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# Exploration of selective recognition of iodide with dipodal sensor: 2,2′-[ethane-1,2-diylbis-(iminoethane-1,1-diyl)]diphenol†

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A dipodal fluorescent receptor, 2,2′-[ethane-1,2-diylbis(iminoethane-1,1-diyl)]diphenol (**2**), with amine and hydroxyl moieties as binding sites has been synthesised and characterized with spectroscopic methods and single crystal X-ray techniques. The recognition of the anions with receptor **2** was studied using UV-Vis and fluorescence spectroscopy. The $^1$H-NMR spectroscopic and DFT studies revealed the distinct recognition of $I^-$ ions over the other surveyed anions.

## Introduction

The advance of innovative molecular arrays for the fluorometric detection of anions,[1–3] cations[4–6] or neutral moieties[7–10] has gained foremost importance due to their application in the material sciences, biology and environmental management. At the present time, active effort towards the development of molecular complexation systems that concurrently bind anions and is cost-effective is still needed.[11] Normally, amide, urea, amine and hydroxyl groups act as binding sites for anions.[12]

Iodide plays a basic role in many important physiological functions, including neurological activity and thyroid function.[13–15] Due to its significance in physiological processes, a method for the rapid, sensitive and selective detection of iodide in food, pharmaceutical products, and biological samples such as urine is of great significance.[16] In addition, elemental iodine is commonly involved in chemical synthesis, including pharmaceuticals and dyes.[17] Literature reports revealed that fluorescent sensing systems measuring the stability of iodide are of considerable significance owing to their high simplicity and sensitivity. Nevertheless, relatively few examples of fluorescent sensors for iodide, based on two recognition strategies including hydrogen-bonding and metal-coordination, have been reported.[18–20] Iodide has a large ionic radius, low charge density and low hydrogen bonding ability, it is challenging to develop specific probes for this entity based on hydrogen bonding.

In the current article, we report a convenient and efficient route for the preparation of the noncyclic receptor **2** and furthermore explore its new application as an anion sensor. For iodide sensing, the synthesized noncyclic receptor **2** provides two amine and two hydroxyl groups as an array of converging recognition sites. To date, there is no report of a synthesis of receptor **2** by the reduction of 2,2′-{ethane-1,2-diylbis[nitrile(1*E*)eth-1-yl-1-ylidene]}diphenol (**2**) which was herein used for the molecular recognition of the $I^-$ ion. The interesting feature of this work is that there is a Turn-ON fluorescence response upon interaction with the iodide anion. In the literature, most sensors reported showed fluorescence quenching upon binding with iodide.[1a,21–24] However, the Turn-ON signal is always preferable over Turn-OFF because it can detect low concentrations relative to a dark background. This increases the sensitivity and authenticity of the receptor towards the analyte.[25,26] Another advantage is the ease of preparation and low detection limit, already existing sensors have complex structures and multistep syntheses, *e.g.* gold nanoclusters, CdSe nanoparticles, use of PVC membranes, complexes of transition metal ions, *etc.*, as shown in Table S1.† However, the present work involves a simple condensation reaction followed by reduction. These points increase the scope of receptor **2** as a highly selective and sensitive chemosensor for iodide anion.

## Results and discussion

2,2′-{Ethane-1,2-diylbis[nitrile(1*E*)eth-1-yl-1-ylidene]}diphenol (compound **1**) was synthesized by refluxing an alcohol solution

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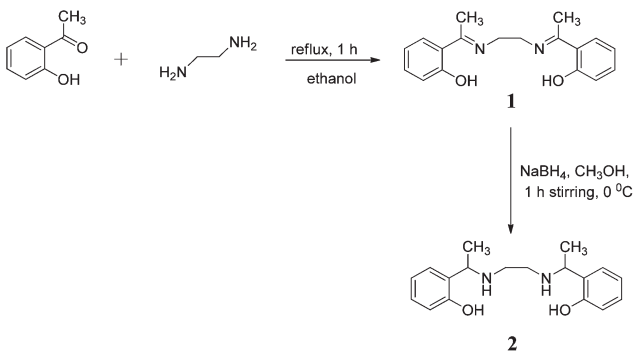
of 2-hydroxyacetophenone and ethane-1,2-diamine (2 : 1 molar ratio) for one hour. The reaction mixture was cooled and bright yellow coloured crystals of compound **1** precipitated. The crystals were filtered off and recrystallized from ethanol to give bright yellow crystals. Compound **1** was obtained with a good yield.[27] A further receptor **2** was obtained from compound **1** by reduction with $NaBH_4$ in a good yield (Scheme 1).

