

Dipyrrolylquinoxaline-bridged hydrazones: a new class of chemosensors for copper(II)

Qian-ni Guo · Cheng Zhong · Yun-guo Lu ·
Chuang Shi · Zao-ying Li

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Abstract Novel 2,3-bis(1*H*-pyrrol-2-yl)quinoxaline-functionalized hydrazones were prepared and characterized as new chemosensors for copper(II) ion. The binding properties of the compounds **4**, **5**, **6** and **7** for cations were examined by UV–vis, fluorescence spectroscopy, and linear sweep voltammetric experiments (LSV). The results indicate that a 1:1 stoichiometric complex is formed between compound **4** (or **5**, **6**, **7**) and copper(II) ion, and the association constant is $1.3 \times 10^5 \text{ M}^{-1}$ for **4**, $2.1 \times 10^6 \text{ M}^{-1}$ for **5**, $4.1 \times 10^5 \text{ M}^{-1}$ for **6** and $8.0 \times 10^5 \text{ M}^{-1}$ for **7**, respectively. The recognition mechanism between compound **4** (or **5**, **6**, **7**) and metal ion was discussed based on their electrochemical properties, absorbance changes, and the fluorescence quenching effect when they interact with each other. Control experiments revealed that compound **4** (or **5**, **6**, **7**) has a highly selective response to copper (II) ion.

Keywords Chemosensor · Selectivity · Sensitivity

Introduction

The design of artificial chemosensors for selective and sensitive quantification of biologically and environmentally important ion species, especially transition-metal ions, has attracted wide-spread interests of chemists, biologists, clinical biochemists and environmentalists in recent years. Because of their advantages of simple instrumentation, high sensitivity and facile analysis, many efficient chemosensors for transition-metal ions have been developed during the last

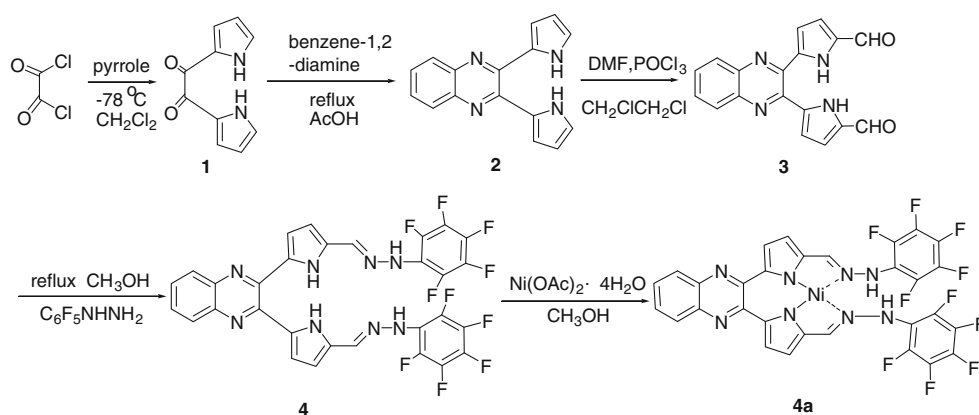
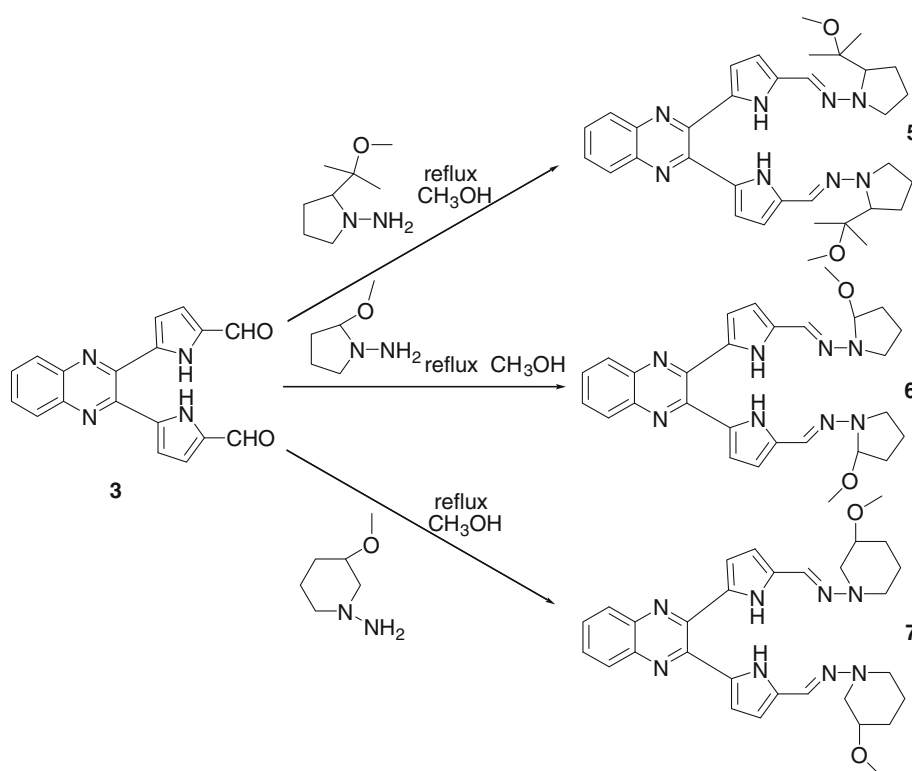
two decades [1–6]. Among the transition metal ions of interest, divalent copper, Cu^{2+} , is particularly attractive, because it is not only an environmental pollutant at high concentrations, [7, 8] but also an essential trace element for many biological process and systems [9, 10]. Therefore, many excellent work of Cu^{2+} sensing by synthesized colorimetric/fluorescent probes has been reported and investigated [11–16]. However, there is still an intense demand for new efficient Cu^{2+} chemosensors, especially those that can work with high selectivity and sensitivity. Work related to this area is of great challenge and increasing interest.

The Schiff bases (SB) are known to form stable complexes with transition metal ions. Almost all of metals form 1:1 metal complexes with SBs. The feature of SBs gives geometric and cavity control of host–guest complexation and modulation of its lipophilicity, and produces remarkable selectivity, sensitivity and stability for a specific ion. The resulting SB complexes have attracted increasing attention in the area of ionic binding due to their unique properties and reactivity. Schiff bases with N and O as donor atoms are well known to form strong complexes with transition metal ions [17]. Since the structure of hydrazones is similar to the Schiff bases, they have similar properties of Schiff bases [18].

