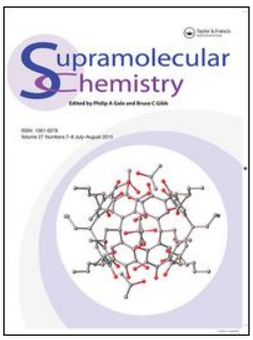

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Two new fluorescent Zn^{2+} sensors exhibiting different sensing mode with subtle structural changes

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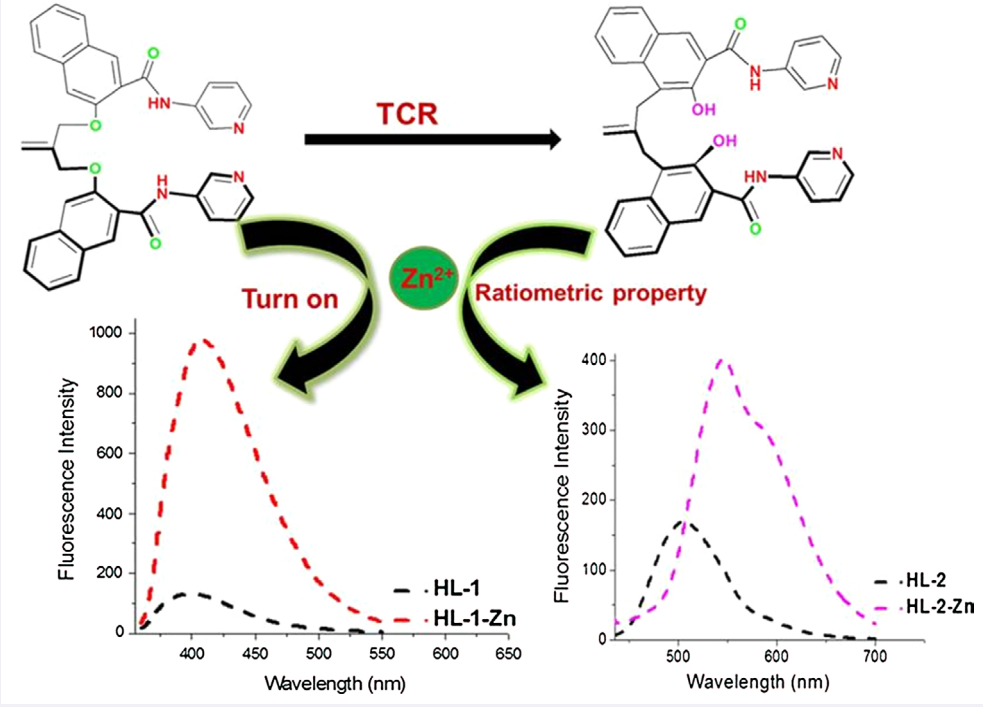
ABSTRACT

Two novel receptors **HL-1** and **HL-2** without and with hydroxyl groups were designed and synthesised. Both receptors showed highly selective coordination towards Zn^{2+} and exhibited diverse sensing behaviour due to the structural variations. **HL-1** showed monotonous 'turn-on' response towards Zn^{2+} while **HL-2** displayed highly Zn^{2+} sensitive 'turn on' and 'ratiometric' properties. Detailed Job plot experiment, single crystal data, ^{1}H NMR, ESI-MS, UV–vis and density functional theory calculation studies were conducted to understand the binding modes of **HL-1** and **HL-2** with Zn^{2+}. These results revealed the binding stoichiometric ratio between receptors and Zn^{2+} were 1:1 with low detection limits and high binding constants.



Two novel receptors **HL-1** and **HL-2** without and with hydroxyl groups were designed and synthesised via TCR reaction. Both of them showed selective coordination to Zn^{2+} ions but exhibited incongruent sensing mode due to structural variations. **HL-1** showed monotonous 'turn-on' whereas **HL-2** displayed highly sensitive 'turn on' and 'ratiometric' properties towards Zn^{2+}.

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1. Introduction

Design and synthesis of efficient fluorescent sensors for metal ions, especially transition metal ions, is a vigorous research area of supramolecular chemistry (*1–3*). During past few years, selective fluorescent sensors for Zn^{2+} have attracted great attention, owing to the biological and environmental significance (*4–6*). As a second most abundant transition metal in human body, Zn^{2+} is responsible for blood sugar (*7*), epilepsy (*8*), ischemic stroke (*9*), abnormal growth (*10*) and Alzheimer's disease (*11*). Furthermore, Zn^{2+} also has an essential role in environmental pollution, and agricultural disorders (*12*).

Although, a variety of Zn^{2+} fluorescent sensors have been designed with di-2-picolylamine (DPA) (*13*), acyclic, cyclic polyamines, quinoline, bipyridine and Schiff-bases (*14–16*). However, most of them suffered from the interference of other heavy metal and transition metal ions such as Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Hg^{+} (*17*), particularly Cd^{2+} is in the same group of the periodic table and displays identical properties to Zn^{2+} (*18, 19*). Accordingly, development of new chelators with unique fluorescent selectivity and sensitivity towards Zn^{2+} is still a hot topic in the supramolecular field.

Tandem claisen rearrangement (TCR) reaction developed by Hiratani, represents a useful strategy to construct various building blocks for supramolecular chemistry (*20*) including macrocycles (*21*), rotaxanes, catenanes (*22*) and helicate-type complexes by the efficient introduction of multiple hydroxyl groups into the structure (*23–26*).

By exploiting these building blocks, some admirable fluorescent chemosensors have been established with potential application towards anions and rare earth metals (*27*). Moreover, the building blocks before TCR and after TCR show diverse structural conformations due to the differences in structural connectivity and existence of hydroxyl groups. So, based on this efficient phenomenon, different supramolecular structures can be constructed (*25, 28*). However, no investigation on metal ion sensing was reported till now.