The synthesized receptor **2** was characterized by melting point, IR, $^1$H-NMR, $^{13}$C-NMR, mass spectroscopy and X-ray crystallographic methods (Fig. S1–S4†). IR, $^1$H-NMR, $^{13}$C-NMR, mass spectroscopy and X-ray crystallographic methods provided confirmation of the structure of receptor **2**. The assigned structure of receptor **2** was further supported with X-ray crystallography and an ORTEP diagram, as shown in Fig. 1, and the crystallographic details for receptor **2** are listed in Table S2.† The CIF file for receptor **2** was deposited in the Cambridge Structure Database with CCDC no 952233.[28]

Examination of the diffraction pattern from a Nonius Kappa CCD diffractometer indicated a tetragonal crystal system. The molecule contains a crystallographic two-fold rotation axis. The N–H and O–H hydrogen atoms were located on electron density maps and refined isotropically. The –OH group is involved in an intermolecular hydrogen bond with a nitrogen atom and the N–H group is involved in an intramolecular hydrogen bond with the oxygen atom. (Table S3†). For the methyl group, the hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5*U_{eq}$ (bonded carbon atom). The torsion angle, which defines the orientation of this methyl group about the C–C bond, was refined. The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2*U_{eq}$ (bonded atom).

The recognition properties of receptor **2** towards various anions were evaluated with different spectroscopic techniques such as UV-Vis, fluorescence and NMR spectroscopy. Firstly, the ability of receptor **2** to bind with anions in $CH_3CN$ was examined using UV-Vis absorption spectroscopy. For the anion binding assay, tetrabutylammonium (TBA) salts of various anions ($F^-$, $Cl^-$, $Br^-$, $I^-$, $HSO_4^-$, $CN^-$, $NO_3^-$, $CH_3COO^-$ and $H_2PO_4^-$) were used in the experiment. The introduction of various anions did not cause a significant change in the absorption profile of **2** except in the case of $I^-$ (Fig. 2). The addition of $I^-$ into the solution of receptor **2** (0.1 mM) produced a dramatic change in the absorption profile (Fig. 2). The receptor **2** showed a ratiometric estimation of $I^-$ having three isosbestic points ($I_E$) at 218, 230 and 260 nm as shown in Fig. 3. To verify this recognition and find out its mechanism of action, a titration was carried out between receptor **2** (0.1 mM) and the $I^-$ anion (Fig. 3). Receptor **2** exhibited a broad absorption band centred at 276 nm. The continuous addition of $I^-$ to the solution of receptor **2** (0.1 mM) resulted in a new band at 245 nm and a simultaneous decrease in intensity at 276 nm (Fig. 3). This new absorption band may arise due to an n–π* type transition, which could be attributed to hydrogen bonding of the $I^-$ ion with receptor **2**.

The well-defined isosbestic points at 218, 230 and 260 nm were observed, indicating the formation of a new species upon treatment of receptor **2** with the $I^-$ ion and it also shows that the **2**·$I^-$ complex is an equilibria system.[29] The crystal structure and DFT optimized structure of **2** reveal that the receptor has a well-defined cavity enriched with an array of hydrogen bonding N–H and O–H groups (Fig. 1 and 7a). Therefore, the driving force behind binding is H-bonding, which is also




**Scheme 1** Synthesis route of receptor **2**.

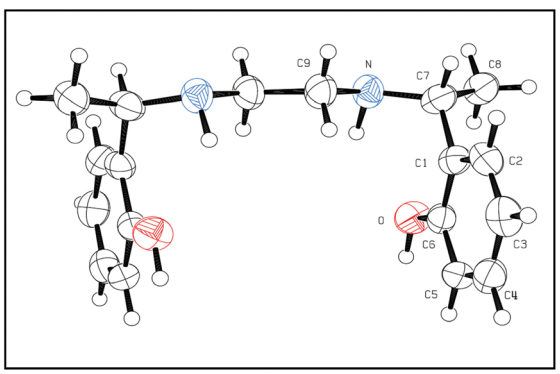



**Fig. 1** ORTEP diagram of receptor **2** drawn with 50% probability displacement ellipsoids. The molecule contains a crystallographic two fold rotation axis.

