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Electronic Supporting information

Highly selective iodide sensing ability of an anthraquinone derived Schiff base in semi-aqueous medium and its performance as antioxidant, anti-inflammatory and HRBC membrane protection

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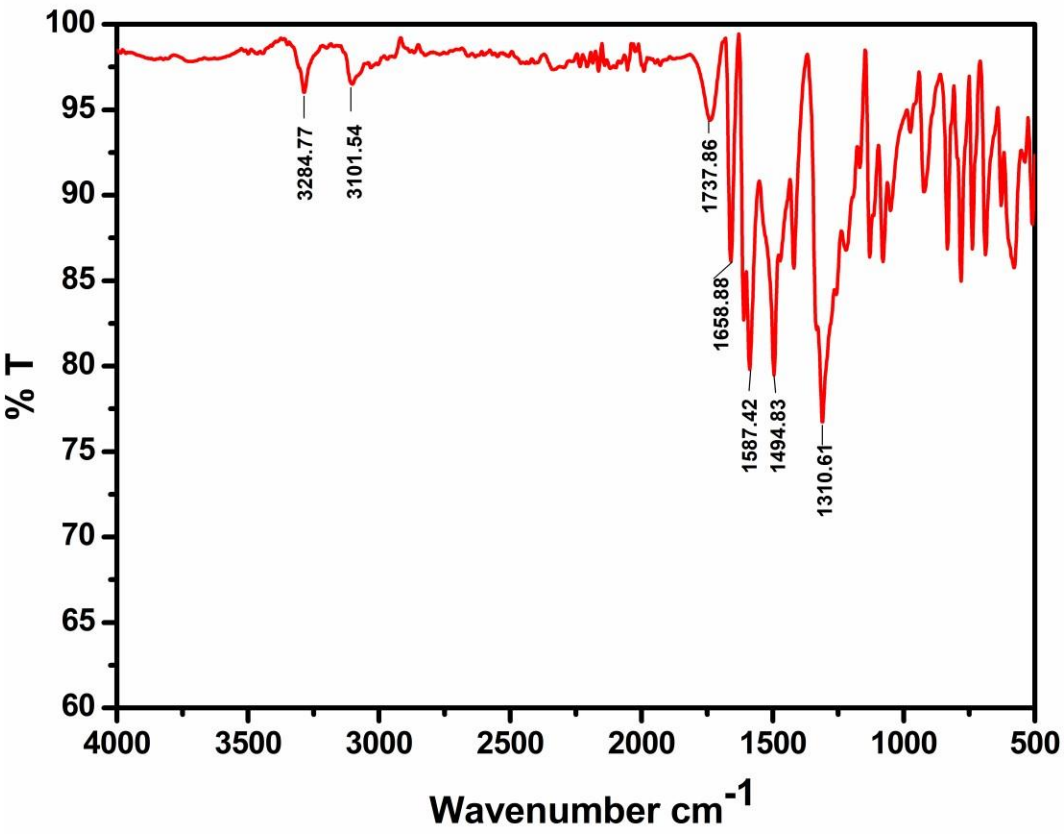