In present work, two novel receptors **HL-1** and **HL-2** were constructed and their selective fluorescent sensing behaviours towards Zn^{2+} ion were investigated. Both **HL-1** and **HL-2** consist of naphthalene fluorophores as signalling part and pyridine moieties act as potential chelating sites with Zn^{2+}. Isobutenyl group was introduced with two aims: (1) introducing multiple hydroxyl groups via TCR reaction readily; (2) producing certain rigidity in structure and reducing free molecular rotations via intramolecular restrictions. The key structural difference in **HL-2** and **HL-1** is relief of two hydroxyl groups via TCR, which would induce clear variation in structural conformations. We expected that this difference will show diverse sensing

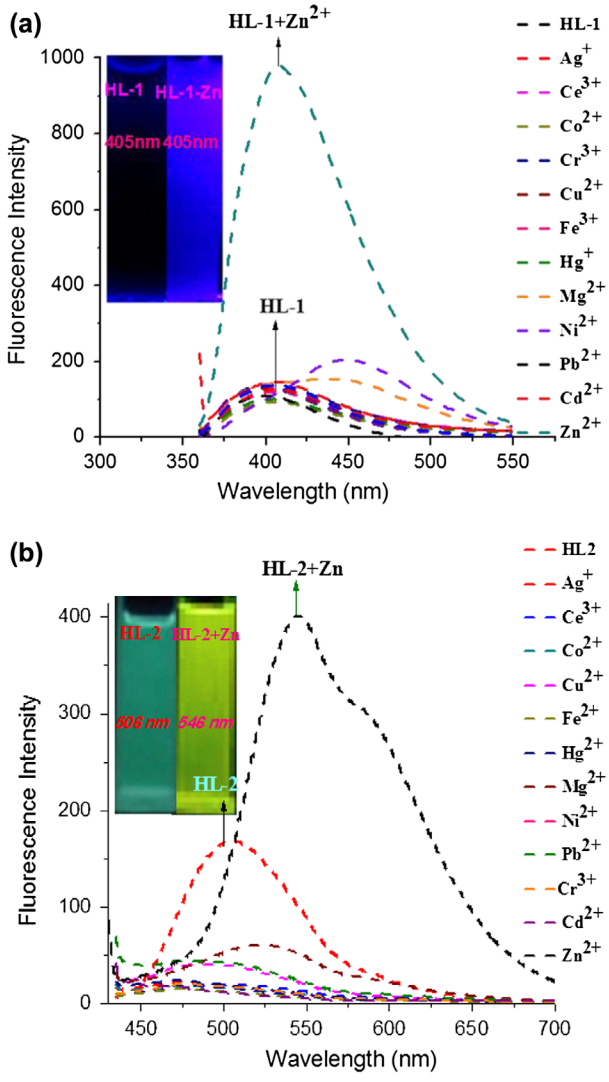


Figure 1. (Colour online) Fluorescence responses of (a) **HL-1,** (b) **HL-2** towards various metal ions (10 μM, CH_3CN /H_2O, 8:2 v/v).

ability towards Zn^{2+}. Just as expected, ligand **HL-1** showed monotonous 'turn-on' response towards Zn^{2+}, while in contrast, receptor **HL-2** displayed highly Zn^{2+} sensitive 'turn-on' along with 'ratiometric' sensing properties. The detailed sensing behaviours of receptors **HL-1** and **HL-2** towards Zn^{2+} have been investigated by fluorescence spectroscopy, UV–vis, ESI-MS experiment, X-ray crystallography, partial ^1H NMR titrations and density functional theory (DFT) calculations.

2. Results and discussion

2.1. *Fluorescence spectroscopic studies of* HL-1 *and* HL-2 *in the presence of various metal ions*

Fluorescence spectroscopic studies were recorded in CH_3CN:H_2O (8:2) with 10 μM solutions of receptors and metal ions**.** As shown in Figure 1(a), receptor **HL-1** displays

weak fluorescence emission. Upon addition of equimolar of Zn^{2+} into receptor **HL-1** showed significant enhancement in fluorescence intensity at 405 nm using excitation maxima at 353 nm, whereas no obvious fluorescent response could be observed by addition of other metal ions such as Mg^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Hg^{+}, Ag^{+} and Ce^{3+}.

This observation clearly demonstrated that receptor **HL-1** showed highly selective responsiveness towards Zn^{2+} among various other metal ions (Figure 1(a)). Unlikely, **HL-1**, receptor **HL** without C=C double bond in structure exhibited weak fluorescence enhancement with Zn^{2+} because of free intramolecular rotations (Figure S9). This result revealed that the remarkable fluorescence emission enhancement of receptor **HL-1** with Zn^{2+} ion is due to the introduction of the rigid environment, which restricted to free intramolecular rotation. Such rigidity in structure of receptor provided opportunity to coordinate with Zn^{2+}.

Interestingly, receptor **HL-2** containing two hydroxyl groups showed quite different sensing mode towards Zn^{2+} compared with receptor **HL-1**. Only receptor **HL-2** displayed weak fluorescence emission at 506 nm. Upon addition of Zn^{2+} into **HL-2** exhibited clear ratiometric fluorescence property via drastically increase in fluorescence intensity along with red shift about 40 nm. A new peak appeared at 546 nm after addition of 1 eq of Zn^{2+} leading to a striking modulation in the colour of solution from blue-green to yellow-green under the UV-lamp at 360 nm. In contrast, for all competitive metal ions, receptor **HL-2** exhibited common quenching effect (Figure 1(b)).

