A reversible E_m-FRET rhodamine-based chemosensor for carboxylate anions using a ditopic receptor strategy†

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A reversible rhodamine-based sensor (**L1**) capable of undergoing excimer-fluorescent resonance energy transfer (E_m-FRET) was designed and synthesized using a ditopic receptor strategy. Addition of Cu^{2+} ions to a solution of L1 induced a ring-open conformation of spirolactam (E_m-FRET *ON*), whilst ring closure was induced upon addition of CH_3COO^- (E_m-FRET *OFF*).

Introduction

The demand for chemosensors that are selective for specific target anions or cations is continuously increasing. Especially important in this regard is a sensor whose receptor can bind either cations, anions or both.[1] A great effort has been concentrated on the development of selective fluorescent chemosensors due to their high sensitivity.[2,3a] Most fluorometric sensors, have been developed to adopt photo-physical changes produced upon guest complexation, including photo-induced electron/energy transfer (PET), charge-transfer (CT) excited state, excimer/exciplex and fluorescence resonance energy transfer (FRET).[3] More recently, FRET has become an active field in supramolecular chemistry research due to its potential practical benefits in cell physiology and optical therapy, as well as the selective and sensitive sensing of specific targeted molecular or ionic species.[4] A variety of chemosensors have been reported based on a FRET signal mechanism.[4] For example, a calix[4]arene containing rhodamine dye and pyrenyl moieties was described as a Hg^{2+}-selective FRET sensor.[5] Recent developments have shown that rhodamine spirolactam is a promising structural scaffold for the design of selective chemosensors. Upon metal binding, its structure can undergo a change from the spirolactam to an open ring amide, resulting in a magenta-colored, highly fluorescent compound.[4b,6] To date, several rhodamine-modified chemosensors for Hg^{2+}, Cu^{2+}, Pb^{2+} and Fe^{3+} ions have been developed.[6] Surprisingly, the potential for a rhodamine-based ditopic receptor remains unexplored despite the indispensable value of them in many biochemical processes.[7] Because of the irreversible Hg^{2+}-promoted desulfurization reaction, Cu^{2+} and Zn^{2+} were chosen in this work. Herein, we report rhodamine derivatives (RhBs) based on excimer-fluorescent resonance energy transfer (E_m-FRET), combined with energy donor from excimer emission (naphthalene excimer)[8] and energy acceptor from dye absorption (rhodamine dye) (**L1**). Using **L1** as a sensitive and selective chemosensor for anions in the absence of cation binding, the **L1** solution is colorless and nonfluorescent, yet in the presence of the cation, a visual color change was observed as well as a fluorescent OFF-ON observation, which constitutes a ditopic selective fluorescent chemosensor. Chemosensor **L1** was synthesized with two steps from the reaction of rhodamine B with ethylenediamine, and the coupling reaction with 1-naphthaleneisothiocyanate and refluxing in $CHCl_3$ for 72 h to afford **L1** at an 84% yield.

As a control experiment, compound **2** was synthesized by reacting butylamine with 1-naphthaleneisothiocyanate. The control compound was used in comparative investigation to explore which structure is preferable to form excimer emission (~500 nm)[8] and can overlap with ring-opened rhodamine B to undergo the E_m-FRET phenomenon (Fig. 1). **L1** and **2** were well characterized by ^1H NMR, FT-IR and MALDI-TOF MS.

The UV-vis spectra and fluorescence intensity changes of **L1** were investigated to determine the anion binding abilities, as

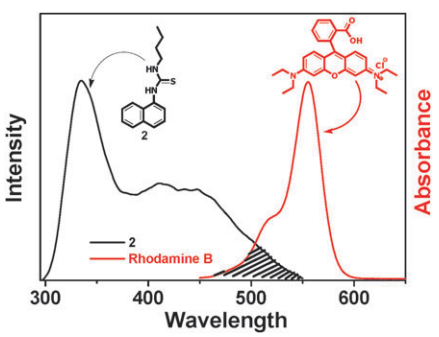

Fig. 1 Spectral overlap between naphthyl emission (black) and ring-opened rhodamine B absorption (red).