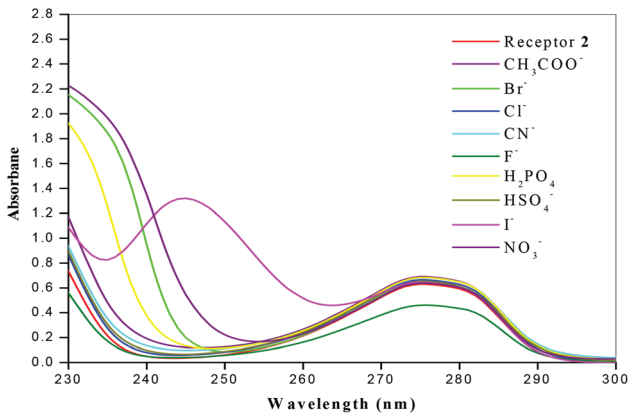



**Fig. 2** The anion binding absorption profile of receptor **2** (0.1 mM) upon addition of tetrabutylammonium salts of various anions (0.5 equiv. of each).

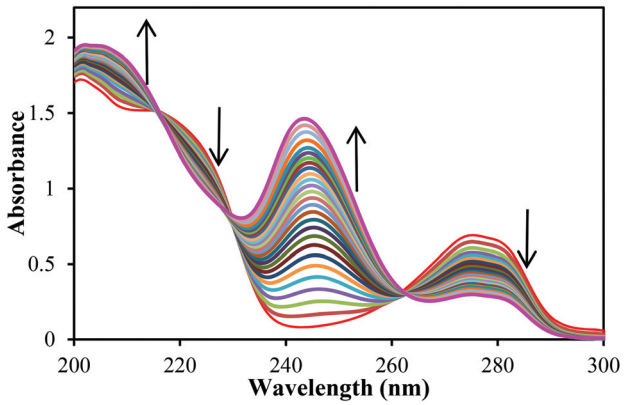



Fig. 3 Changes in absorption spectra of **2** (0.1 mM) upon addition of various amounts of $I^-$ anion (1 mM) in $CH_3CN$ solution (0–3 equivalents).

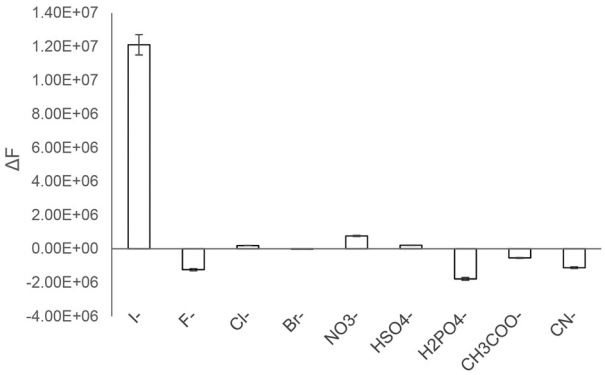



Fig. 5 Fluorescence response ($\Delta F = F - F_0$) of receptor **2** (0.1 mM) upon addition of 0.5 equiv. of tetrabutylammonium iodide ion and 3 equiv. of other tetrabutylammonium anion salts in $CH_3CN$.

supported by the DFT optimized structure of **2**·$I^-$ (Fig. 7b). Nevertheless, the weaker binding of the iodide ion among halides on the basis of its basicity is well known. There are many examples where $Cl^-$, $Br^-$ and $I^-$ ions bind principally because of the complementary size of the pseudocavity formed within the receptor.[30] From the above investigation, we find that the flexible cavity size in receptor **2**, which is confirmed by the single crystal X-ray structure and DFT calculations, was more compatible with the $I^-$ ion than with other anions.

Next we studied the fluorescence properties of receptor **2** upon the addition of various tetrabutylammonium salts of the $F^-$, $Cl^-$, $Br^-$, $I^-$, $HSO_4^-$, $CN^-$, $NO_3^-$, $CH_3COO^-$ and $H_2PO_4^-$ ions in $CH_3CN$ solution. Fig. 4 and 5 show the emission spectra of receptor **2** upon addition of various anions. The addition of $I^-$ caused an enhancement along with a blue shift in the emission profile of receptor **2** (Fig. 4 and 5). However, other anions remain almost silent upon excitation at 260 nm.