The fluorescent emission intensity of both receptors **HL-1** and **HL-2** are remarkably increased with increasing the concentrations of Zn^{2+} until 1.0 eq, while the emission intensity tends to be the same with further increasing the concentrations of Zn^{2+}. Furthermore, a good linear relationship ($R^2 = 0.99$) in both cases were obtained between the maximum fluorescence intensity and the minimum fluorescence intensity (Figure 2(a), Figure S6). In addition, to investigate the counter ions effect, salts other than $Zn(ClO_4)_2$ such as $Zn(NO_3)_2$, $ZnCl_2$ and $Zn(SO_4)_2$ were used which showed similar spectral changes (Figure S10).

To validate the high selectivity of **HL-1** and **HL-2** as a turn on and ratiometric chemosensors for the detection of Zn^{2+}, competitive experiments were carried out by the addition of 1.0 eq of Zn^{2+} into the **HL-1** and **HL-2** solutions in the presence of 1.0 eq of other metal ions. Receptors **HL-1** and **HL-2** could easily detect Zn^{2+} in the presence of interfering metal ions. These results demonstrated that **HL-1** and **HL-2** displayed excellent selectivity and sensitivity towards Zn^{2+} from the interference of other heavy and transition metal ions such as Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Cd^{2+} (Figure 2(b) and Figure S8).

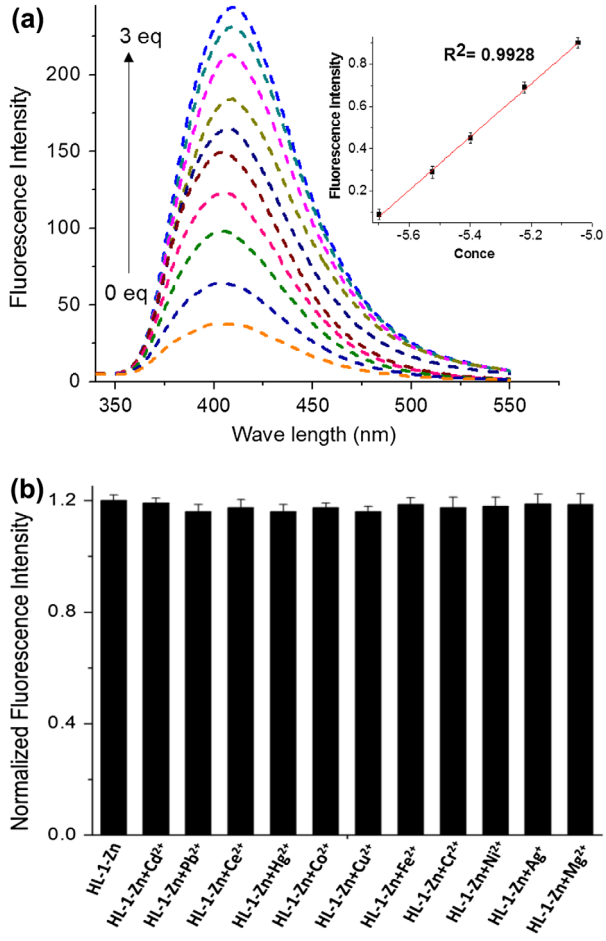


Figure 2. (Colour online) (a) Fluorescence spectra of **HL-1** with increasing the concentration of Zn^{2+}. (b) Fluorescence spectra of **HL-1-Zn** in the presence of various metal ions.

Moreover, high binding constants and low detection limits of **HL-1** and **HL-2** towards Zn^{2+} were calculated as $4.7 \times 10^7\ M^{-1}$, $2.5 \times 10^7\ M^{-1}$, and 1.29×10^{-6} M, 1×10^{-6} M by fluorescence titration experiment respectively. In order to quantify the binding ratio between both receptors **HL-1** and **HL-2** with Zn^{2+}, fluorescence Job plot experiments were carried out. The results indicated that the stoichiometric complex ratio of **HL-1** and **HL-2** with Zn^{2+} ion was 1:1 (Figure S11).

2.2. Absorption spectroscopic studies

UV–vis spectroscopic measurements were also conducted in CH_3CN:H_2O (8:2) with 10 μM solutions. Receptor **HL-1** exhibited an absorption peak at 285 nm whereas **HL-2** showed two prominent absorption peaks at 295 and 360 nm which originating from high electronic transition and long conjugation system (Figure 3(a)). Upon addition of above-mentioned metal ions into the receptors **HL-1** and **HL-2**, only Zn^{2+} induced a noticeable change in the

absorption spectra over other common metal ions (Figure S7).

As for receptor **HL-1**, absorption peak recorded at 285 nm, while after the addition of Zn^{2+} exhibited a remarkable enhancement in the absorption intensity. Upon gradual addition of Zn^{2+} into **HL-1**, its absorbance intensity was significantly enhanced with the absorption peak centred at 285 nm. This process was indicating the formation of a well-defined complex between **HL-1** and Zn^{2+} (Figure S7c). Furthermore, upon incremental addition of Zn^{2+} into receptor **HL-2,** both bands showed clear bathochromic shift from 295 to 305 and 360 to 370 nm along with red shift about 10 nm (Figure 3(b)). Essentially, these absorption spectra also demonstrated that the receptors **HL-1** and **HL-2** have unique, diverse and outstanding selectivity and sensitivity response towards Zn^{2+}.

2.3. Partial ^{1}H NMR of HL-1 and HL-2 with Zn^{2+}

To further investigate the differences in molecular structure of **HL-1** and **HL-2**, we recorded ^{1}H NMR spectra, which showed the characteristic distribution in chemical shifts. In previous studies, Hiratani et al. reported ^{1}H NMR signal of several compounds based on conformational changes in isobutylene chain. These compounds were classified into three groups such as (a) skew–skew (b) syn–skew (c) syn–syn conformers with respect to conformation–chemical shift relationship (*29, 30*).