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demonstrated in Fig. S1 and S2, respectively.† Upon addition of 30 equiv. of anions to the solution of **L1**, hypochromic shifts of all anions were observed. Moreover, in the case of F^-, $H_2PO_4^-$ and CH_3COO^-, the new absorption bands appeared at 410 nm, red-shifted by a $\Delta\lambda_{max}$ of 95 nm. These shifts are ascribed to the occurrence of the H-bond interaction involving the two N–H fragments of the thiourea subunit and anions.[9] Fluorescent spectra showed a small enhancement in the monomer and excimer emission at 370 and 490 nm, respectively. UV-vis spectroscopy was employed to determine the stoichiometry and stability constant for the complexes using the SIRKO program.[1b,8c,10]

According to the extent of the observed absorption spectra changes, the association constants of **L1** were obtained, and are summarized in Table 1. **L1** prefers to bind with $PhCOO^-$ selectively (log β = 4.44, Fig. 2) over all the other anions which form structurally similar 1:1 complexes, suitably described as 2:2 complexes owing to the evident dimeric fluorescent nature of naphthalene (Fig. 1 and S2†). The selectivity can be explained by the geometry of $PhCOO^-$ and the π–π stacking interaction as demonstrated in proposed binding modes in Fig. 3 and S3.† To further elucidate the binding mode, ^1H NMR-titration experiments were conducted. As shown in Fig. 4, the downfield shift of the N*H* thiourea proton and upfield shift of the naphthyl proton were observed, which may be due to anion complexation and conformational organization.[11] Upon addition of 2 and 5 equiv. of Zn^{2+} and Cu^{2+}, respectively, to the solution of **L1**, the solution turned from colorless to pink (Fig. 4A), and the absorbance was significantly enhanced with a new peak appearing at around 558 nm. (Fig. 5), clearly suggesting the formation of the ring-open amide form of **L1** as a result of cations binding.[12]

The addition of 5 equiv. of Cu^{2+} induced a relatively larger change in both the spectrometric and colorimetric results than that of 2, 5 equiv. of Zn^{2+} and 2 equiv. of Cu^{2+}, as demonstrated in Fig. 5a. The SIRKO program of the UV-vis titration curve assumed a 1:1 stoichiometry for the **L1**-Cu^{2+} complex with log β = 5.78. This binding mode was also supported by the data of Job's plots and mole ratio plots evaluated from the absorption and emission spectra of **L1** and Cu^{2+} (Fig. S4 and S5†).

Table 1 Stability constants (log β)[a] of 1:1 complexes of **L1** and **L1**·Cu^{2+} with anions in MeCN by UV-visible titration method (T = 25 °C)

Anions	**L1**	**L1**·Cu^{2+}
F^-	2.56 (0.08)	4.09 (0.08)
Cl^-	2.59 (0.03)	nc[b]
Br^-	2.74 (0.09)	nc[b]
I^-	2.61 (0.02)	nc[b]
NO_3^-	2.76 (0.09)	nc[b]
ClO_4^-	2.74 (0.01)	nc[b]
$H_2PO_4^-$	2.12 (0.04)	4.05 (0.05)
CH_3COO^-	3.12 (0.09)	5.15 (0.07)
$PhCOO^-$	4.44 (0.09)	3.92 (0.03)

[a] Mean values derived from at least three independent determinations with the standard deviation σ_{n-1} in parentheses. [b] nc = no observable change in the UV-vis and fluorescent spectrum upon addition of the indicated anions.

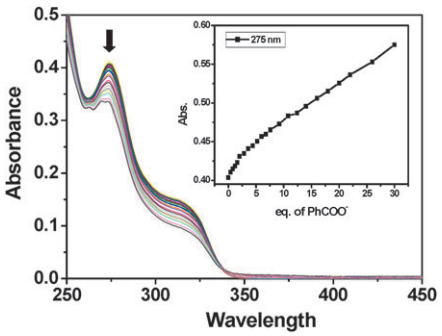


Fig. 2 Spectral change in the UV-vis absorption of **L1** (C_L = 10 μM) upon addition of $PhCOO^-$ (C_A = 0.4 mM) in MeCN ($0 \le C_A/C_L \le 30$).