Fig. 1S: FT-IR spectra of **3**

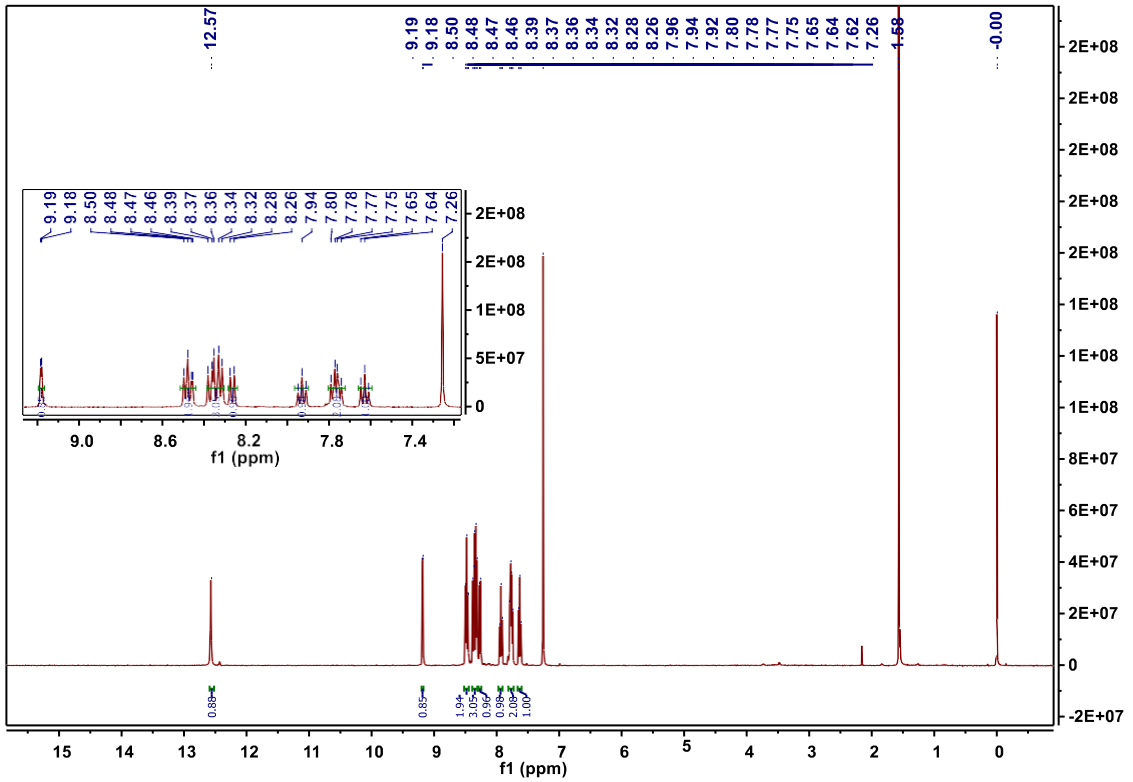


Fig. 2S: ^{1}H NMR spectra of **3**