Based on the conformation–chemical shift correlation, we were able to follow the key structural differences between two receptors. According to the theoretical calculation (DFT), receptor **HL-1** (C=C–C–O) adopted syn–skew, while **HL-2** (C=C–C– (Neph) followed syn–syn conformation with respect to the isobutylene chain (Figure 4). In this study, we focused on isobutylene protons such as H-1 and H-2 which showed comparatively large changes in chemical shift.

In receptor **HL-1**, the chemical shift of protons H-1 and H-2 were recorded at δ 5.70 and δ 5.04 ppm, while shifts of **HL-2** were observed at δ 4.41 and δ 4.03 ppm, respectively. This result indicates that in receptor **HL-2**, protons H-1 and H-2 undergo more shielded due to the presence of two –OH groups and ring current effect. The upfield shifting of H-1 and H-2 revealed that receptor **HL-2** follows syn–syn conformation which is fully consistent with its dihedral angle of calculated structure (3°, 9°). While the chemical shifts of receptor **HL-1** adopted syn–skew conformation. Interestingly, this result was also in agreement with the conformations of the isobutenylene moiety, which was observed via dihedral angle of calculated structure (9°, 111°). This conformation–chemical shift correlation results suggested that these two receptors have different structural conformations.

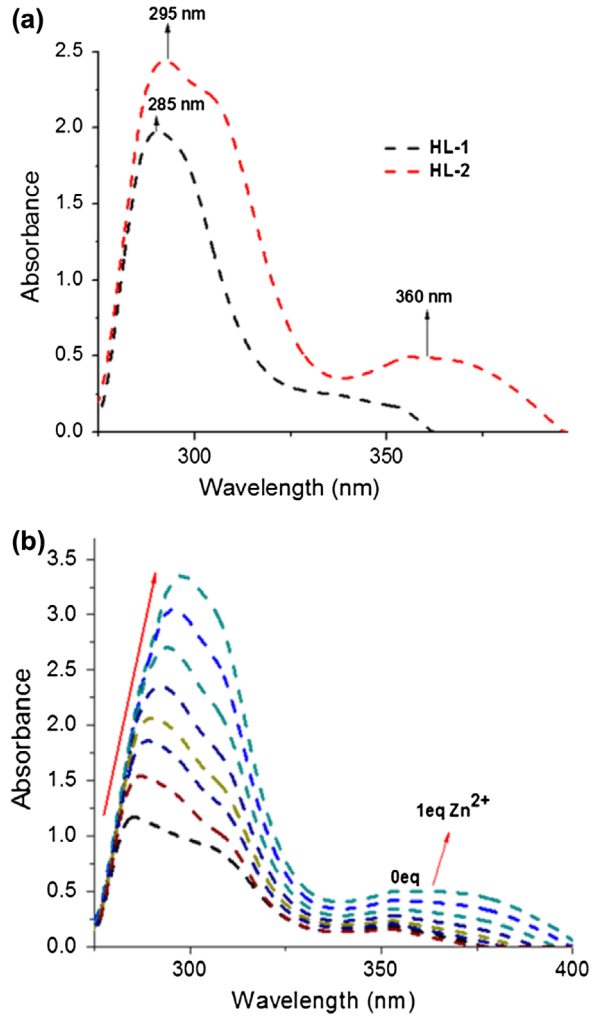


Figure 3. (Colour online) (a) Absorption spectroscopy of **HL-1** and **HL-2** (10 μM) in CH_3CN:H_2O (8:2) and (b) with incremental addition of Zn^{2+} into receptor **HL-2**.

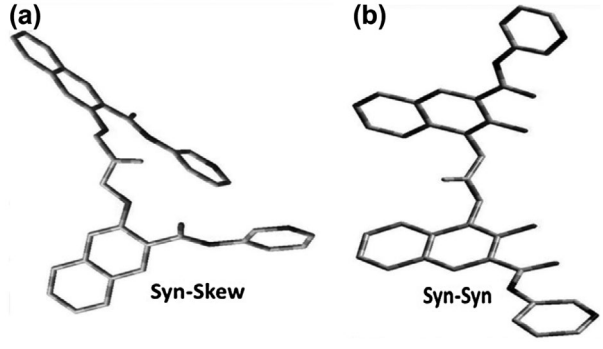


Figure 4. Proposed conformational structure of receptors (a) **HL-1** and (b) **HL-2**.

To further elucidate the nature of coordination and conformational changes of **HL-1** and **HL-2** after binding with Zn^{2+}, we carried out partial ^{1}H NMR titrations in CD_3CN. Chemical shifts of H-1 and H-2 of both free receptors