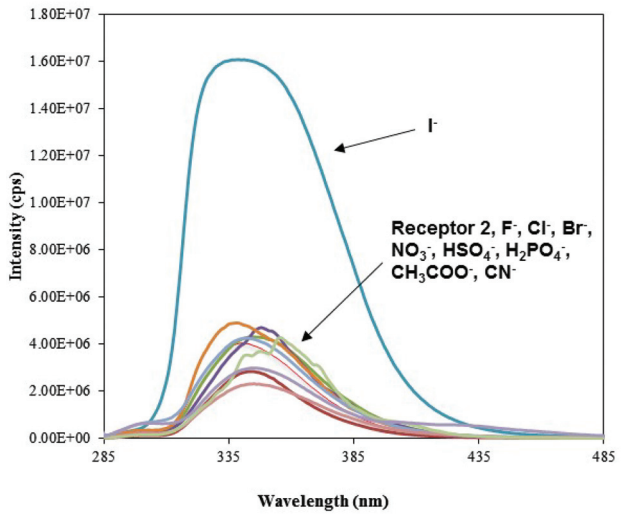



Fig. 4 Changes in fluorescent intensity of receptor **2** (0.1 mM) upon the addition of various tetrabutylammonium salts of $F^-$, $Cl^-$, $Br^-$, $I^-$, $HSO_4^-$, $CN^-$, $NO_3^-$, $CH_3COO^-$ and $H_2PO_4^-$ in $CH_3CN$ ($\lambda_{ex}$ = 276 nm).

The sensing properties of receptor **2** towards $I^-$ ion were further investigated with a titration using fluorescence spectroscopy and the results are shown in Fig. S5.† Upon progressive addition of $I^-$ (0 to 3 equiv.) to the solution of receptor **2**, a gradual enhancement in the fluorescence emission maximum at 340 nm can be observed along with a blue shift of 4 nm. The enhancement and blue shift could be attributed to intramolecular charge transfer (ICT) interaction between the $I^-$ ion, having a low charge density, and the electron rich donor array of amine and hydroxyl groups.

In order to investigate the sensing of $I^-$ in a real environment competitive titrations were performed. The competition experiments were conducted in the presence of 0.5 equiv. of $I^-$ mixed with an excess of different anions (3 equiv.). It was observed that receptor **2** selectively recognized $I^-$ even in the presence of other competing anions with moderately low interference from the other ions (Fig. S6†). These results indicate that receptor **2** shows a good sensitivity and selectivity towards the $I^-$ ion *versus* other competitive anions. The binding constant was calculated to be $8.6 \pm 0.01 \times 10^4$ $M^{-1}$ (Benesi–Hildebrand, Scatchard and Connor's fitting methodology, Fig. S7–S9†).[31] The binding stoichiometry between receptor **2** and $I^-$ ion was measured with the continuous variation method (Job's plot).[32] The total concentration of host and guest was kept constant while mole fractions were varied. A graph was plotted between [HG] and [H]/([H] + [G]) which has a maximum at 0.5 which corresponds to a 1 : 1 stoichiometry of **2**·$I^-$ (Fig. S10†).

The LC-MS mass spectrum of complex **2**·$I^-$ ion shows a peak at *m*/*z* 437.40 [$(C_{18}H_{25}N_2O_2I)$·1/2$H_2O$], corresponding to [**2**·$I^-$] fragment pattern also supports the formation of a 1 : 1 complex (Fig. S11†).[33] Thus, receptor **2** can be used for the selective recognition of $I^-$, and it can detect $I^-$ up to a low concentration of 1.38 μM. Besides selectivity and sensitivity, response time is the third most important parameter for ON-site detection of an analyte. An ideal receptor should have high selectivity, sensitivity, low detection limit and a short response time. Fig. S12† represents the response time of receptor **2** towards the iodide anion. It is observed that the fluorescence intensity becomes stable after 50 s upon addition of

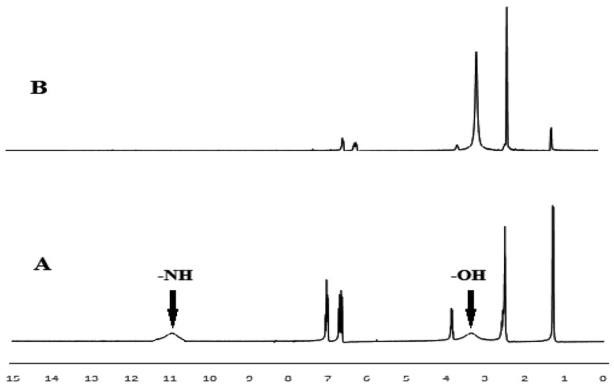



Fig. 6 Partial $^1$H-NMR spectrum of (A) only receptor **2** and (B) presence of 1 equivalents of $[n\mathrm{Bu}_4\mathrm{N}]\mathrm{I}^-$ ion in receptor **2**.