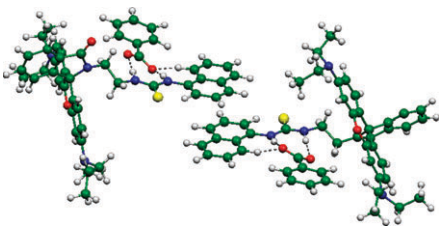


Fig. 3 Proposed binding modes of **L1** + $PhCOO^-$ (2:2).

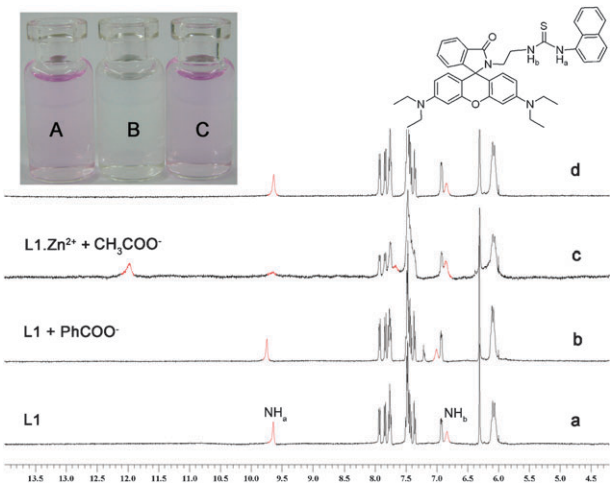


Fig. 4 ^1H NMR spectra (400 MHz, DMSO-d_6) of (a) **L1**, (b) **L1** ⊃ $PhCOO^-$ 1.5 equiv., (c) **L1**·Zn^{2+} ⊃ CH_3COO^- 5 equiv., (d) **L1**·Zn^{2+} after treatment with dilute NaOH and eluted through a silica column. Inset: Visible color changes of (A) **L1** (10 μM) after the addition of 5 equiv. of Cu^{2+} and **L1**·Cu^{2+} after the addition of (B) CH_3COO^-, $PhCOO^-$, F^-, $H_2PO_4^-$ and (C) other anions.

Upon irradiation at 300 nm, the fluorescent spectrum of **L1** shifted to 584 nm, the region of the energy acceptor (E_m-FRET *ON*). A statistically significant increase (almost 300-fold enhancement of I_F/I_0) of fluorescence at 584 nm was observed, that is, Cu^{2+} ion induced the formation of ring-opened RhBs[11] with a strong fluorescence E_m-FRET process (Scheme 1, Fig. 5). To confirm that FRET was originated from excimer formation, Cu^{2+} was added to **1** at the same condition and the spectrum was recorded. The spectrum showed no evident emission at 548 nm as