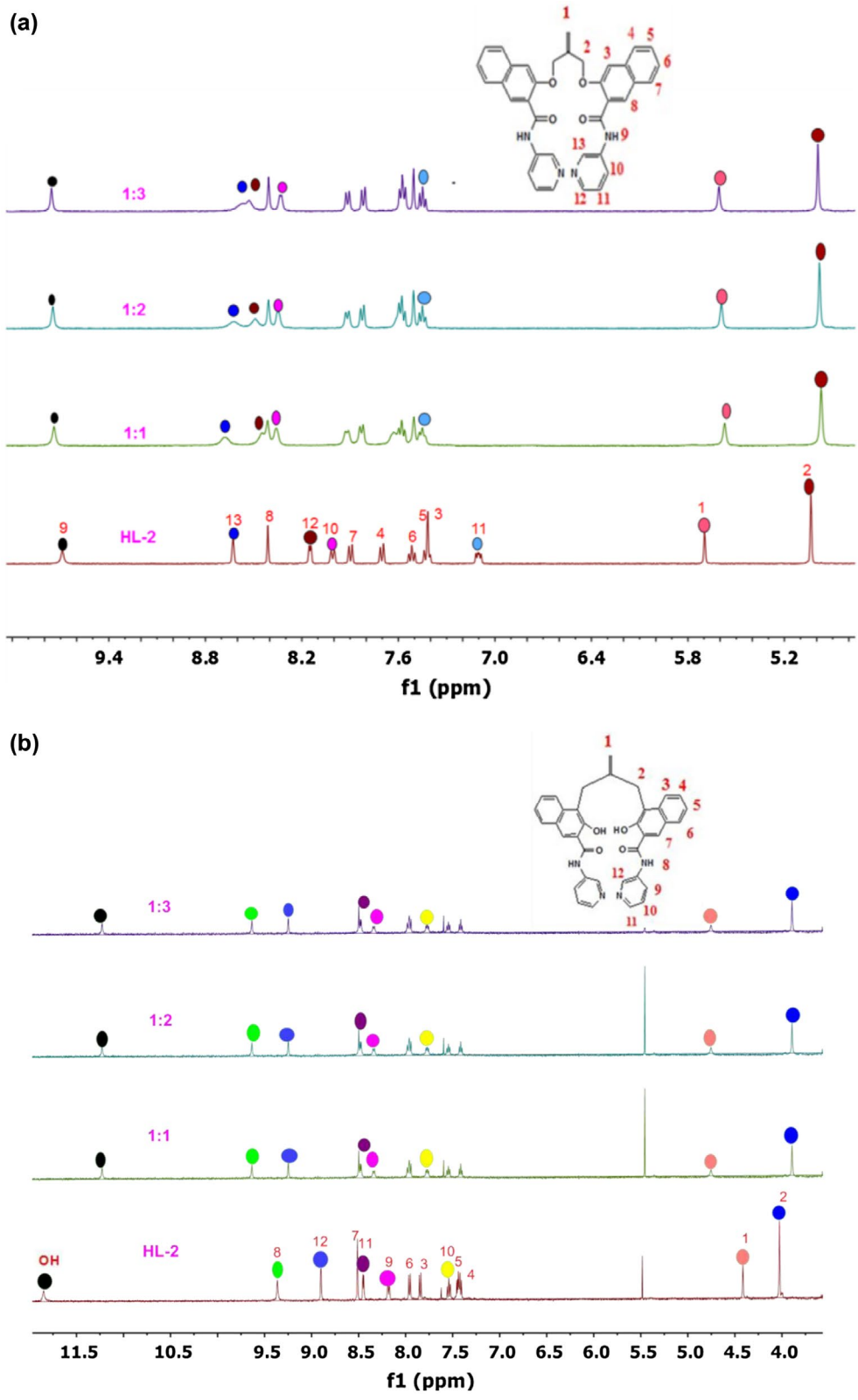


Figure 5. (Colour online) Partial ^{1}H NMR with increasing concentration of Zn^{2+} in CD_3CN at room temperature (a) **HL-1** and (b) **HL-2.**

and their Zn-complexes are shown in Figure 5. For **HL-1**, upon addition of Zn^{2+} protons H-1 and H-2 were shifted towards upfield from 5.70 to 5.55 ppm and 5.04–4.95 ppm, respectively.

This result indicated that conformational structure of **HL-1-Zn** adopted as syn–syn which deviated from syn–skew conformation of free receptor **HL-1**. Whereas in **HL-2** upon addition of Zn^{2+}, H-1 and H-2 shifted quite opposite

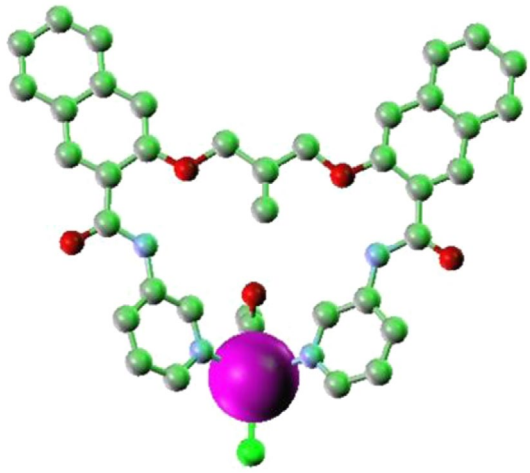


Figure 6. (Colour online) X-ray crystal structure of **HL-1-Zn.**

to each other, H-1 experienced downfield shift from 4.41 to 4.75 ppm and H-2 shifted towards upfield 4.03–3.89 ppm due to the non-equivalent chemical and electronic environments. This result revealed that the conformation of the complex **HL-2-Zn** adopted as skewed-trans (50°, 30°) C=C–C–C (Neph) which diverged from the syn–syn conformation of the free receptor through the steric effect of two –OH groups, anisotropic effect, γ-steric effect and ring current effects. On the other hand, upon addition of Zn^{2+} in **HL-1**, all pyridine protons shifted towards downfield along with a reduction in intensity, such as H-13, H-12, H-11 and H-10 from δ 8.63, 8.15, 7.11, and 8.02 ppm to 8.67, 8.46, 7.50 and 8.36 ppm. Similarly, in **HL-2** clear downfield shifting were noted in pyridine moieties, while –OH protons shifted towards upfield from 11.85 to 11.22. Hence, both receptors showed minute changes in naphthalene platform as compared to the other protons within the system. Collectively, ^{1}H-NMR titration suggested the *N*-atoms of pyridine moieties are strongly coordinated with Zn^{2+}.