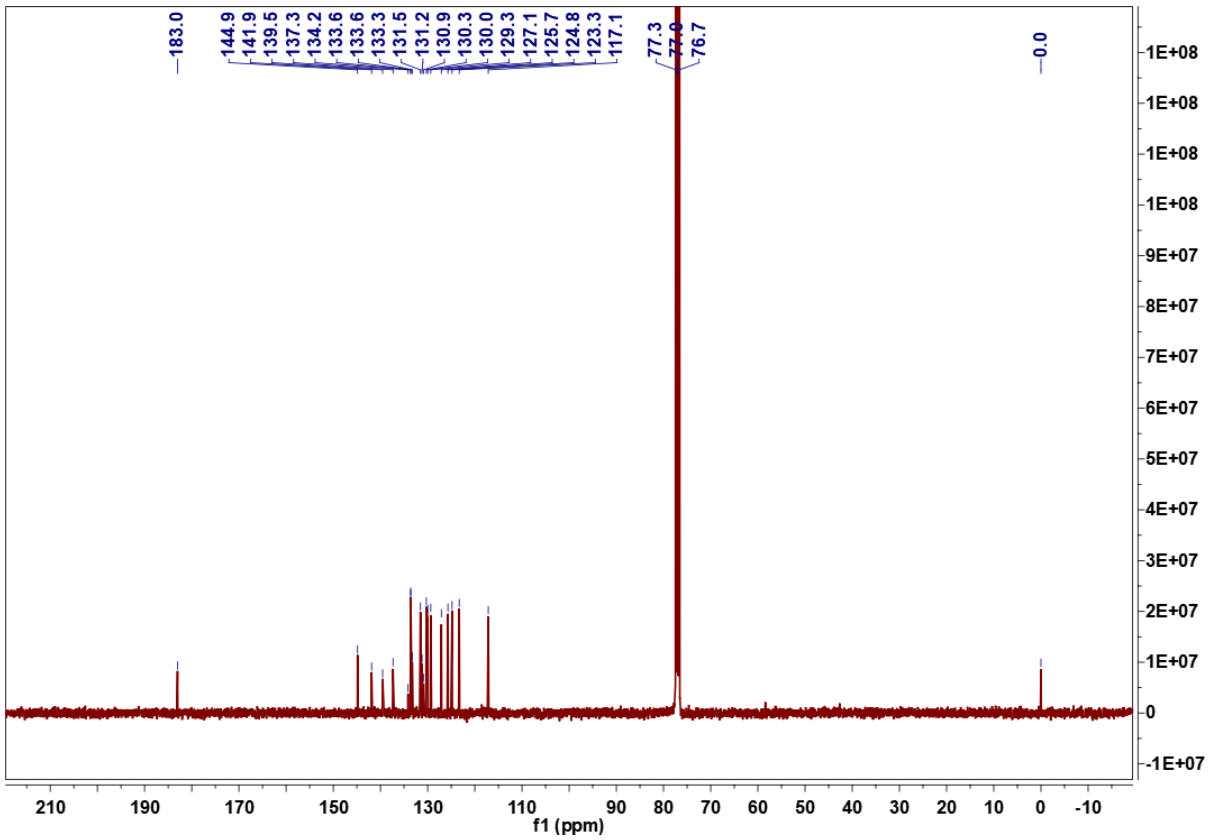


Fig. 3S: ^{13}C NMR spectra of **3**

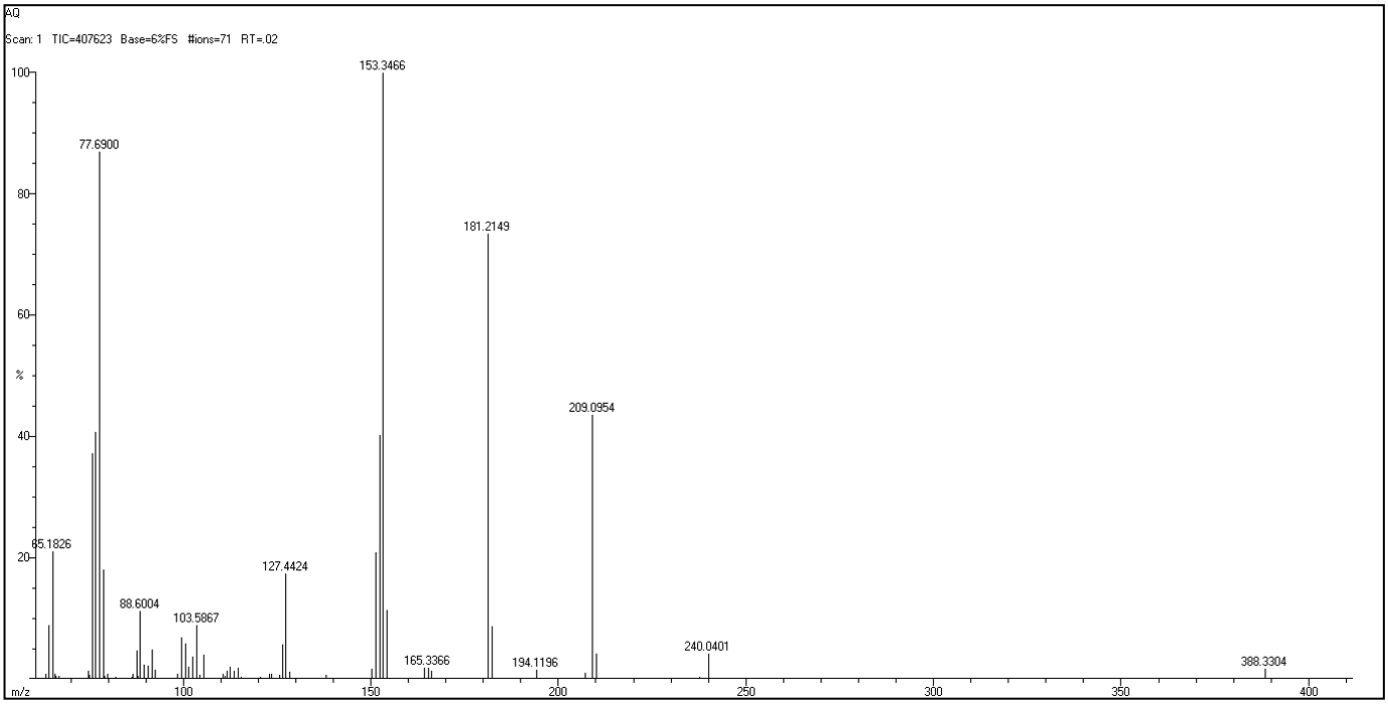


Fig. 4S: HR-MS spectra of **3**