The dipyrrolylquinoxaline (DPQ) derivatives have been reported as anion receptors,[19–22] but to the best of our knowledge, they have only been employed as cation receptors for mercury(II) [23].

In this article, we wish to develop a new chemosensor by using dipyrrolylquinoxaline as the basic fluorophore, pyrrole and the hydrazone as the recognition site. Due to the change in the electronic density of the chromophore induced by complexation, when the ionophore moiety is complexed to a metal ion, remarkable changes in the fluorescence intensity and the absorption spectra appear [24, 25]. Since the recognition site is now part of the fluorophore, when it is

Q. Guo · C. Zhong · Y. Lu · C. Shi · Z. Li (✉)
College of Chemistry and Molecular Sciences, Wuhan
University, Wuhan 430072, People's Republic of China
e-mail: zyliwuc@whu.edu.cn

Scheme 1 Synthesis of ligand **4** and complex **4a****Scheme 2** Synthesis of ligands **5**, **6**, and **7**

conjugated with the cation in solution, the analytical potential of the system should be greatly enhanced. The metal ion binding affinity is adequately controlled by the cavity size of the molecular clamp. As expected, synthetic compounds have the advantage of detecting Cu^{2+} ion. The cation binding can be visualized by changes in the UV–vis absorption spectrum, fluorescence spectrum, linear sweep voltammetric experiments (LSV), and can be observed by naked eyes.

Results and discussion

Synthesis and characterization of the compounds

The synthetic routes for compounds **4**, **5**, **6**, **7** and **4a** were depicted in Schemes 1 and 2. The new fluorescent sensor **4**

(or **5**, **6**, **7**) was synthesized by refluxing the methanol solution of 2,3-bis(5-formylpyrrolyl)quinoxaline and an equivalent molar amount of 1-(perfluoro-phenyl)hydrazine (or 2-(2-methoxypropan-2-yl)pyrrolidin-1-amine, 2-methoxy pyrrolidin-1-amine, 3-methoxypiperidin-1-amine) in the presence of triethylamine. The products were obtained as an orange (or red) powder in a high yield and characterized by IR, ^1H NMR, MALDI-TOF, FAB-MS and elemental analysis.

Absorbance change of **4**, **5**, **6** and **7** with copper(II) and other metal ions

As shown in Figs. 1, 2, 3 and 4, an obvious absorption of ligands **4**, **5**, **6** and **7** appeared at 396, 408, 418 and 422 nm, respectively, in acetonitrile solution, and their absorption

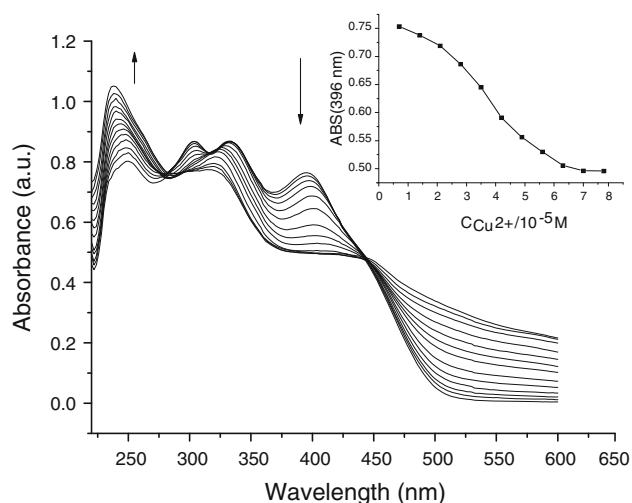


Fig. 1 UV absorbance spectra of **4** (3.0×10^{-5} mol/L) upon the addition of various amounts of Cu^{2+} . The inset shows the absorbance intensity at $\lambda_{\text{max}} = 396$ nm as a function of copper concentration

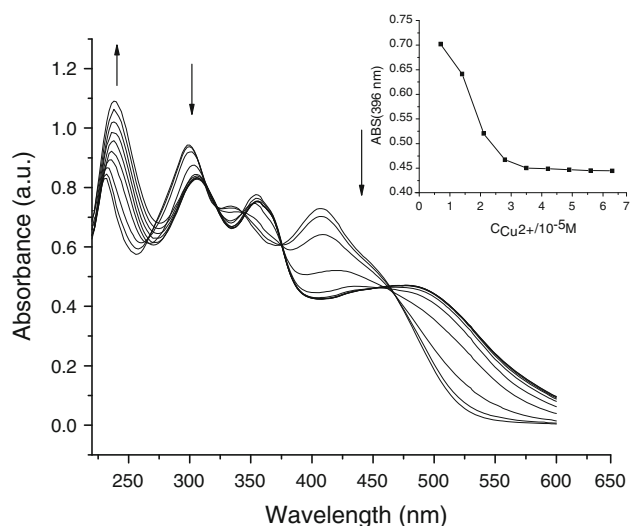


Fig. 2 UV absorbance spectra of **5** (3.0×10^{-5} mol/L) upon the addition of various amounts of Cu^{2+} . The inset shows the absorbance intensity at $\lambda_{\text{max}} = 408$ nm as a function of copper concentration

intensity also decreased gradually with an increase in Cu^{2+} ion concentration (about 10^{-6} – 10^{-5} M, linearly dependent coefficient $R^2 = 0.9896, 0.9679, 0.9890$ and 0.9742 for **4**, **5**, **6** and **7** respectively). With Cu^{2+} /ligand mole ratio $> 1:1$, a clear red shift (up to 20 nm) was observed. Isosbestic points were observed at 442, 466, 465 and 484 nm respectively for ligands **4**, **5**, **6** and **7**. As more and more Cu^{2+} solution was added to the ligand solution, the absorbance intensity got a minimum and did not change obviously any more. When considered the value of R^2 of **4**, **5**, **6** and **7**, we can find all of them were more than 0.9500, which were so closed to 1. The results showed the formation of a complex with a 1:1 stoichiometry for **4** (or **5**, **6**, **7**) and Cu^{2+} .

