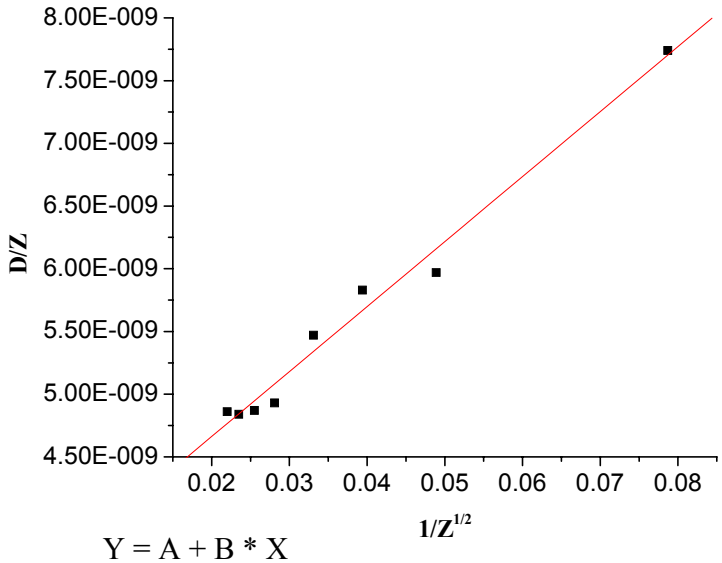
R	SD	N	P
0.99416	9.55287E-11	8	<0.0001

K_a for **2**-urea complex = 1.97 x 10^6 M^{-1}

Quantum yield (Φ) of receptor **2** = 0.0147

Calculation for approximate binding constant (K_a) determination from dilution method for the thiourea complex of 2 in $CHCl_3$ by fluorescence method

System	Concentration (d) M	Fluorescence Intensity (F) At 425 nm	Ouantum Yield (Φ)	F/ Φ = Z	(d/Z) = Y	$1/Z^{1/2}$ = X
Thiourea complex of receptor **2** (TUCR **2**	1×10^{-5}	74.94	0.0364	2058.79	4.86×10^{-9}	0.022
TUCR **2**: $CHCl_3$ (3.5:0.5) by vol.	0.875×10^{-5}	49.02	0.0271	1808.85	4.84×10^{-9}	0.0235
TUCR **2**: $CHCl_3$ (3:1) by vol.	0.75×10^{-5}	40.16	0.0261	1538.7	4.87×10^{-9}	0.0255
TUCR **2**: $CHCl_3$ (2.5:1.5) by vol.	0.625×10^{-5}	41.94	0.0331	1267.07	4.93×10^{-9}	0.0281
TUCR **2**: $CHCl_3$ (2:2) by vol.	0.50×10^{-5}	21.22	0.0232	914.65	5.47×10^{-9}	0.0331
TUCR **2**: $CHCl_3$ (1.5:2.5) by vol.	0.375×10^{-5}	14.42	0.0224	643.75	5.83×10^{-9}	0.0394
TUCR **2**: $CHCl_3$ (1:3) by vol.	0.25×10^{-5}	7.70	0.0184	418.78	5.97×10^{-9}	0.0489
TUCR **2**: $CHCl_3$ (0.5:3.5) by vol.	0.125×10^{-5}	4.48	0.0278	161.51	7.74×10^{-9}	0.0787



Y = A + B * X

Parameter	Value	Error
A	3.62561E-9	1.15805E-10
B	5.18218E-8	2.79749E-9

R	SD	N	P
0.99137	1.40402E-10	8	<0.0001

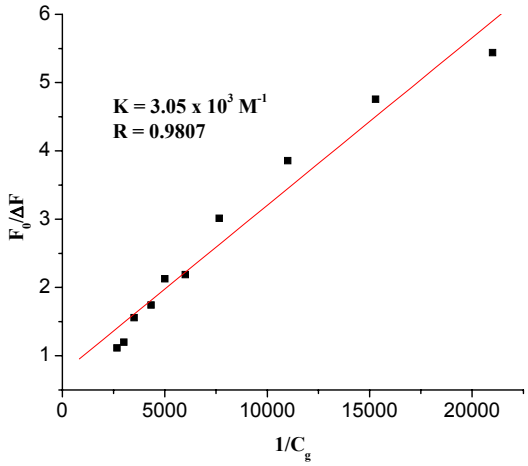
K_a for **2**-thiourea complex = 1.35 x 10^6 M^{-1}