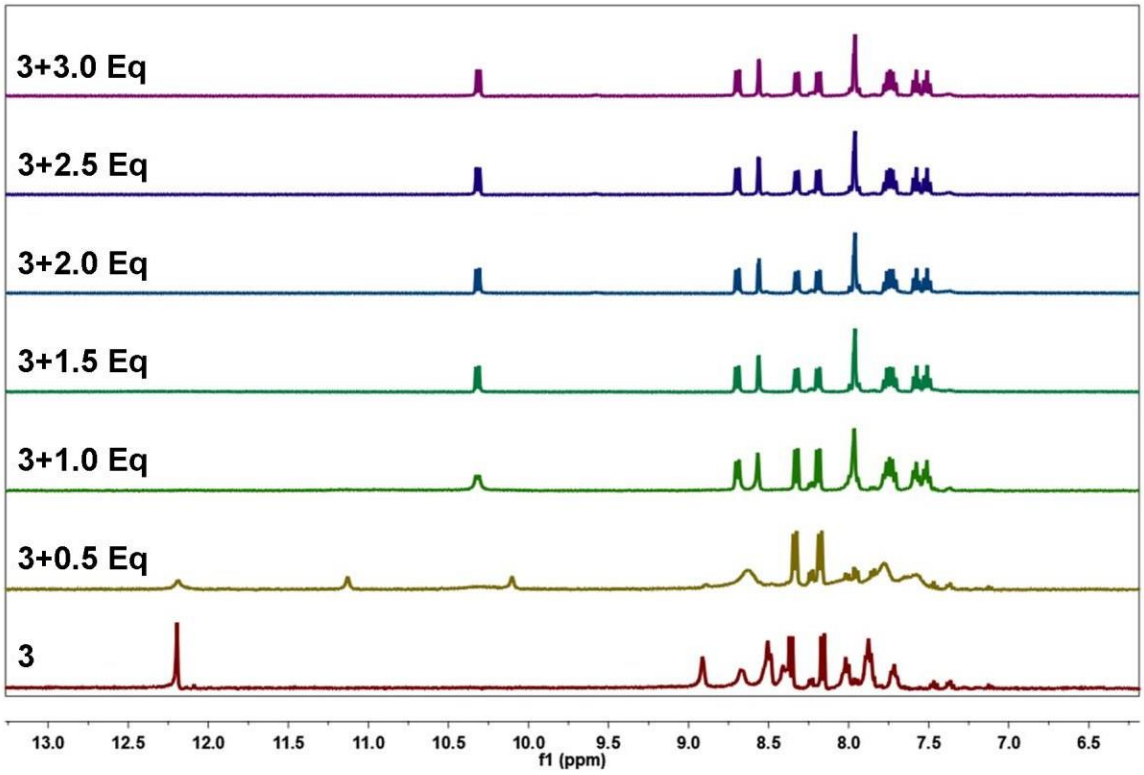


Fig. 5S. ^{1}H NMR titration of receptor **3** with TBAF in DMSO-d_6.