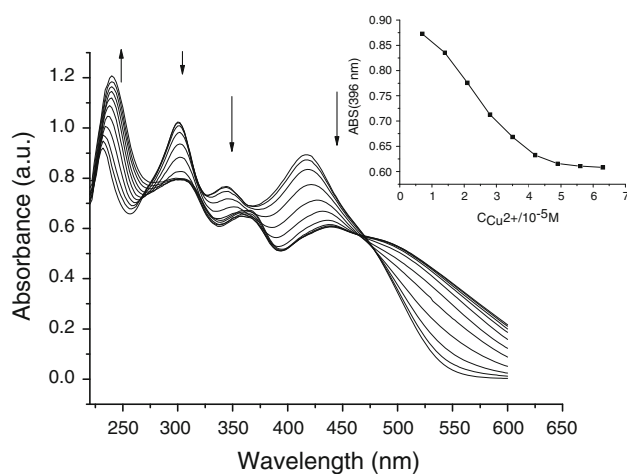


Fig. 3 UV absorbance spectra of **6** (3.3×10^{-5} mol/L) upon the addition of various amounts of Cu^{2+} . The inset shows the absorbance intensity at $\lambda_{\text{max}} = 418$ nm as a function of copper concentration

The selectivity experiments

To explore the utility of **4**, **5**, **6** and **7** as an ion-selective chemosensor for Cu^{2+} , the control experiments were conducted with Co^{2+} , Ni^{2+} , Zn^{2+} , at increase concentration (about 10^{-6} – 10^{-5} M). As shown in Fig. 5, there was virtually no obvious change of the absorbance intensity and no remarkable isosbestic point can be observed when other cations (e.g. Co^{2+} , Ni^{2+} , Zn^{2+}) were used instead of Cu^{2+} with ligand **4**. Ligand **5**, **6** and **7** showed similar properties in this context. Because cations Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} were near each other in the same periods of the elements periodic table, the sizes of them were different. The phenomenon suggested that only the size of copper (II) could fit with the ligands' cave, which indicated their prominent selectivity towards Cu^{2+} .

Determination of the association constants (K_{ass}) of complexes

For a metal complex of 1:1 stoichiometry, the association constant (K_{ass}) can be estimated according to the following relation: [26, 27]

$$X = X_0 + (X_{\text{lim}} - X_0)/2c_0 \left\{ c_{\text{H}} + c_{\text{G}} + 1/K_{\text{ass}} - \left[(c_{\text{H}} + c_{\text{G}} + 1/K_{\text{ass}})^2 - 4c_{\text{H}}c_{\text{G}} \right]^{1/2} \right\}$$

where X represents the absorbance intensity, c_{H} and c_{G} are the corresponding concentration of the host and guest. The association constants obtained by a non-linear least-square analysis of X vs. c_{H} and c_{G} are listed in Table 1. The data shows that receptors **4**, **5**, **6** and **7** have an excellent selectivity for Cu^{2+} ion.

Fluorescence titration of 4, 5, 6 and 7 with copper(II)

The sensitive signal response of compounds **4**, **5**, **6** and **7** toward Cu^{2+} were carried out in acetonitrile solution. As shown in Fig. 6, with a gradual increase of Cu^{2+} ion

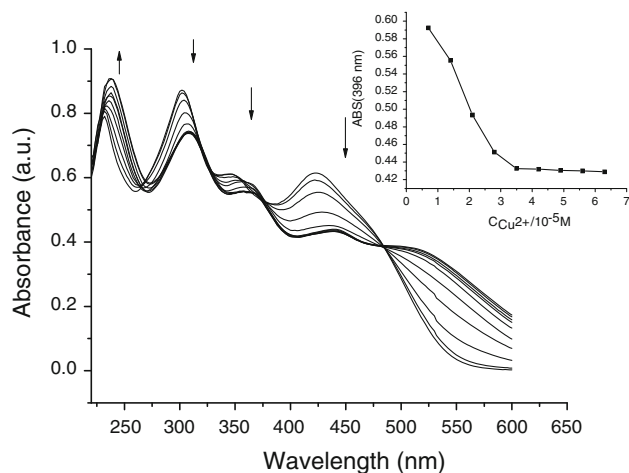


Fig. 4 UV absorbance spectra of **7** (3.4×10^{-5} mol/L) upon the addition of various amounts of Cu^{2+} . The inset shows the absorbance intensity at $\lambda_{\text{max}} = 422$ nm as a function of copper concentration

Fig. 5 a UV absorbance spectra of **4** (3.0×10^{-5} mol/L) upon the addition of various amounts of Co^{2+} , **b** UV absorbance spectra of **4** (3.0×10^{-5} mol/L) upon the addition of various amounts of Ni^{2+} , **c** UV absorbance spectra of **4** (3.0×10^{-5} mol/L) upon the addition of various amounts of Zn^{2+} , **d** UV absorbance intensity of compound **4** (3.0×10^{-5} mol/L) at $\lambda_{\text{max}} = 396$ nm as a function of cobalt (filled square), nickel (filled circle), copper (filled triangle) and zinc (filled inverted triangle) concentration

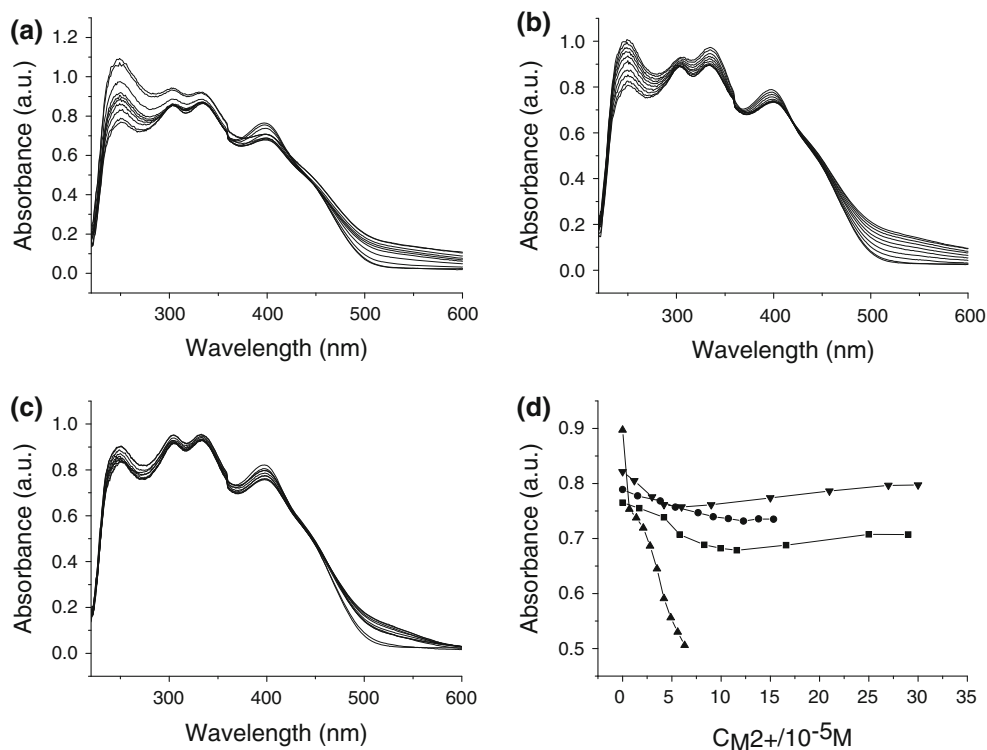


Table 1 Association constants K_{ass} of receptors **4**, **5**, **6** and **7** with guest cations