3 equiv. of iodide into a solution of receptor **2**. Further, to strengthen the mechanism of binding of $\mathrm{I}^-$, $^1$H-NMR spectra of receptor **2** were recorded in the presence and absence of iodide. It is observed that the signals of the –NH and –OH protons at $\delta$ 11.38 and $\delta$ 1.67–1.75 vanish upon addition of 1 equivalent of $\mathrm{I}^-$ as shown in (Fig. 6). These results clearly show that the –NH and –OH protons of receptor **2** form hydrogen bonds with iodide.

We also tried to grow a single crystal of the $\mathrm{I}^-$ complex of receptor **2**. Unfortunately, we did not get crystals which are suitable for a diffraction study. Therefore, to understand the electronic environment and changes in structure of receptor **2** upon complexation with $\mathrm{I}^-$, DFT calculations were performed using the B3LYP/LANL2DZ basis set.[34] The optimized structure of receptor **2** has more or less a similar geometry to the structure obtained from crystallography (Fig. 7a). The two pods of receptor **2** have –OH groups in opposite directions. Three electronegative atoms (O22, N26 and N25) arrange in a particular way for the encapsulation of the analyte as shown in Fig. 7a. This sensor has a selectivity for the iodide anion; therefore optimization is performed with the iodide complex of receptor **2**. The optimized structure of **2**·$\mathrm{I}^-$ showed that two benzene rings are very far from each other due to the large size of iodide (Fig. 7b). Table S4† illustrates some of the structural parameters for comparison of receptor **2** with the **2**·$\mathrm{I}^-$ complex. The optimization energy is also calculated for each structure and is listed in Table S4.†

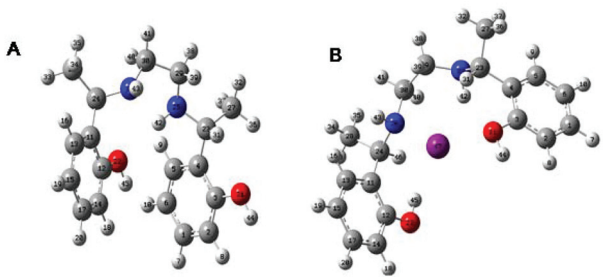



Fig. 7 The DFT optimized structure of (A) receptor **2** and (B) the **2**·$\mathrm{I}^-$ complex calculated at the B3LYP/LANL2DZ level. The red, blue, gray, purple and dark pink spheres refer to O, N, C, $\mathrm{I}^-$ atoms, respectively.

In conclusion, we have synthesized an easy-to-make dipodal fluorescent anion receptor **2** based upon amine and hydroxyl moieties which is confirmed by a single crystal X-ray technique, and investigated its anion binding using UV-visible and fluorescence spectroscopy. Receptor **2** exhibited ratiometric estimation of iodide using absorption spectroscopy and an enhancement in fluorescence intensity upon addition of the $\mathrm{I}^-$ anion. The stoichiometry of the **2**·$\mathrm{I}^-$ complex (1 : 1) was confirmed by a Job's plot and mass spectroscopy. The binding constant, detection limit, short response time and interference studies advocate the selectivity and sensitivity of receptor **2** towards $\mathrm{I}^-$.

## Experimental

All commercial grade chemicals and solvents were procured and used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a Varian NMR mercury system 300 spectrometer operating at 300 and 75 MHz, respectively, in $\mathrm{CDCl}_3$ and DMSO-$\mathrm{d}_6$. The fluorescence and UV-visible spectra were recorded in $\mathrm{CH}_3\mathrm{CN}$ on a fluoromax-4 spectrofluorometer and a Shimadzu UV-24500 in the range of 200–600 nm, respectively, at room temperature using a 1 cm path length cell. X-ray crystallographic data was measured on a Nonius Kappa CCD diffractometer at 150 K using an Oxford Cryosystems Cryostream Cooler. The data collection strategy was set up to measure an octant of reciprocal space with a redundancy factor of 4.6, which means that 90% of these reflections were measured at least 4.6 times. Phi and omega scans with a frame width of 0.5° were used. Data integration was done with Denzo and scaling and merging of the data was done with Scalepack.[35] The structure was solved with the direct methods procedure in SHELXS-97.[36] Full-matrix least-squares refinements based on $F^2$ were performed in SHELXL-2013,[37] as incorporated in the WinGX package.[38] Neutral atom scattering factors were used and include terms for anomalous dispersion.[39]