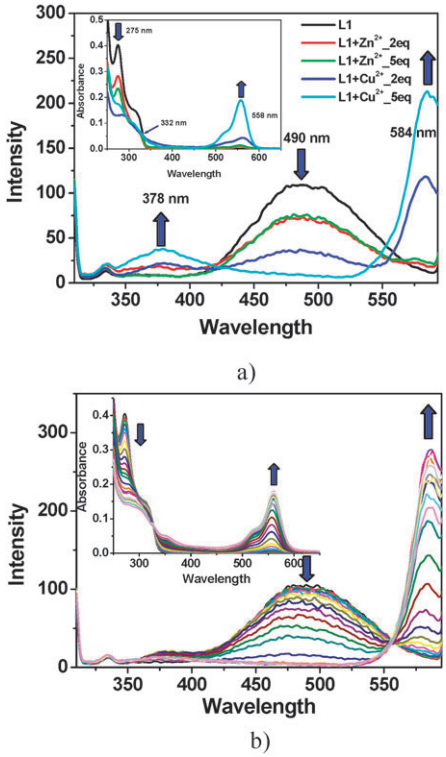
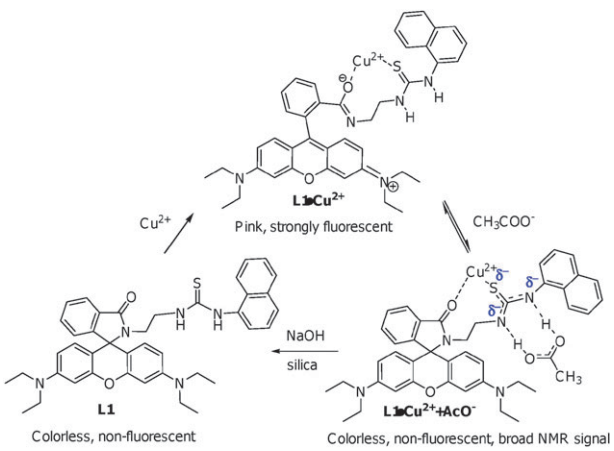


Fig. 5 (a) Absorption and fluorescence spectra of **L1** (10 μM) in MeCN upon addition of 2 and 5 equiv. of Cu^{2+} and Zn^{2+} ions, and (b) upon addition of different amounts of Cu^{2+} ions (λ_{ex} = 300 nm, λ_{em} = 584 nm).

demonstrated in Fig. 6. In addition, we further investigated the time evolution of the responses of **L1** (10 μM) in the presence of 5.0 equiv. of Cu^{2+} in MeCN. As shown in Fig. S6,† the recognition interaction was completed after addition of the Cu^{2+} for 3 h.

In order to verify that **L1** can accommodate substrates as a ditopic receptor, the selectivity of **L1** for anions in the present of Cu^{2+} was studied. Upon addition of 2.5 equiv. of CH_3COO^- to the solution of **L1**·Cu^{2+}, the color changed from pink to colorless, and the fluorescence and UV-vis spectra were immediately turned off (E_m-FRET *OFF*), which



Scheme 1 Proposed Cu^{2+}-promoted ring opening and CH_3COO^--promoted ring closing of spirolactam on RhBs.

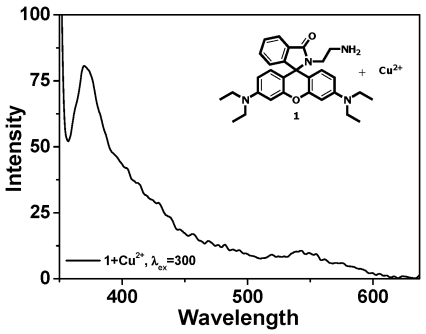


Fig. 6 Fluorescence spectra of **1** (10 μM) in MeCN upon addition of 5 equiv. of Cu^{2+}; λ_{ex} = 300 nm.

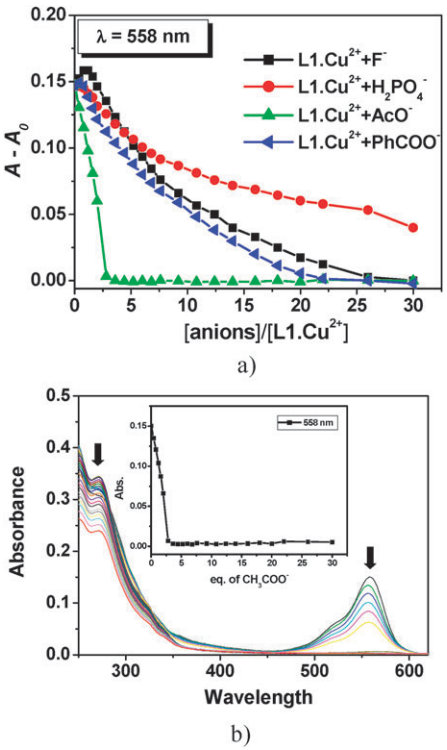


Fig. 7 (a) Mole ratio plot of **L1**·Cu^{2+} with anions at 558 nm, (b) spectral change in the UV-vis absorption of **L1**·Cu^{2+} (C_L = 10 μM) upon addition of CH_3COO^- (C_A = 0.4 mM) in MeCN ($0 \leq C_A/C_L \leq 30$).