Ligand	4	5	6	7
R^2	0.9896	0.9679	0.9890	0.9742
K_{ass}	$1.3 \times 10^5 \text{M}^{-1}$	$7.2 \times 10^6 \text{M}^{-1}$	$4.1 \times 10^5 \text{M}^{-1}$	$8.0 \times 10^5 \text{M}^{-1}$

concentration, the fluorescence intensity of **7** at 496 nm was gradually reduced. Meanwhile, a blue shift was distinctly observed. The fluorescence intensity decreased linearly ($0.7\text{--}7.0 \times 10^{-5}$ M, linearly dependent coefficient $R^2 = 0.9646$ for **7**) with an increase in Cu^{2+} ion concentration. Ligands **4**, **5**, and **6** showed similar properties in this context. When the hydrazone group (the electron donor) interacts with Cu^{2+} ion, the latter reduces the electron-donating character of this group due to the reduction of conjugation, and a decrease of the extinction coefficient was expected [28, 29]. Careful analysis of the evolution of the emission spectra revealed that a 1:1 complex was formed between Cu^{2+} and compound **4** (or **5**, **6**, **7**). The sensors exhibited fluorescence quenching according to the concentration of Cu^{2+} , with a dynamic working arrange of $0.7\text{--}7.0 \times 10^{-5}$ M, respectively. In other words, the ligands **4**, **5**, **6** and **7** have remarkable sensitive fluorescence responses to Cu^{2+} .

Figure 7 showed the Job's plot of compound **5** with Cu^{2+} . The total concentration of the host and guest was constant (3.0×10^{-5} mol·L $^{-1}$) in acetonitrile, with a continuously variable molar fraction of the guest ($([\text{G}]/([\text{H}] + [\text{G}]))$). When the molar fraction of the guest

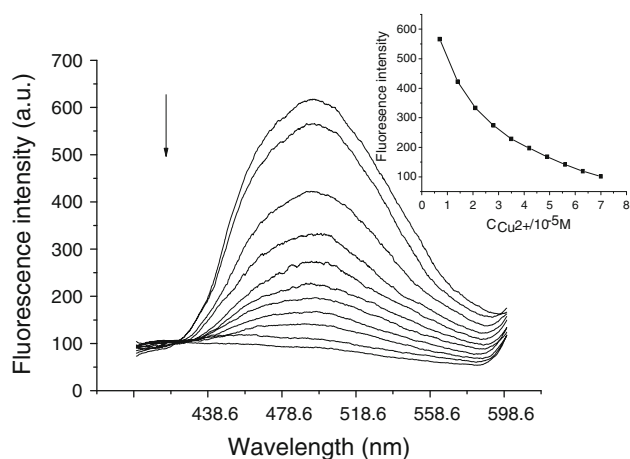


Fig. 6 Fluorescence spectra of **7** (3.4×10^{-5} mol/L) upon the addition of various amounts of Cu^{2+} , $\lambda_{\text{ex}} = 310$ nm. The inset shows the fluorescence intensity at $\lambda_{\text{max (em)}} = 503$ nm as a function of Cu^{2+} ion concentration

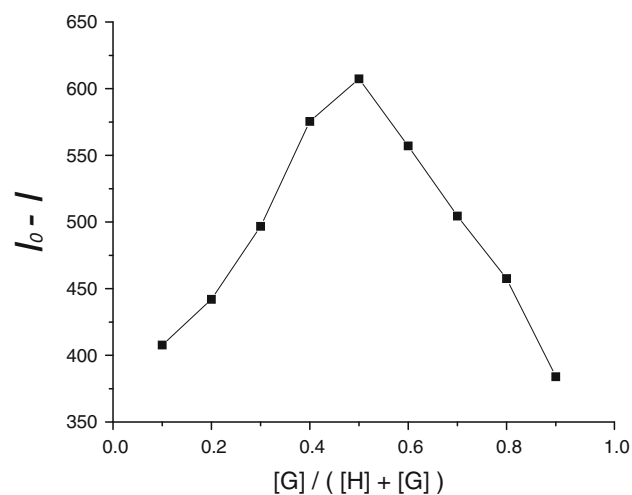


Fig. 7 Job plot of compound **5** with Cu^{2+} . The total concentration of the host and guest is 3.0×10^{-5} mol L^{-1} in acetonitrile solution. I_0 : fluorescence intensity of the host; I : fluorescence intensity of host in the presence of the guest

was 0.50, the difference of fluorescence intensity between the host and the guest reached a maximum, which demonstrated that compound **5** formed a 1:1 complex with Cu^{2+} , respectively. Ligands **4**, **6**, and **7** showed similar properties in this context.

Linear sweep voltammetric experiments (LSV)

Further, linear sweep voltammetric experiments (LSV) with compounds **3**, **4**, **5**, **6** and **7** in the presence of Ni^{2+} , Cu^{2+} and Zn^{2+} respectively were performed to ascertain the interaction between the ligands and Cu^{2+} , while compound **3** was used as control. These experiments were carried out in a solution which contained 10^{-5} M ligands in