### Synthesis of receptor 2

Compound **1** was synthesized by refluxing one mole of ethane-1,2-diamine (0.60 g, 10 mmol) with two moles of 2-hydroxy acetophenone (2.72 g, 20 mmol) in ethanol (50 mL) with stirring for 1 h. Compound **1** was obtained and appears as a yellow crystalline powder in a 70% yield, mp > 250 °C. Further, receptor **2** was obtained from compound **1** by reduction under $\mathrm{NaBH}_4$ in $\mathrm{CH}_3\mathrm{OH}$ in a good yield. The X-ray quality crystal of receptor **2** was obtained by a slow evaporation of a chloroform solution. Yield 81%, mp ≥ 250 °C. IR (KBr, $\mathrm{cm}^{-1}$): $\nu$ = 3291, 2841, 2556, 1900, 1815, 1591, 1450, 1352, 1242, 1197, 1032, 968, 932, 873, 760 $\mathrm{cm}^{-1}$; $^1$H-NMR (300 MHz, $\mathrm{CDCl}_3$): $\delta$ = 1.42–1.46 (d, 6H, 2-$\mathrm{CH}_3$), 1.67–1.75 (bs, 2H, 2-OH), 2.72–2.80 (t, 4H, 2-$\mathrm{CH}_2$–), 3.80–3.89 (q, 2H, 2=CH–), 6.74–7.17 (m, 8H, Ar-H), 11.38 (s, 2H, NH). $^{13}$C NMR (75 MHz, $\mathrm{CDCl}_3$ = few drops of DMSO): $\delta$ = 21.1, 46.8, 58.9, 116.5, 119.0, 126.4, 127.9, 128.2,

156.9. LC-MS ($M + H^+$) calcd for $C_{18}H_{25}N_2O_2$ = 301.19, found for $C_{18}H_{25}N_2O_2$ = 301.07. CHN analysis; calcd C, 71.97; H, 8.05; N, 9.33; found C, 71.82; H, 8.19; N, 9.37.

### Anion recognition studies

The anion recognition studies were performed at room temperature, and the solution was shaken before recording absorption and emission spectra to ensure uniformity. The anion binding ability of receptor **2** in a $CH_3CN$ media was studied by adding fixed amounts (0.5 equivalent) of a tetrabutylammonium salt (1 mM) to a standard solution of receptor **2** (0.1 mM, 2 mL) in $CH_3CN$ and by keeping the solvent ratio constant throughout the experiment. The binding study was explored by using fluorescence spectroscopy.

### Stoichiometry determination

Consecutively, to determine the stoichiometry of the receptor **2**·$I^-$ ion binding, solutions of receptor **2** and the $I^-$ ion were prepared at ratios of 3.0 : 0.0, 2.7 : 0.3, 2.4 : 0.6, 2.1 : 0.9, 1.8 : 1.2, 1.5 : 1.5, 1.2 : 1.8, 0.9 : 2.1, 0.6 : 2.4, 0.3 : 2.7 and 0.0 : 3.0. These solutions were allowed to stand for 1 h with frequent shaking in between. The fluorescence spectra were recorded for each mixture. The plot of [HG] *versus* $X_i$ was used to determine the stoichiometry of the complex formed. The fluorescence intensity of the emission peak maximum at 341 nm was used for the stoichiometry calculations. The concentration of [HG] was calculated by the equation of $[HG] = (\Delta F/F_0)\,[H]$ and $X_i$ = Mole Fraction = $[H]_v/[H]_v + [G]_v$.