indicates a closed-ring form of RhB (Fig. 4B, 7, 8 and S7†). No significant changes were, however, promoted by any of the other tested anions (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-) (Fig. 4C and S7†). The order of effect of anions on the E_m-FRET *OFF* process was $CH_3COO^- > F^- \approx PhCOO^- > H_2PO_4^-$ (Fig. 8). This order is the result of two phenomena, the strength of hydrogen bonding and the inductive effect. The stronger the hydrogen bond is, the easier the closure of the ring is. This also results in the stronger interaction of S of thiourea with Cu^{2+}.

The calculated association constants are summarized in Table 1. In certain cases, the presence of a metal cation increased the anion affinity of the thiourea subunit by more than 20 times, except for the $PhCOO^-$. It is possible that the

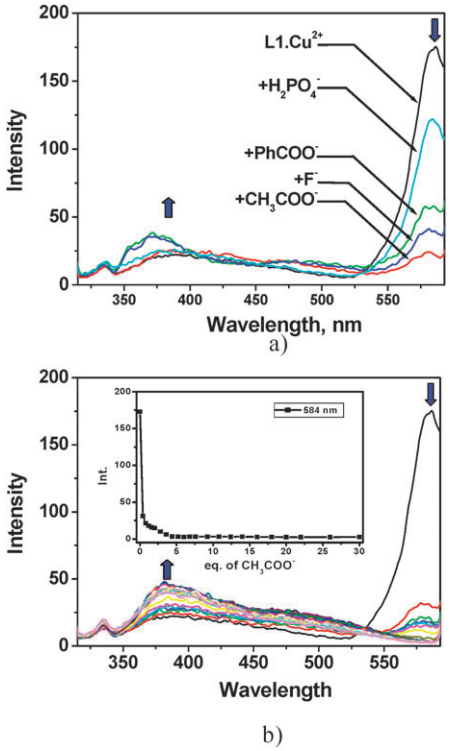


Fig. 8 Fluorescent spectral change of **L1**·Cu^{2+} (C_L = 10 μM) (a) upon addition 0.2 equiv. of various anions, (b) upon addition of different amounts of CH_3COO^- (C_A 0.4 mM) in MeCN ($0 \leq C_A/C_L \leq 30$) (λ_{ex} = 300 nm, λ_{em} = 584 nm).

steric hindrance, **L1** preorganized to bind with Cu^{2+}, blocks the $PhCOO^-$ anion. However, from the absolute values of association constants, the following cooperative factors[13] can be calculated: F^-, 1.68; $H_2PO_4^-$, 1.91; CH_3COO^-, 1.65; $PhCOO^-$, 0.88. A value <1 indicates that host/anion binding is inhibited by the steric hindrance, whereas a cooperativity factor >1 reflects host/anion binding enhancement due to the ion-pair recognition,[12] allosteric effects (induced fit)[14] and/or through-bond electrostatic effects.[8,15]

The ^{1}H-NMR spectrum (Fig. 1c) of **L1**·Zn^{2+} instantly after addition of CH_3COO^- gave rise to two sets of distinguishable broad signals for the N*H* thiourea proton at δ = 9.65 and 6.84 ppm and at δ = 11.98 and 7.67 ppm, respectively. These peaks were ascribed to the anion-free and acetate-bound forms **L1**·Zn^{2+} and were consistent with the anion-binding/decomplexation equilibrium shown on the ^{1}H-NMR time scale. Furthermore, after treated with dilute NaOH and eluted through a silica column, ^{1}H-NMR gave solid evidence for the reversible process (Fig. 4d).