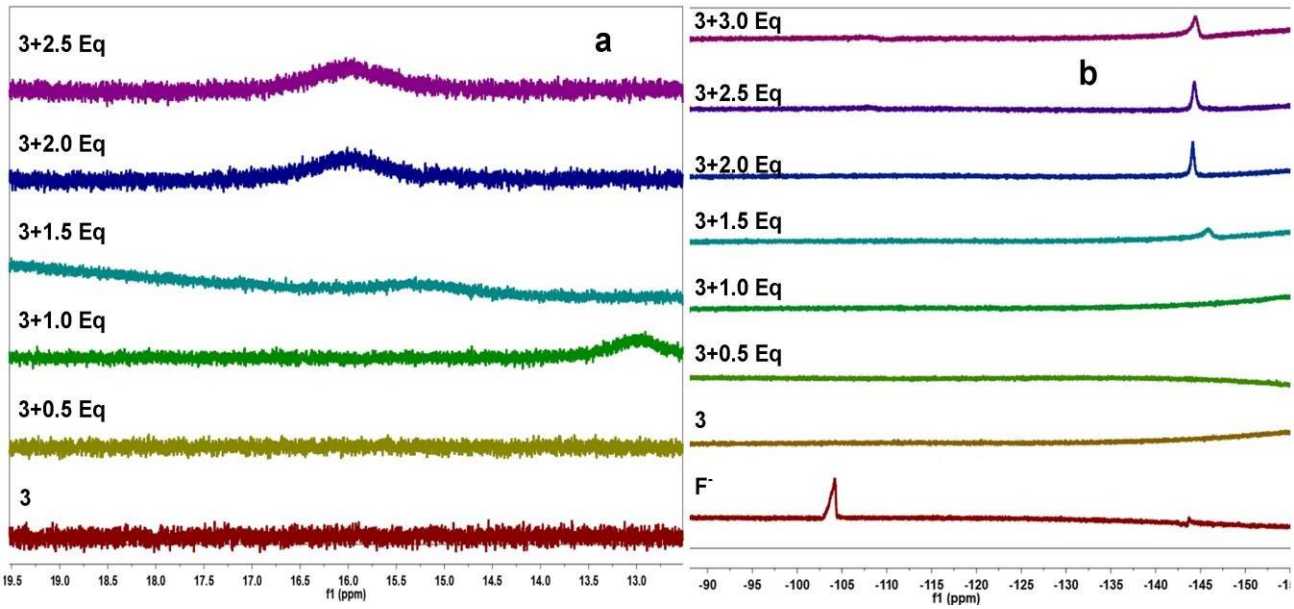


Fig. 6S. (a) ^{1}H NMR titration (downfield region) of receptor **3** and (b) ^{19}F NMR of receptor **3** with TBAF in DMSO-d_6.

Table 1S. Anthraquinone based ligands for anion selective sensors.

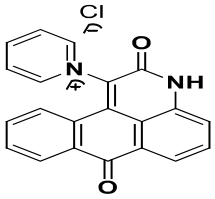
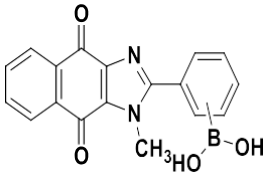
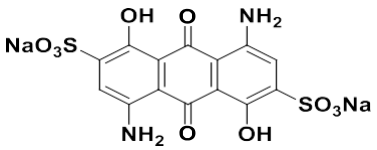
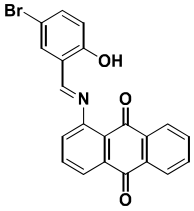
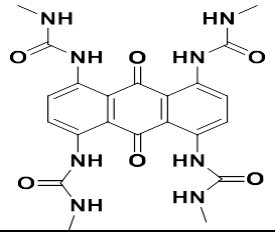
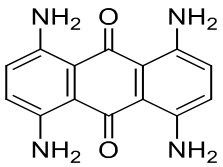
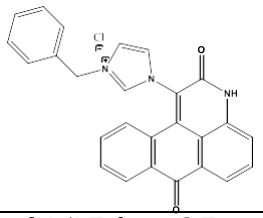
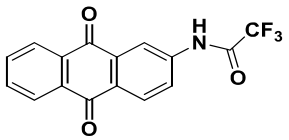
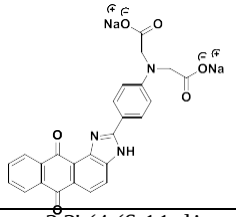
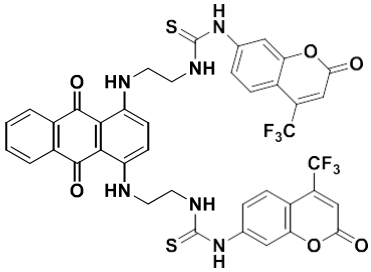
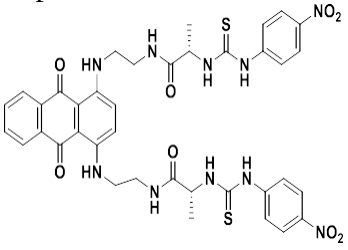
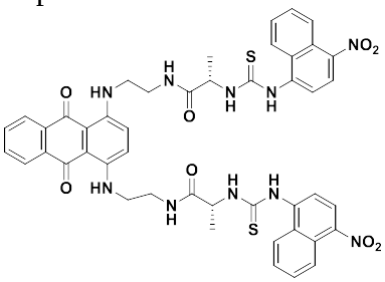
F^- 	CN^- 	F^- and CN^- 
1-(2,7-dioxo-3,7-dihydro-2H-naphtho[1,2,3-de]quinolin-1-yl)pyridinium chloride [24a]	1-methyl-2-phenyl-1H-naphtho[2,3-d]imidazole-4,9-dione methylboronate[24b]	sodium 4,8-diamino-1,5-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2,6-disulfonate [24c]
F^- 	F^- 	F^- 
(E)-1-(5-bromo-2-hydroxybenzylideneamino)anthracene-9,10-dione [24d]	1,1',1",1'"-(9,10-dioxo-9,10-dihydroanthracene-1,4,5,8-tetrayl)tetrakis(3-methylurea) [24e]	1,4,5,8-tetraaminoanthracene-9,10-dione [24e]
F^- and AcO^- 	CN^- 	F^- and CN^- 
3-benzyl-1-(2,7-dioxo-3,7-dihydro-2H-naphtho[1,2,3-de]quinolin-1-yl)-1H-imidazol-3-ium chloride [24f]	N-(9,10-dioxo-9,10-dihydroanthracen-2-yl)-2,2,2-trifluoroacetamide [24g]	sodium 2,2'-(4-(6,11-dioxo-6,11-dihydro-3H-anthra[1,2-d]imidazol-2-yl)phenylazanediyl)diacetate[24h]
Citrate 	Aspartate and malate 	Aspartate and malate 
1,1'-(2,2'-(9,10-dioxo-9,10-dihydroanthracene-1,4-diyl)bis(azanediyl)bis(ethane-2,1-diyl))bis(3-(2-oxo-4-(trifluoromethyl)-2H-chromen-7-yl)thiourea) [24i]	(S)-2-(3-(4-nitrophenyl)thioureido)-N-(2-(4-(2-((R)-2-(3-(4-nitrophenyl)thioureido)propanamido)ethylamino)-9,10-dioxo-9,10-dihydroanthracen-1-ylamino)ethyl)propanamide [24j]	(S)-2-(3-(4-nitronaphthalen-1-yl)thioureido)-N-(2-(4-(2-((R)-2-(3-(4-nitronaphthalen-1-yl)thioureido)propanamido)ethylamino)-9,10-dioxo-9,10-dihydroanthracen-1-ylamino)ethyl)propanamide [24j]