2.4. ESI-MS experiment

The binding mode of **HL-1** and **HL-2** with Zn^{2+} were also investigated by ESI-MS. Mass spectra of complexes **HL-1-Zn** [$C_{36}H_{28}N_4O_4$ + Zn] and **HL-2-Zn** [$C_{36}H_28N_4O_4$ + Zn] recorded at '321.9888' and '643.1281', respectively (Figure S2 and Figure S4). So ESI-MS results, single crystal data, DFT calculations were consistent with the results of emission spectroscopy, UV–vis, and partial ^{1}H NMR titrations, which revealed that the stoichiometric ratio was 1:1 in complexes **HL-1-Zn** and **HL-2-Zn**.

2.5. Signalling mechanisms of Zn^{2+} ion with HL-2 and HL-1

Initially, the weak fluorescence of receptors **HL-1** and **HL-2** may be due to the free molecular rotation, less conjugation system, non-planer structures in solution. The turn-on and ratiometric fluorescence properties of receptors **HL-1** and **HL-2** after coordinating with Zn^{2+} may be attributed to different signalling mechanisms. As for **HL-1**, fluorescence enhancement can be ascribed to the conformational restriction by CHEF effect, while for **HL-2**, ratiometric fluorescence change can be attributed to the binary signalling mechanism like ICT and conformational restriction via CHEF effect.

As illustrated in single crystal structure (Figure 6), complex **HL-1-Zn** followed by chelation of the Zn^{2+} with the N-atoms of pyridine groups. Consequently, the free rotation of receptor gets restricted and the system becomes more rigid and planar. Additionally, due chelation of Zn^{2+} with *N*-atoms of pyridine moieties drastically increased the electronic mobility through conjugations resulting in remarkable enhancement in the fluorescence intensity (*31*).

Moreover, in the presence of Zn^{2+}, emission colour readily modulated from blue (**HL-1-Zn**) to yellow-green (**HL-2-Zn**) under the UV-lamp at 360 nm, which is critically dependent on the molecular structure and higher electron mobility in the π-conjugation system. Compared with **HL-1**, receptor **HL-2** has two additional –OH groups and two newly formed C–C bonds which were introduced via TCR reaction. These –OH groups do not get involved in the binding processes but only acted as electron-donating groups to regulate the electronic system, and promote electrons from donor to acceptor via excitation. Furthermore, according to the theoretically optimised structure, as **HL-1**, receptor **HL-2** also chelated with Zn^{2+} by *N*-atoms of pyridine moieties, owing to changes in the structural conformation of **HL-2-Zn**. These results subsequently lead to binary sensing mechanism as ICT and conformational restrictions via CHEF effect. The molecular restrictions via CHEF effect in the combination with ICT process upon interacting with Zn^{2+} perhaps results in the enhancement of the fluorescence intensity along with a red shift of ~40 nm.

Further, above evidence of our proposed sensing mechanism were verified by the theoretical calculation of **HL-1**, **HL-2,** and complexes **HL-1-Zn**, **HL-2-Zn**. To identify the optical response of receptors towards Zn^{2+} and the association between the structural changes of receptors and complexes, we carried out DFT calculations with the B3LYP/6-31 + G (d, p). The optimised geometries along with highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) of both receptors (**HL-1, HL-2**) and complexes (**HL-1-Zn, HL-2-Zn**) were calculated and presented in Figure 7. HOMO and LUMO energy diagrams showed that the energy gap for the complexes **HL-1-Zn** and **HL-2-Zn** were reduced as compared to the free receptors. This result revealed the fluorescence enhancement due to strong coordination with

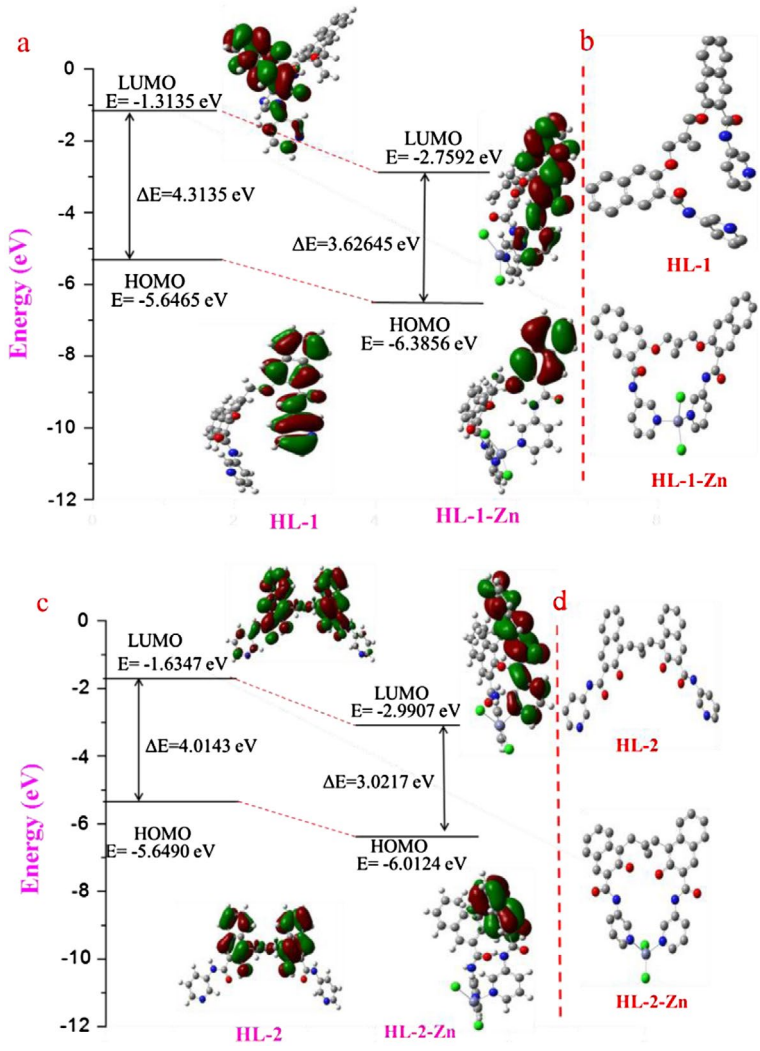


Figure 7. (Colour online) Energy diagrams of HOMO and LUMO orbitals of **HL-1** and **HL-1– Zn** (a) **HL-2** and **HL-2-Zn** (c). Optimised structures of **HL-1** and **HL1–Zn** (b) **HL-2** and **HL-2–Zn** (d).