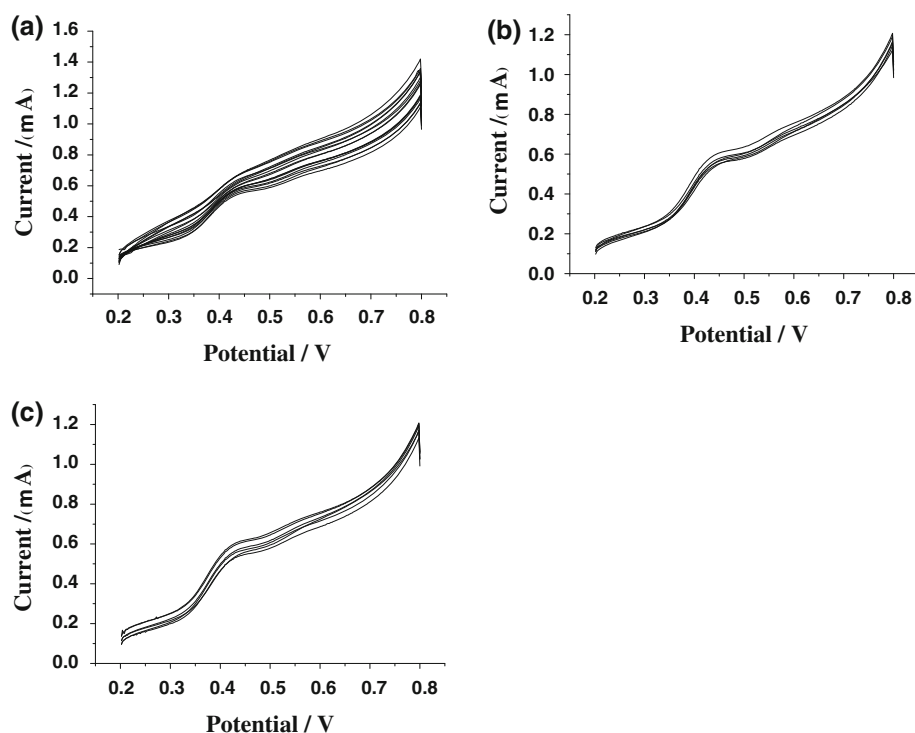
50% (v/v) acetonitrile/(0.1 M KNO_3 aqueous solution as supporting electrolyte) with a modified glassy carbon (3 mm in diameter) working electrode, and the auxiliary and reference electrodes were platinum wire and saturated calomel electrode (SCE), respectively. Deoxygenation of the solutions was achieved by bubbling nitrogen gas for at least 5 min and the working electrode was cleaned after each run. The linear sweep voltammograms were recorded with a scan rate of 100 mV S^{-1} . The Cu^{2+} was added at an increase concentration (1.05–15.75 μM). The Fig. 8 exhibited an irreversible oxidation wave at ca. + 0.43 V which may be assigned to the oxidation of the pyrrol-hydrazone group of compound **6**, since the compound **3** had no signal toward it. The addition of Ni^{2+} and Zn^{2+} caused no significant influence in the oxidation potential (+ 0.43 V) compared to the free receptor. Additionally, the oxidation wave of pyrrol-hydrazone group is anodically shifted with respect to the free receptor after the addition of Cu^{2+} . Further, the current intensity of the oxidation wave increased linearly with an increase in Cu^{2+} ion concentration. Ligands **5**, and **7** showed similar properties in this context. However, no obvious signal can be detected for ligand **4**, the possible explanation can be speculated because of the presence of the F, which made the compound difficult to be oxidated and deoxidated. Both properties above might support the formation of the complexed species and the selectivity of the ligands for Cu^{2+} . By the way, in the case of Cu^{2+} an additional redox process was observed, which was quasi-reversible. Since this was not observed in the case of Ni^{2+} and Zn^{2+} , it seemed to be metal based. However, the electrochemical instrument was not as sensitive as spectroscopic analysis, the properties of the ligands can be detected by linear sweep voltammetric experiments (LSV), which additionally supported the sensitivity of the ligands we synthesized.

Binding characteristics of computational explanation

To shed light on the binding model between various hosts (**4**, **5**, **6** and **7**) and guests (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}), their corresponding binding structures were optimized by quantum theory method, based on the crystal structure of compound **3** (CCDC 782078) we made. Worthy of note here, the optimized structures shown in Fig. 9(a–d) represented only one of the possible canonical forms for **4**, **5** **6** and **7**, respectively, and the detailed resonance structures for them are depicted in Chart 1.

In each optimized structure of the complex between the host and the guest, the metal atom was bound to four nitrogen atoms, two from the deprotonated pyrroles and two from the adjacent imines, and was almost coplanar to the respective N_4 plane. The geometry at each metal centre was square planar. When interact with Cu^{2+} , the bond length

Fig. 8 **a** LSV of **6** (3.3×10^{-5} mol/L) upon the addition of various amounts of Cu^{2+} , **b** LSV of **6** (3.3×10^{-5} mol/L) upon the addition of various amounts of Ni^{2+} , **c** LSV of **6** (3.3×10^{-5} mol/L) upon the addition of various amounts of Zn^{2+}



is the shorter than other three metal ions (Co^{2+} , Ni^{2+} , Zn^{2+}). This result was based on the optimized structure, which demonstrated the metal ions binding affinity of the ligands was molecular clamp cavity size related.

At the B3LYP/6-31 + G(d) level, the binding energy between Cu^{2+} and hosts **4**, **5**, **6** and **7** ranged from 83 to 3635 kJ/mol. This binding energy, included with zero-point correction and thermal correction at 298 K, was calculated as the electronic energy of the binding structures relative to free host and guest molecules. The binding energies obtained in the theoretical predictions are in line with the significantly large binding constants measured for Cu^{2+} and hosts **4**, **5**, **6** and **7**.

In contrast, the molecular modelling revealed that the two oxygen atoms in host **5** can serve as electrostatic force donors to interact with Cu^{2+} (bond length was 2.6 Å) as shown in Fig. 10(b) while **4** didn't have any oxygen atom and the distance between the atoms in **6** and **7** was too long (> 3.2 Å), as shown in Fig 10(a, c, d), leading to the formation of the most stable complex. As reflected in its binding constant, this additional electrostatic force interaction was comparable to that of the normal binding.

Discoloration experiments

We studied the color changes of ligands **4**, **5**, **6** and **7** in acetonitrile upon addition of various cations (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} added as their acetate salts). Significantly, as shown in Fig. 11, the yellow solutions of ligands **5**, **6** and **7** in acetonitrile all changed to red-brown upon

addition of excess of the Cu^{2+} . However, the discoloration of ligand **4** is not as obvious as others, which can be ascribed to the electron withdraw effect of F. In contrast, other cations could not trigger any color changes of the above four receptors under the same experimental conditions. The dramatic color changes made ligands **5**, **6** and **7** to be efficient colorimetric sensors for the detection of Cu^{2+} .