Table 2S. Comparison of **3** sensing towards iodide ions with previously reported work.

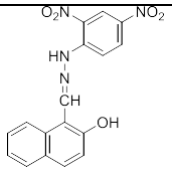
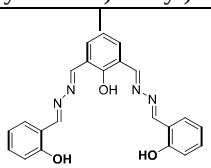
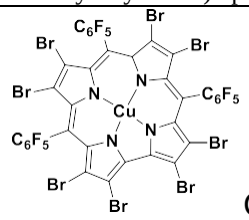
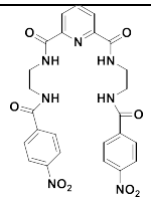
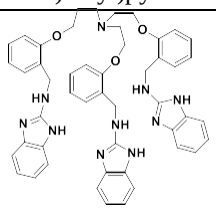
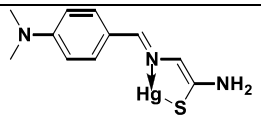
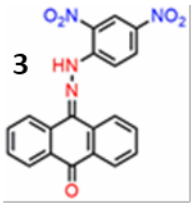
Structures	λ_{max}, nm	LOD, (M)	Environmental analysis
 1-((2-(2,4-dinitrophenyl) hydrazono)methyl)naphthalen-2-ol [19]	424	1.1×10^{-6}	Iodide content in urine
 2,2'-(1E,1'E)-((2E,2'E)-(2-hydroxy-5-methyl-1,3-phenylene)bis(methan-1-yl-1-ylidene)bis(hydrazine-2,1-diylidene))bis(methan-1-yl-1-ylidene)diphenol [17]	636	1.2×10^{-7}	Iodide recovery in water and urine
 Cu-Corrole[36]	441	7×10^{-6}	---
 N2,N6-bis(2-(4-nitrobenzamido)ethyl)pyridine-2,6-dicarboxamide [37]	365	1×10^{-6}	---
 N-(2-(2-((2-(2-((1H-benzo[d]imidazol-2-ylamino)methyl)phenoxy) ethyl)(3-(2-((1H-benzo[d]imidazol-2-ylamino)methyl)phenoxy) propyl) amino)ethoxy)benzyl)-1H-benzo[d]imidazol-2-amine [15]	495	2.1×10^{-6}	---
 ((Z)-1-amino-2-((E)-4-(dimethylamino)benzylideneamino) vinylthio) mercury [38]	468	4.5×10^{-7}	-
Present work 	615 nm	2.7×10^{-6} M	Iodide recovery in water

Table 3S. Validation of method using actual and spiked system.