Calculation for binding constant (K_a) determination from direct titration method in CH_3CN by fluorescence method

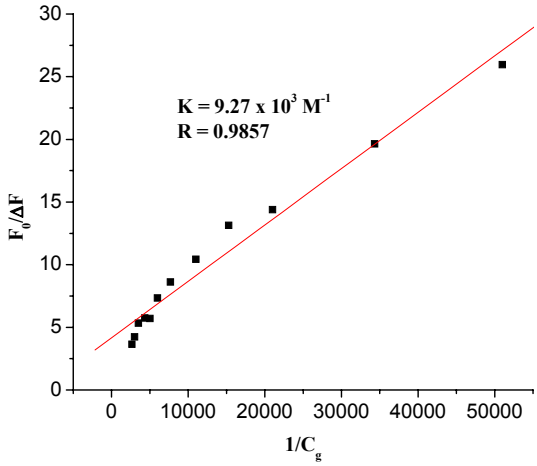
Working formula[7]: $F_0/(F-F_0) = [\Phi_M \epsilon_M/(\Phi_p \epsilon_p - \Phi_M \epsilon_M)][(1/K_a C_g) + 1]$

Where F_0 and F denote the measured fluorescence intensity prior and after adding guest. Here, Φ_M and Φ_p are fluorescence quantum yields of the monomer and complex, respectively. The measured relative fluorescence intensities $[F_0/(F-F_0)]$ as a function of the inverse of guest concentrations (C_g) were plotted to ascertain the binding constant values. The ratio of the intercept to the slope gave the binding constant (K_a).

Receptor 1 with urea:



Receptor 2 with urea:

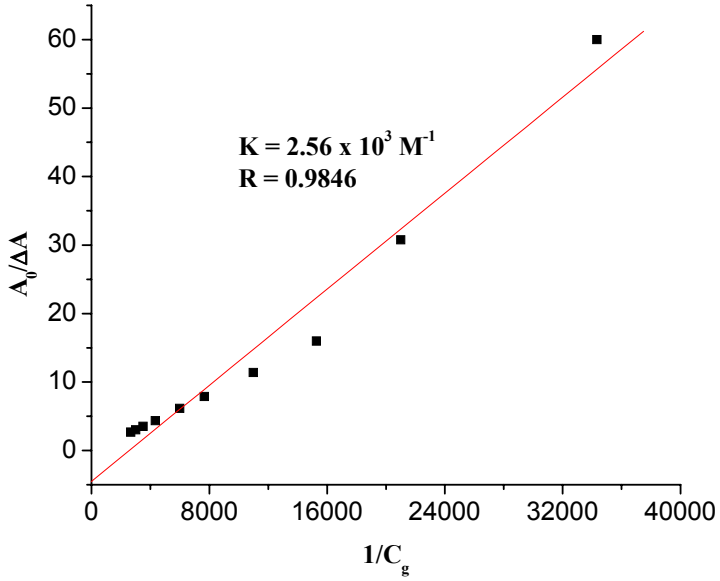


Calculation for binding constant (K_a) determination from direct titration method in CH_3CN by UV-vis method