Conclusion

In summary, four novel chemosensors for Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} metal ions including dipyrrolylquinoxaline as chromophore **4**, **5**, **6** and **7** were successfully designed and synthesized. Compound **4**, **5**, **6** and **7** exhibited high selectivity and sensitivity for Cu^{2+} at the concentration of 10^{-5} M. A 1:1 stoichiometry was obtained from non-linear fitting of the UV–visible titration curves. The photophysical studies also revealed interesting properties of this new family when interact with Cu^{2+} : an intense absorption change around 410 nm and an obvious fluorescence quenching around 500 nm. The binding properties of the ligands can be detected by linear sweep voltammetric (LSV) titration experiments supported the sensitivity of the ligands we synthesized additionally. Meanwhile, the computational explanation demonstrated the binding characteristics from the quantum theory by bond length and binding energy. On the other hand, since the acetonitrile system can be dissolved with water, our findings will help

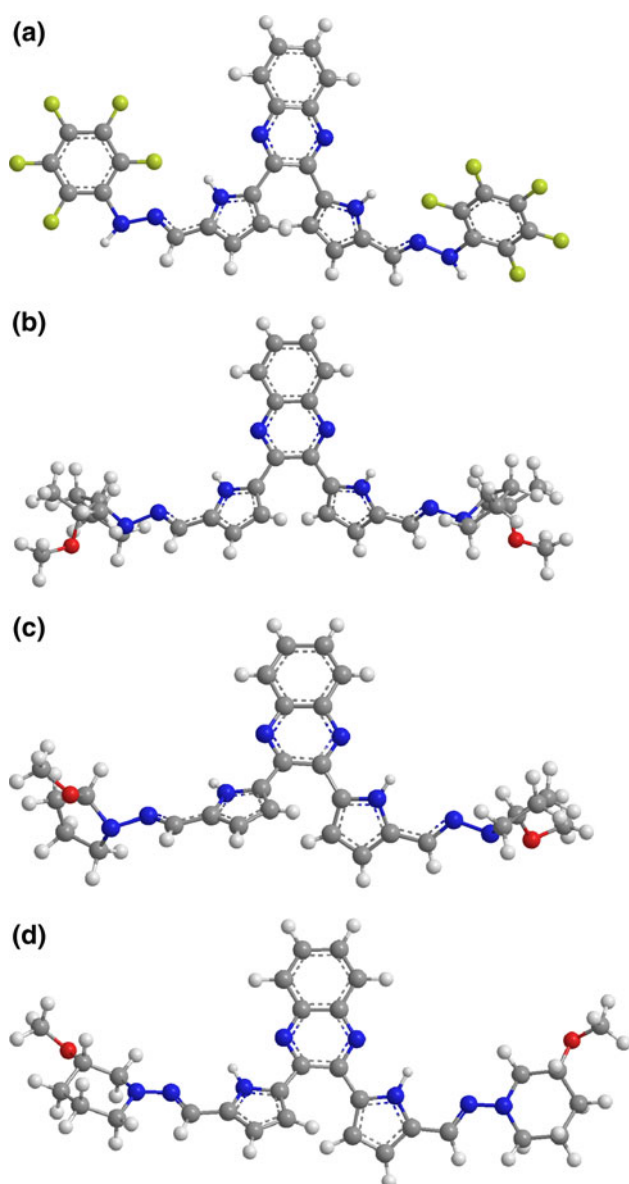


Fig. 9 The computational optimised structures of compounds 4(a), 5(b), 6(c) and 7(d)

to improve the direct detection of Cu^{2+} ion in the environment. Exploration along this direction in chemsensor development is in progress.

Experimental

General information

Unless otherwise indicated, all commercially available starting materials were used directly without further purification. Pyrrole was dehydrated and distilled prior to use. DMF and 1,2-dichloroethane were distilled from CaH_2 and stored over

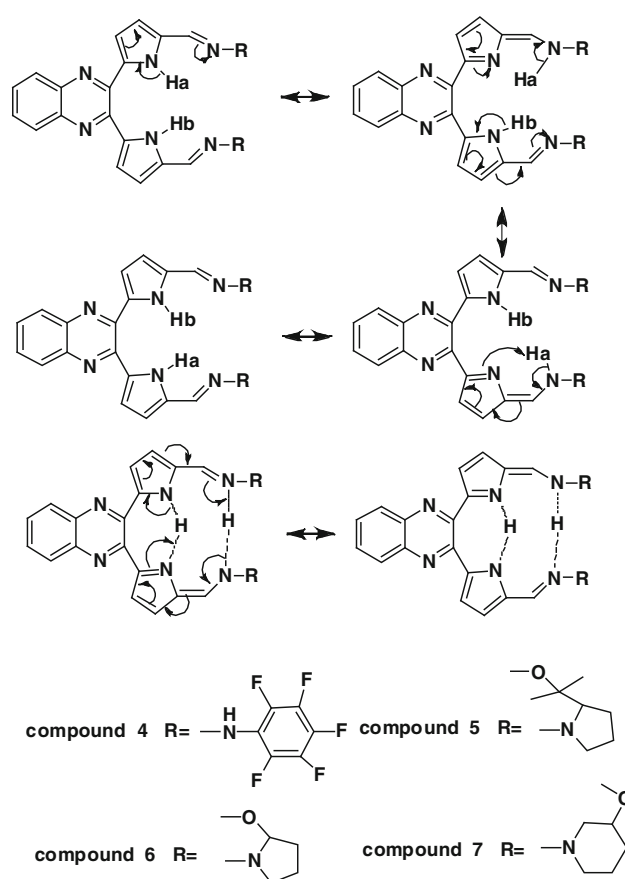


Chart 1 Resonance structures of compound 4, 5, 6, and 7

activated molecular sieves prior to use. Pyridine was distilled from NaOH and stored over activated molecular sieves prior to use. Methanol and dichloromethane were distilled from CaH_2 . The 1-(perfluorophenyl)hydrazine, (\pm)-2-(2-methoxypropan-2-yl)-pyrrolidin-1-amine, (\pm)-2-methoxypyrrolidin-1-amine, and (\pm)-3-methoxypiperidin-1-amine were bought from UniPharm Ltd. The infrared spectra were measured on a Shimadzu FT-IR 3000 spectrometer. ^1H NMR spectra was recorded on a Varian Mercury-VX 300 spectrometer, high-resolution mass spectra on a API-Qstar-LCMS/MS in MALDI-TOF mode, and low-resolution mass spectra on a Finnigan MAT SSQ-710 in FAB (positive) mode. Fluorescence spectra were obtained on a Hitachi Model F-4500 FL Spectrophotometer. UV-vis spectra were taken on a TU-1901 spectrometer. Linear sweep voltammetric experiments (LSV) were performed with a CHI 660B electrochemical workstation (CH Instrument Co. (Shanghai, China)).