In conclusion, a reversible-ditopic fluorescent and colorimetric chemosensor based on RhBs has been discovered and used as an E_m-FRET probe. Complexation studies showed that L1 was a selective chemosensor for $PhCOO^-$ due to the geometry of $PhCOO^-$ and π–π stacking interaction and turned out to bind CH_3COO^- in the presence of Cu^{2+} due to the allosteric effect, ion-pair recognition and/or through-bond electrostatic effects (Table 1, Fig. 9). The results provided a useful design strategy for the future synthesis and application of new fluorescent sensors as ditopic receptors.

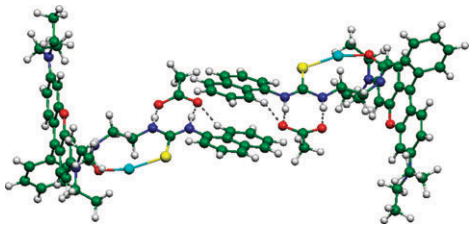


Fig. 9 Proposed binding modes of **L1**·Cu^{2+} + CH_3COO^- (2 : 2).

Experimental

General methods

NMR spectra were recorded on a Varian 400 MHz spectrometer in deuterated chloroform and DMSO-d_6. MALDI-TOF mass spectra were recorded on a Biflex Bruker Mass spectrometer using 2-cyano-4-hydroxycinnamic acid (CCA) or 2,5-dihydroxy-benzoic acid (DHB) as the matrix. ESI mass spectra were recorded on a Bruker Daltonics microTOF. UV-vis absorption measurements were performed on a Perkin Elmer Lambda 25 UV/VIS spectrometer. Fluorescent spectra were recorded using a Perkin Elmer luminescence spectrometer LS50B. Infrared spectra were obtained on a Nicolet Impact 410 using KBr pellet. Column chromatography was carried out using silica gel (Kieselgel 60, 0.063–0.200 mm, Merck). All reagents were standard analytical grade and used without further purification.

Commercial grade solvents, such as acetone, hexane, dichloromethane, methanol and ethyl acetate, were distilled before use. MeCN was dried over CaH_2 and freshly distilled under a nitrogen atmosphere prior to use.

Syntheses

Synthesis of *N*-(rhodamine B)lactam-ethylenediamine (1). This was synthesized in a manner similar to literature procedure.[16] Rhodamine B (0.20 g, 0.42 mmol) was dissolved in 30 mL of ethanol and ethylenediamine (0.22 mL, excess) was added dropwise to the solution and refluxed overnight (24 h) until the solution lost its red color. The solvent was removed by evaporation. Water (20 mL) was added to the resultant residue and the solution extracted with CH_2Cl_2 (20 mL × 2). The combined organic phase was washed twice with water and dried over Na_2SO_4. The solvent was removed by evaporation and dried *in vacuo*, affording a pale-yellow solid of **1** (0.17 g, yield 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.81 (m, 1H, Ar*H*), 7.45–7.32 (m, 2H, Ar*H*), 7.08–7.03 (m, 1H, Ar*H*), 6.42 (s, 1H, Ar*H*), 6.39 (s, 1H, Ar*H*) 6.37 (s, 2H, Ar*H*), 6.38–6.21 (m, 2H, Ar*H*), 3.32 (q, J = 6.8 Hz, 8H, NCH_2CH_3), 3.12 (t, J = 6.8 Hz, 2H, NCH_2CH_2), 2.23 (t, J = 6.8 Hz, 2H, $NCH_2CH_2NH_2$), 2.05 (s, 2H, $CH_2CH_2NH_2$) and 1.16 (t, J = 7.2 Hz, 12H, NCH_2CH_3). MS (MALDI-TOF); Calcd for $[C_{30}H_{36}N_4O_2]^+$: m/z 484.63. Found: m/z 485.91 $[M+H]^+$.