## Notes and references

1 (*a*) N. Singh and D. O. Jang, *Org. Lett.*, 2007, **9**, 1991; (*b*) D. O. Youn, N. Singh, M. J. Kim and D. O. Jang, *Org. Lett.*, 2011, **13**, 3024.
2 S. O. Kang, S. Llinares, V. W. Day, V. W. James and K. B. James, *Chem. Soc. Rev.*, 2010, **39**, 3980.
3 P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486.
4 J. L. Sessler, P. A. Gale and W. S. Cho, *Anion Receptor Chemistry*, RSC, Cambridge, 2006.
5 P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79.
6 M.-L. Lehaire, R. Scopelliti, H. Piotrowski and K. Severin, *Angew. Chem., Int. Ed.*, 2002, **41**, 1419.
7 P. D. Beer and J. Cadman, *Coord. Chem. Rev.*, 2000, **205**, 131.
8 F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609.
9 P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79.
10 H. T. Ngo, X. Liu and K. A. Jolliffe, *Chem. Soc. Rev.*, 2012, **41**, 4928.
11 M. Haldimann, B. Zimmerli, C. Als and H. Gerber, *Clin. Chem.*, 1998, **44**, 817.
12 G. Aumont and J. C. Tressol, *Analyst*, 1986, **111**, 841.
13 F. Jalali, M. J. Rajabi, G. Bahrami and M. Shamsipur, *Anal. Sci.*, 2005, **21**, 1533.
14 K. Wygladacz and E. Bakker, *Analyst*, 2007, **132**, 268.
15 E. C. V. Butler, *Trends Anal. Chem.*, 1996, **15**, 45.
16 S. Jayaraman, L. Teiltler, B. Skalski and A. S. Verkman, *Am. J. Physiol. Cell Physiol.*, 1999, **277**, C1008.
17 B. S. Hetzel, The conquest of iodine deficiency: a special challenge to Australia from Asia, *Proc. Nutr. Soc. Austr*, 1991, **16**, 69.
18 B. Ma, F. Zeng, F. Zheng and S. Wu, *Chem.–Eur. J.*, 2011, **17**, 14844.
19 Z. He, H. Li and Z. Li, *J. Org. Chem.*, 2010, **75**, 4636.
20 L. Xu, Y. Xu, W. Zhu, Z. Xu, M. Chen and X. Qian, *New J. Chem.*, 2012, **36**, 1435.
21 H. Wang, L. Xue and H. Jiang, *Org. Lett.*, 2011, **13**, 3844.
22 Z. B. Shang, Y. Wang and W. J. Jin, *Talanta*, 2009, **78**, 364.
23 R.-H. Yang, K.-M. Wang, D. Xiao and X.-H. Yang, *Analyst*, 2000, **125**, 1441.
24 Y. Wang, H. Zhu, X. Yang, Y. Dou and Z. Liu, *Analyst*, 2013, **138**, 2085.
25 L.-R. Lin, W. Fang, Y. Yu, R.-B. Huang and L.-S. Zheng, *Spectrochim. Acta, Part A*, 2007, **67**, 1403.
26 L. J. Fan and W. E. Jones, *J. Am. Chem. Soc.*, 2006, **128**, 6784.
27 R. M. Ramadan, M. S. A. Hamza and S. A. Ali, *J. Coord. Chem.*, 1998, **43**, 31–39.
28 These data can be obtained free of charge from The Cambridge Crystallographic Data centre via www.ccdc.cam.ac.uk/data_request/cif.
29 K. Ghosh and T. Sen, *Tetrahedron Lett.*, 2008, **49**, 7204.
30 V. Muthalagu, N. Rajagopal and V. Suresh, *Macromolecules*, 2006, **39**, 8303.
31 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703; G. Scatchard, The Attractions of proteins for small molecules and ions, *Ann. N. Y. Acad. Sci.*, 1949, **51**, 660; K. A. Connors, in *Binding constants, The measurements of molecular complex stability*, Wiley, New York, 1987.
32 P. Job, *Ann. Chim.*, 1928, **9**, 113.
33 V. K. Bhardwaj, N. Aliaga-Alcalde, M. Corbella and G. Hundal, *Inorg. Chim. Acta*, 2010, **363**, 97.
34 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
35 Z. Otwinowski and W. Minor, Methods in Enzymology, in *Macromolecular Crystallography, Part A*, ed. C. W. Carter Jr. and R. M. Sweet, Academic Press, 1997, vol. 276, pp. 307–326.
36 G. M. Sheldrick, *SHELXS-97*; G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
37 G. M. Sheldrick, *SHELXL-2013*; G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
38 L. J. Farrugia, *WinGX-Version 1.70.01*; *J. Appl. Crystallogr.*, 1999, **32**, 837.
39 *International Tables for Crystallography*, Kluwer Academic Publishers, Dordrecht, 1992, vol. C.