Syntheses

1,2-Bis(1H-pyrrole-2-yl)ethane-1,2-dione(1): This compound was prepared according to the published procedure [19].

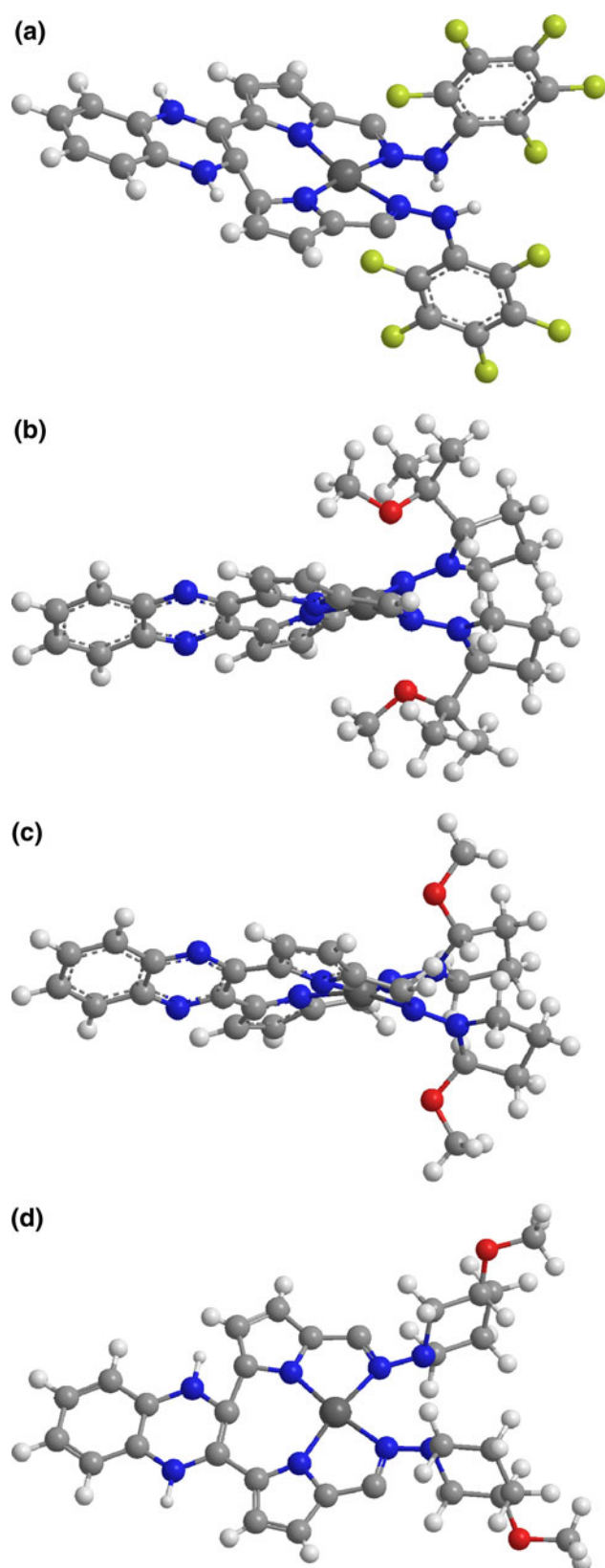


Fig. 10 The computational optimised structures of complexes **4(a)**, **5(b)**, **6(c)** and **7(d)** with Cu^{2+}

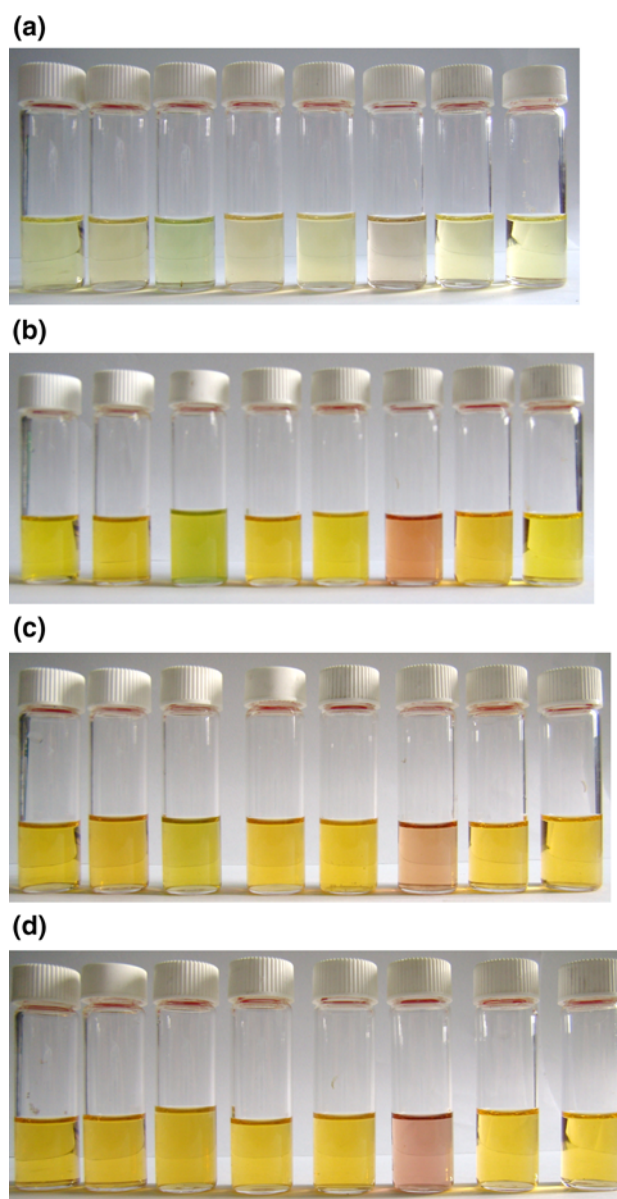


Fig. 11 **a** The colour changes of ligand **4** (3.0×10^{-5} mol/L in acetonitrile) after addition of various cations. **b** The colour changes of ligand **5** (3.0×10^{-5} mol/L in acetonitrile) after addition of various cations. **c** The colour changes of ligand **6** (3.3×10^{-5} mol/L in acetonitrile) after addition of various cations. **d** The colour changes of ligand **7** (3.4×10^{-5} mol/L in acetonitrile) after addition of various cations. (From left to right: free, Co^{2+} , 1 equiv, 5 equiv; Ni^{2+} , 1 equiv, 5 equiv; Cu^{2+} , 1 equiv; Zn^{2+} , 1equiv, 5 equiv.)