Target ions	**Sample**	**I^- Added (µM)**	**I^- Found (µM)**	**Recovery (%)**
Iodide ions determination	Drinking water	20	19.77	98.85
	Drinking water	50	48.23	96.46
	Bore well water	20	18.83	94.15
	Bore well water	50	47.37	94.74

Table 4S. Anthraquinone based ligands for biological evaluation.

Name of the receptors	**Biological properties studied**			
	antioxidant	**anti-inflammatory**	**HRBC membrane protection ability**	**Other properties**
Anthraquinone-2-Carboxylic Acid [40]	--	reported	--	Antinociceptive activities
4,5-Dihydroxy-9,10-dioxo-9,10-dihydro anthracene-2-carboxylic acid [41]	--	reported	--	Antiarthritic activity
Anthraqinone [42]	reported	Reported (IC 50- 213 ± 22 µM)	--	--
1, 8-Dimethoxy Anthraquinone-2-Methyl Carboxylate [43]	reported	reported	--	--
Anthraquinone chalcone hybrids [44]	--	--	--	DNA interaction studies
2-hydroxy-9,10-anthraquinone [45]	--	--	--	Anti-microbial studies
Anthraquinone-Derived Small Molecules [46]	--	--	--	Anti-cancer
Present work	70.18%	73.42%	72%	--

General procedure used in the spectrophotometric experiments

The receptor **3** of $2x10^{-5}$M in THF:H_2O (1:1, v/v) was interacted with appropriate amount of various anions (F^-, Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$ and OH^-) of $1x10^{-4}$ M in THF:H_2O (1:1, v/v) in separate vials and kept for 1-2 minutes. Then the UV-visible spectra of each individual solutions were taken in the region of 300-800 nm using THF:H_2O (1:1, v/v) solvent medium as blank solution. The receptor **3** ($2x10^{-5}$M, 2 mL) in THF:H_2O (1:1, v/v) was taken in quartz cell and to this solution KI of $1x10^{-4}$ M was added incrementally in THF:H_2O (1:1, v/v). After each increment addition of KI, the absorbance was recorded. For reversibility studies, the UV-visible spectra of receptor **3** ($2x10^{-5}$ M) in THF:H_2O (1:1, v/v) was recorded. To this solution, 1 eq of KI solution was added and the UV-visible spectra was recorded. In the next step, to the above solution, added 0.5 eq. of $CaNO_3$ and the spectra was recorded. Finally to complete the reversibility cycle further added 1eq of KI and spectra was recorded. For interference studies, the receptor **3** of $2x10^{-5}$ M was taken in THF:H_2O (1:1, v/v) and KI of same concentration was added. Followed by, the other anions were taken in three different concentrations (1eq, 5 eq and 10 eq) and the spectra were recorded. The detection limit of **3** from the absorption spectral titration with I^- was determined by following the equation: LOD: 3σ/slope and LOQ: 10 σ/slope. Were σ = standard deviation of the blank solution and s = slope of the calibration curve. From the calibration curve plotted at 615 nm, we get slope = 3017, and the σ value of 0.002711 was obtained from the ten reading of the blank sample. Thus using the formula we get the LOD and LOQ for I^- = 2.7×10^{-6} M µM and 8.99×10^{-6} M respectively

The binding constant value of I^- with **3** was obtained from UV-visible titration data with the Benesi–Hildebrand equation.

$$1 / (A - A_0) = 1/ (A_{max} - A_0) + (1 / K_a[I^-])[1 / (A_{max} - A_0)]$$

Here, K_a is the association constant or binding constant. A_0 is the minimum absorbance at 615 nm, i.e. the absorbance at 615 nm in absence of KI or receptor **3** ($2x10^{-5}$ M) alone in THF/H_2O (1:1, v/v) medium. A_{max} is the maximum absorbance at the saturation point obtained after gradual addition of KI solution ($1x10^{-4}$ M) and A is the absorbance observed after each addition of KI (20 to 400 µL). The association constant (K) was determined from the slope of the straight line of the plot of 1/(A-Ao) against $1/[I^-]_n$. The association constant (K_a) as determined by UV-vis titration method for sensor with I^- was found to be 1.37×10^4 M^{-1}

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