Synthesis of *N*-(Rhodamine B)lactam-*N*′-naphthylthiourea-ethylenediamine (L1). A portion of **1** (0.17 g, 0.35 mmol) and 1-naphthyl isothiocyanate (0.08 g, 0.46 mmol) were combined in fresh distilled acetonitrile (30 mL). The reaction solution was refluxed for 24 h under a N_2 atmosphere and stirred for

another 2 h at room temperature to form a white precipitate. The solid was filtrated, washed with acetonitrile three times. Crude product was purified by recrystallization from acetonitrile to give 0.15 g of **L1** (white crystal) in 65% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (s, 1H, N*H*CS), 7.92 (d, J = 7.2 Hz, 1H, Ar*H*), 7.83 (d, J = 7.2 Hz, 1H, Ar*H*), 7.79–7.73 (m, 2H, Ar*H*), 7.50–7.21 (m, 6H, Ar*H*), 7.00 (s, 1H, CSN*H*), 6.30 (s, 2H, Ar*H*), 6.09 (d, J = 7.2 Hz, 4H, Ar*H*) 3.23 (t, J = 9.6 Hz, 8H, NCH_2CH$_3$), 3.17–3.08 (m, 4H, NCH_2CH_2NH) and 1.03 (t, J = 6.8 Hz, 12H, NCH$_2$CH_3). ^{13}C NMR (100 MH$_Z$, DMSO-d_6) δ 182.0, 168.0, 154.0, 152.9, 148.8, 134.5, 133.3, 130.3,128.7, 128.6, 128.3, 127.5, 126.9, 126.7, 126.2, 125.9, 123.9, 123.2, 122.9, 108.5, 105.1, 97.8, 64.4, 44.1, 42.9, 38.8 and 12.8. IR (KBr) ν 3367, 3249, 2972, 1683, 1616, 1559, 1519, 1386, 1333, 1267, 1222, 1119, 786 and 701 cm^{-1}. MS (MALDI-TOF) Calcd for $[C_{41}H_{43}N_5O_2S]^+$: m/z 669.3137. Found: m/z 670.94 $[M+H]^+$. EI-MS m/z 670.3301 $(M+H)^+$, m/z 692.3131 $(M + Na)^+$.

Synthesis of 1-butyl-3-(naphthalen-1-yl)thiourea (2). This was synthesized by a modified literature method.[17] To a solution of butylamine (0.50 g, 0.68 mL, 6.76 mmol) in dried $CHCl_3$·(20 mL) was added 1-naphthyl isothiocyanate (1.0 g, 5.41 mmol). The reaction mixture was stirred at room temperature for 15 h and then water (40 mL) was added. The organic layer was separated, washed with brine (40 mL), dried with anhydrous $MgSO_4$ and the product purified by recrystallization from acetonitrile to give 0.15 g of **2** (white crystal) in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H, ArN*H*CS), 7.87–7.78 (m, 3H, Ar*H*), 7.54–7.36 (m, 4H, Ar*H*), 5.60 (s, 1H, CSN*H*CH$_2$), 3.51 (t, J = 7.2 Hz, 2H, NCH_2CH$_3$), 1.39–1.32 (m, 4H, NCH$_2$CH_2CH$_2$), 1.18 (m, 2H, CH$_2$CH_2CH$_3$) and 0.76 (t, J = 7.2 Hz, 3H, CH$_2$CH$_2$CH_3). IR (KBr) ν 3391, 3155, 2934, 1676, 1559, 1536, 1509, 1277, 1203, 788 and 640 cm^{-1}.

Complexation studies of ligands by using UV-vis titrations

The complexation abilities of ligand **L1** with anions in the presence and absence of bound cations were investigated by spectrophotometric titration in MeCN at 25 °C. 2 mL of the 10 μM·**L1** solution were placed in a spectrophotometric cell (1 cm path length) and the spectrum was recorded from 250–650 nm. The solutions of a cation or an anion were added successively into the cell from a microburette. The mixture was stirred for 40 s after each addition and its spectral variation was recorded. The stability constants were calculated from spectrometric data using program SIRKO.[10]

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