2,3-Bis(1H-pyrrol-2-yl)quinoxaline (2): It was prepared by the literature method.[20].

2,3-Bis(5-formylpyrrol-2-yl)quinoxaline (3): It was synthesized under the guiding of the literature.²³

Compound 4: A solution of 2,3-bis(5-formylpyrrol-2-yl)-quinoxaline (**3**) (50.4 mg, 0.16 mmol) and triethylamine (80 μL) in dry methanol (50 mL) was stirred at

reflux for 30 min. After that, 1-(perfluorophenyl)hydrazine (63.1 mg, 0.32 mmol) in dry methanol (2 mL) was added dropwise to the solution. The resulting mixture when refluxed over night, the color of which was changed to orange from yellow. Evaporated the resulting solution to dryness, and recrystallized from CH_2Cl_2 /hexane to furnish an orange solid (91 mg, 84%). $^1\text{H NMR}$ (300 MHz; CDCl_3) δ : 10.05 (br, 2H, NH), 8.00–7.97 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.76 (br, 2H, = N–NH), 7.67–7.64 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.19 (s, 2H, –CH = N), 6.91 (br, 2H, pyrrole), 6.41 (br, 2H, pyrrole). IR (KBr, cm^{-1}): 3433(b), 2825(w), 2359(w), 1632(s), 1602(s), 1384(vs), 1115(b), 611(b). HR-MS (MALDI-TOF): ($M + 1$)⁺ requires 677.1182, found 677.1228. Anal. calcd for $\text{C}_{30}\text{H}_{14}\text{F}_{10}\text{N}_8$: C, 53.26; H, 2.09; N, 16.56. Found: C, 53.29; H, 2.02; N, 16.59.

Compound 5: This compound was prepared similarly as for **4** except that 2-(2-methoxypropan-2-yl)pyrrolidin-1-amine (50.3 mg, 0.32 mmol) was used in place of 1-(perfluorophenyl)hydrazine to give a red powder (75.9 mg, 79.8%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 9.90 (br, 2H, NH), 7.89–7.86 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.57–7.53 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.19 (s, 2H, –CH = N), 6.97 (br, 2H, pyrrole), 6.18 (br, 2H, pyrrole), 3.55 (t, $J = 7.5$ Hz, 2H, pyrrolidine), 3.32 (s, 6H, –OCH₃), 3.25 (t, $J = 6.0$ Hz, 4H, pyrrolidine), 3.01–2.95 (m, 4H, pyrrolidine), 2.03–1.93 (m, 4H, pyrrolidine), 1.62 (s, 12H, –CH₃). IR (KBr, cm^{-1}): 3449(b), 2924(w), 2853(w), 1631(s), 1490(w), 1384(vs), 1351(w), 997(w), 762(w). HR-MS (MALDI-TOF): ($M + 1$)⁺ requires 597.3587, found 597.3646. Anal. calcd for $\text{C}_{34}\text{H}_{44}\text{N}_8\text{O}_2$: C, 68.43; H, 7.43; N, 18.78. Found: C, 68.47; H, 7.40; N, 18.75.

Compound 6: Similar to preparation of **4**, 2-methoxy-pyrrolidin-1-amine (37.2 mg, 0.32 mmol) was used in place of 1-(perfluorophenyl)hydrazine in this reaction to afford **6** as a red solid (65.7 mg, 80%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 9.97 (br, 2H, NH), 7.92–7.89 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.57–7.53 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.14 (s, 2H, –CH = N), 6.95 (br, 2H, pyrrole), 6.20 (br, 2H, pyrrole), 4.22 (br, 2H, pyrrolidine), 4.04 (br, 4H, pyrrolidine), 3.54 (t, $J = 5.1$ Hz, 4H, pyrrolidine), 3.42 (s, 6H, –OCH₃), 2.18–2.11 (m, 4H, pyrrolidine). IR (KBr, cm^{-1}): 3342(b), 2925(w), 1631(s), 1384(vs), 1352(w), 1096(b). FAB-MS: m/z 512.4 M⁺. Anal. calcd for $\text{C}_{28}\text{H}_{32}\text{N}_8\text{O}_2$: C, 65.61; H, 6.29; N, 21.86. Found: C, 65.67; H, 6.20; N, 21.88.

Compound 7: It was prepared by the method similar to the preparation of **4** when 3-methoxypiperidin-1-amine (41.8 mg, 0.32 mmol) substituted the place of 1-(perfluorophenyl)-hydrazine to get **7** as a red powder (71.6 mg, 82.9%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 10.04 (br, 2H, NH), 7.92–7.90 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.60–7.58 (dd, $J = 3.6$ Hz, 2H, quinoxaline), 7.50 (s, 2H, –CH = N),

6.93 (br, 2H, pyrrole), 6.26 (br, 2H, pyrrole), 4.22 (br, 2H, piperidine), 3.67 (d, $J = 11.7$ Hz, 4H, piperidine), 3.50 (br, 4H, piperidine), 3.46 (s, 6H, –O–CH₃), 3.39–3.35 (m, 4H, piperidine), 2.89–2.78 (m, 4H, piperidine). IR (KBr, cm^{-1}): 3452(s), 2969(w), 2360(w), 1632(s), 1384(vs), 1351(w), 1139(w). FAB-MS: m/z 540.3 M⁺. Anal. calcd for $\text{C}_{30}\text{H}_{36}\text{N}_8\text{O}_2$: C, 66.64; H, 6.71; N, 20.73. Found: C, 66.67; H, 6.70; N, 20.70.

Compound 4: Compound **4** (30 mg, 0.044 mmol) was dissolved in dry methanol (30 mL) and a solution of $(\text{CH}_3\text{CO}_2)_2\text{Ni}\cdot 4\text{H}_2\text{O}$ (11.03 mg, 0.044 mmol) in dry methanol (15 mL) was added. The mixture was stirred for 30 min at refluxing temperature. The mixture was evaporated to dryness. The residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ to give an orange solid (31.9 mg, 98%). IR (KBr, cm^{-1}): 3434(b), 2927(w), 2359(w), 1631(s), 1605(s), 1384(vs), 1094(w), 1050(w), 613(b). HR-MS (MALDI-TOF): ($M + 1$)⁺ requires 733.0379, found 732.9702. Anal. calcd for $\text{C}_{30}\text{H}_{12}\text{F}_{10}\text{N}_8\text{Ni}$: C, 49.15; H, 1.65; N, 15.28. Found: C, 49.19; H, 1.60; N, 15.22.

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