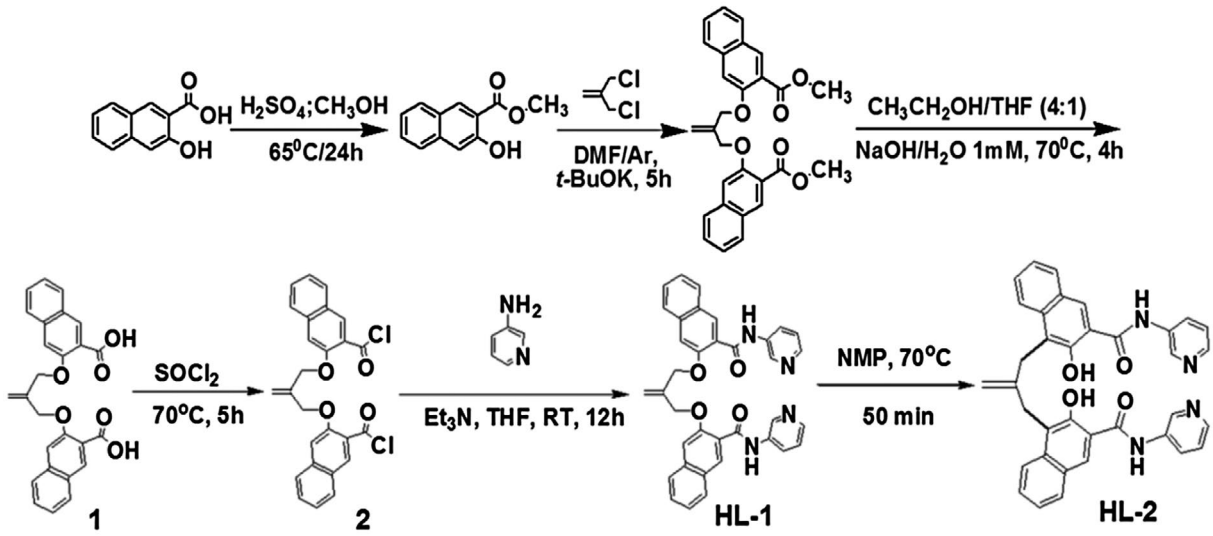
Zn^{2+}. Besides that, the HOMO–LUMO energy gap of the complexes **HL-1-Zn** and **HL-2-Zn** were also decreased successively from 3.626 to 3.021 eV. This result perhaps led to the fluorescence enhancement along with red shift (40 nm) upon chelation of the **HL-2** with Zn^{2+} ions in the proposed fashion. These results indicated that receptors **HL-1** and **HL-2** are strongly coordinated with Zn^{2+} formed stable complexes with significant changes in geometry and structural conformations. Furthermore in **HL-1-Zn** distances of N1–Zn (2.13Å) and N2–Zn (2.14 Å), while in complex **HL-2-Zn** distance between N1–Zn (2.13Å) and N2–Zn (2.15 Å) were in the range of typical coordination bond distances, besides that, clear variations were also recorded in dihedral angles of free receptors and complexes. (Figure S13). These results expected to play an essential role in stabilising the molecules. Selected orbitals and their corresponding energies for both receptors and Zn-complexes shown in Figure 7 might have been playing a vibrant role in the optical spectral outcome.

3. Experimental

3.1. Instruments and reagents

All required chemicals were obtained from commercial suppliers unless otherwise specified. Solvents such as dichloromethane, ethyl acetate, petroleum ether and methanol were used without distillation. Anhydrous DMF and THF were dried and distilled immediately prior to use. ^{1}H NMR spectra were recorded on Bruker AVANCE-400 spectrometer. Mass spectra were obtained on Agilent 6310 MS spectrometer and Q-TOF MS spectrometer. UV–vis spectra were recorded using HITACHI U-4100 spectrophotometer. Fluorescence spectroscopic measurements were conducted on JASCO FP-8500 spectrofluorimeter.

For absorption and fluorescence measurements, receptors were dissolved in CH_3CN to obtain 1 mM stock solutions. These stock solutions were diluted about 10 µM with CH_3CN/H_2O (8:2 v/v) solution.



Scheme 1. Synthetic route of receptors **HL-1** and **HL-2.**

Receptor **HL-1** was synthesised according to the literature (*28*) and used as a starting material to obtain receptor **HL-2** via TCR reaction with two additional hydroxyl groups and newly formed C–C bonds. As a comparison, receptor **HL** without C=C bond was synthesised (Scheme S1) in order to explore the effect of coordination capability of receptors towards metal ions due to molecular restrictions in free intramolecular rotation. The synthetic routes to receptors **HL-1** and **HL-2** are shown in Scheme 1.