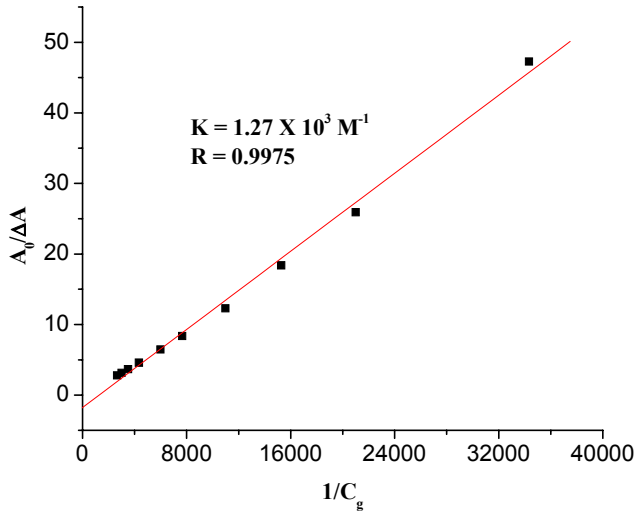
Working formula[7]: $A_0/(A-A_0) = [\epsilon_M/(\epsilon_C - \epsilon_M)][(1/K_aC_g) + 1]$

Where A_0 and A denote the measured absorbance prior and after adding guest. Here, ϵ_M and are molar extinction coefficients of monomer and hydrogen-bonded complex. The measured relative absorbance $[A_0/(A-A_0)]$ as a function of the inverse of guest concentrations (C_g) were plotted to ascertain the binding constant values. The ratio of the intercept to the slope gave the binding constant (K_a).

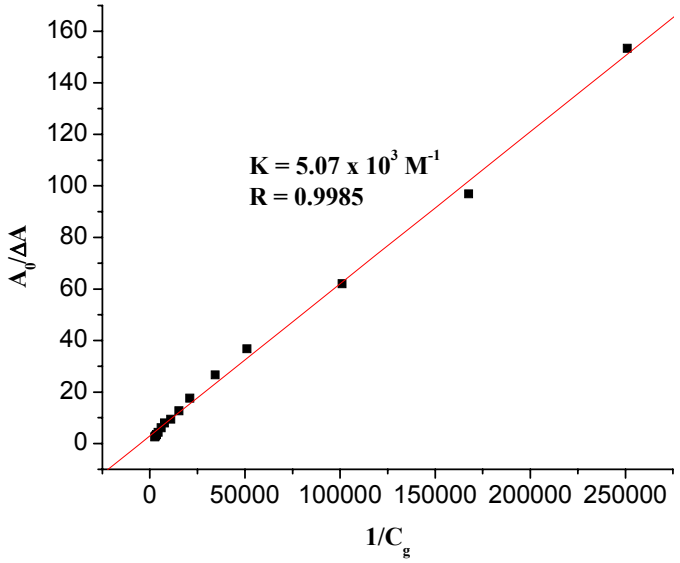
Receptor 1 with urea



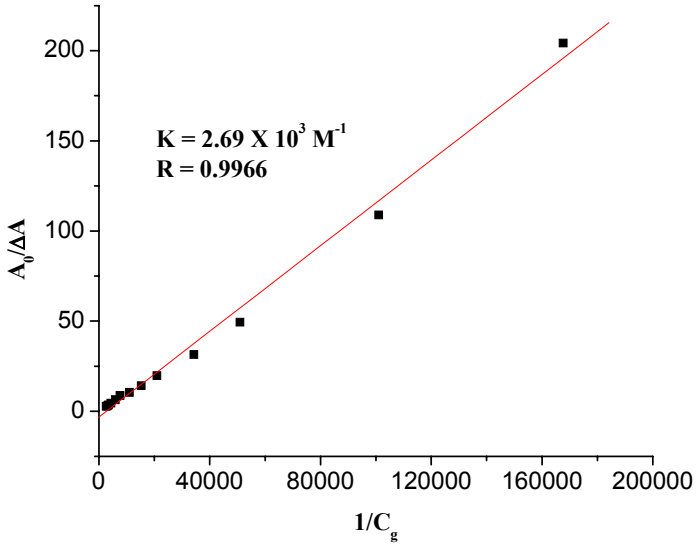
Receptor 1 with thiourea



Receptor 2 with urea



Receptor 2 with thiourea



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