3.2. *Synthesis of compound* HL-1

Compound **2** prepared according to the literature (*28*) and used as a starting material for receptor **HL-1**. As like in literature, compound **2** (0.23 g, 0.5 mmol) was dissolved into dried THF and added dropwise into 3-aminopyridine (0.3 g, 1 mmol) containing triethylamine (0.2 g, 2 mmol) with continuous stirring at 0 °C. Subsequently, reaction mixture was stirred for 12 h at 25 °C. THF was evaporated under reduced pressure. Purification was performed by column chromatography through CH_2Cl_2/ethyl acetate (3:2) and obtained **HL-1** with 74% yield. ESI-MS m/z '603.9048' (M^++Na). ^{1}H NMR (400 MHz, CD_3CN) δ 9.69 (s, 2H, –NH2), 8.63 (s, 2H, Py-H13), 8.41(s, 2H, Nep-H8), 8.15 (d, *J* = 4, 2H, Py-H12), 8.02 (d, *J* = 8 Hz, 2H, Py-H10), 7.91 (d, *J* = 8 Hz, 2H, Nep-H7), 7.71(d, *J* = 8 Hz, 2H, Nep-H4), 7.52(t, *J* = 8 Hz, 2H, Nep-H6), 7.44–7.42 (m, 4H, Nep- H5, H3), 7.12–7.08 (m, 2H, Py-H11), 5.74 (s, 2H, H-1), 5.08 (d, 4H, H-2). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.35, 152.60, 144.42, 141.04, 139.62, 135.79, 134.69, 129.36, 128.22, 127.67, 127.39, 126.55, 126.34, 124.54, 123.62, 114.81, 107.63, 68.50 ppm.

3.3. *Preparation of* HL-1-Zn

HL-1 (0.058 g, 0.1 mmol) was dissolved in CH_2Cl_2 and was added into the CH_3CN solution of $ZnCl_2$ (0.013 g, 0.1 mmol). After two weeks, transparent X-ray crystals of **HL-1-Zn** were obtained by diffusion of diethyl ether into solution.

3.4. *Synthesis of compound* HL-2

Receptor **HL-1** (0.580 g, 1 mmol) was dissolved in 5 ml of NMP (N-methyl-2-pyradone) under the argon with constant stirring at 160 °C for 50 min. After addition of H_2O into reaction mixture, we obtained precipitations of **HL-2**, filtered and washed three times with H_2O yielded 80% pure product. ESI-MS m/z '603.2021' (M^++Na). ^{1}H NMR (400 MHz, CD_3CN) δ 11.85 (s, 2H, –H,), 9.36 (s, 2H, –NH), 8.90 (s, 2H, Py-H12), 8.51 (s, 2H, Nep-H7), 8.45 (d, *J* = 8 Hz, 2H, Py-H11), 7.97 (d, *J* = 8 Hz, 2H, Py-H9), 7.85 (d, *J* = 4 Hz, 2H, Py-H6), 7. 56 (d, *J* = 8.0 Hz, 2H, Nep-H3), 7.53 (t, *J* = 8.0 Hz, 2H, Py-H10), 7.48–7.37 (m, 4H, Nep-H5 & Nep-H4), 4.41 (s, 2H, H-1), 4.03 (s, 4H, H-2). ^{13}C NMR (100 MHz, DMSO-d6) δ 169.50, 153.69, 146.31, 145.81, 143.39, 135.71, 134.84, 129.88, 129.82, 129.74, 129.82, 127.63, 126.74, 123.94, 119.26, 117.48, 110.21 ppm.

3.5. *Synthesis of compound* HL

Synthetic procedure of **HL** is same as **HL-1.** ESI-MS m/z '569.2179', ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 2H, –NH), 8.97 (s, 2H, Py-H12), 8.29 (s, 2H, Nep-H8), 8.22 (d, 2H, *J* = 8.0 Hz Py-H11), 8.03 (d, *J* = 8.0 Hz, 2H, Py-H9), 7.97 (t, *J* = 4 Hz, 2H, Py-H10), 7.84 (d, *J* = 8.1 Hz, 2H, Nep-H7), 7.63 (m, 4H, Nep-H5, Nep-H6), 7.63 (m, 2H, Nep-H4), 7.46 (s, 2H, Nep-H3), 4.40 (s, 4H, H-2), 2.38 (s, 2H, H-1). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.80, 152.74, 143.78, 140.44,

129.42, 128.61, 127.90, 127.42, 127.10, 126.65, 126.10, 124.04, 123.35, 106.90, 64.79, 28.00 ppm.

3.6. Preparation of sample solution for analysis

About 1 mM stock solutions of receptors **HL**, **HL-1,** and **HL-2** were prepared in CH_3CN solvent. Wherein prepared 10 μM dilute solution in CH_3CN/H_2O (8:2 v/v) for sample analysis. Meanwhile, solutions of metals salts were also prepared in CH_3CN:H_2O. All the metal ions were mixed with receptors **HL**, **HL-1,** and **HL-2** in 1:1 ratio at 25 °C to investigate the recognition properties.

4. Conclusion

In conclusion, we synthesised and demonstrated two novel receptors **HL-1** and **HL-2** exhibiting incongruent sensing mode due to dissimilar conformational structures. Based on conformational–chemical shift described the structural variations in both receptors. Furthermore, differences in molecular conformation in **HL-1** and **HL-2** were also observed after coordination with Zn^{2+}. Complex **HL-1-Zn** changed towards syn–syn while **HL-2-Zn** adopted as skewed-trans from syn–skew and syn–syn conformations of free receptors, respectively.

The Job's plots, ^{1}H NMR, ESI-MS experiments, single crystal data and DFT calculations showed the stoichiometric ratio of receptors and Zn^{2+} ion were 1:1. Further due to differences in molecular structure of both receptors exhibited different signalling mechanisms. The working signalling mechanism in **HL-1** is conformational restriction through CHEF effect. Conversely for **HL-2,** the sensing mechanism functions via binary signalling mechanisms like ICT in combination with conformational restriction via CHEF effect. Investigations along these lines for the development of more sophisticated systems based on the same signalling mechanisms for recognition of cations and anions are in progress in our laboratory.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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