A novel class of Cd(II), Hg(II) turn-on and Cu(II), Zn(II) turn-off Schiff base fluorescent probes[†]

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N,N'-((5,5'-(Quinoxaline-2,3-diyl)bis(1H-pyrrole-5,2-diyl))bis(methanylylidene))bis(4-methoxyaniline) 4 and <math>N,N'-((5,5'-(quinoxaline-2,3-diyl)-bis(1H-pyrrole-5,2-diyl))bis(methanylylidene))dianiline 5 have been prepared and structurally characterized. The X-ray crystal structures of compounds 4 and 4a have been determined. These compounds displayed good sensitivity toward transition metal ions with Cd(II), Zn(II) turn-on and Cu(II), Hg(II) turn-off in fluorescence. It is an elegant example of on/off behavior like a lamp. When Cd(II) or Zn(II) is added into compounds 4 or 5, the lamp will switch on, and then when Cu(II) or Hg(II) is added into the mixture, the lamp will switch off. The binding properties of 4 and 5 for cations were examined by fluorescence spectroscopy. The fluorescence data and crystal structure indicate that a 1 : 1 stoichiometry complex is formed between compound 4 (or 5) and metal ions, and the binding affinity is very high. The recognition mechanism between compound 4 (or 5) and metal ion was discussed based on the their chemical constructions and the CHEF/CHEQ effect when they interacted with each other.

Introduction

In recent years, the design of fluorescent probes for selective and sensitive quantification of biologically and environmentally important ion species, especially transition metal ions, has attracted considerable attention in the realms of chemistry, biochemistry and environmental chemistry.¹ Among the cations, developing probes for transition metal ions is the focus, since they usually symbolize an environmental concern when present in uncontrolled amounts, for example, cadmium, lead, mercury, while at the same time some of them such as iron, cobalt, copper and zinc are considered as essential elements in biological systems.² The design and synthesis of probes that have notable capabilities of recognizing and sensing cations are becoming one of the most challenging realms, not only from the viewpoint of organic and supramolecular chemistry but also from its potential environmental and biological applications.³

Cadmium has found extensive use in the fields of Ni–Cd batteries, phosphate fertilizers, pigments, and semiconducting quantum dots and rods.⁴ The detrimental effects of cadmium on human health are, however, being increasingly recognized: chronic cadmium exposure can cause renal dysfunction, calcium metabolism disorders, and an increased incidence of certain forms of cancer,⁵ possibly due to direct inhibition of DNA mismatch repair.⁶ Mercury contamination is widespread and arises from a variety of natural sources, such as oceanic and volcanic emission, as well as anthropogenic sources,⁷ such as gold mining and the combustion of solid waste and fuels. The development of an easy mercury determination system for monitoring its concentration in

polluted areas has attracted considerable attention in the field of supramolecular chemistry. $^{\rm 8}$

In addition, zinc is, after iron, the second most abundant transition metal in mammals,⁹ where it plays important roles in various biological processes such as neurotransmission, signal transduction and gene expression.^{10,11} copper is not only a significant metallic pollutant, but also an essential element for living organisms.¹²⁻¹⁴ Deficiency of copper or zinc can lead to growth and metabolism disorders, such as Menkes syndrome, Wilson disease, hereditary spinal lateral sclerosis, Alzheimer's disease, and so on.¹⁵

Due to their toxic effects and importance to organisms, it is important to develop new chemosensors to be able to monitor the presence of cadmium, mercury, zinc and copper quantitatively.¹⁶⁻¹⁸

Dipyrrolylquinoxaline (DPQ) derivatives have emerged as a new class of ion receptors that exhibit a remarkable selectivity toward anions,^{19–25} but to the best of our knowledge, few of them have been employed as cation receptors.^{26–28}

Previously, we have reported DPQ-bridged Schiff bases²⁸ (Fig. 1) as strong fluorescent quenching sensors. They display remarkable selective and sensitive fluorescence quenching responses (about 90% intensity quenched) toward mercury(II) ions among ten different metal ions.²⁸ In order to investigate and compare the properties of open-chain DPQ Schiff bases, benzene groups were introduced into the DPQ derivatives to break the restriction of the cavity. It is found that ligand **4** (or **5**) shows a 5-fold (or 6-fold) fluorescence emission increase in the presence of Cd(II) and 3-fold



Fig. 1 DPQ-bridged Schiff bases.

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in the presence of Zn(II). The results obtained will be discussed in this paper.

Experimental

General information

All starting materials and solvents were purchased from Sinopharm Chemical Reagent Co. Ltd., and used without further purification unless otherwise stated. Pyrrole was distilled under N_2 prior to use. N,N-dimethylformamide and 1,2-dichloroethane were distilled from CaH₂ and stored over activated molecular sieves prior to use. Pyridine was distilled from NaOH and stored over activated molecular sieves prior to use. 4-Methoxyaniline and aniline were recrystallized from petroleum prior to use. Methanol, dichloromethane and tetrahydrofuran were distilled from CaH₂ under N₂. The infrared spectra were performed on a Nicolet 670 FT-IR spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury-VX 300 spectrometer in CDCl₃. Mass spectra were obtained on a Finnigan MAT SSQ-710 in FAB (positive) mode. Fluorescence spectra were obtained on a Perkin Elmer LS-55 Luminescence spectrometer. Elemental analyses were determined by Finnigan FLASH EA 1112 elemental autoanalyzer. The synthetic procedures to obtain compound 4, 5 and 4a are depicted in Scheme 1.

Syntheses

Compounds **1**, **2** and **3** were prepared according to the published procedure and confirmed.^{27,29}

N,N'-((5,5'-(Quinoxaline-2,3-divl)bis(1H-pyrrole-5,2-divl))bis-(methanylylidene))bis(4-methoxyaniline) (4). 2,3-Bis(5'formylpyrrol-2'yl)-quinoxaline (3) (32 mg, 0.1 mmol) and 4-methoxyaniline (271 mg, 0.22 mmol) were dissolved in methanol (10 mL). The mixture was refluxed for 2 h; no solid appeared. After cooling to room temperature, the mixture was evaporated to dryness. The residue was subjected to chromatography over silica gel (eluent, CH_2Cl_2 : $CH_3OH = 100$: 1, v/v) to afford a yellow solid (51 mg, 97%). ¹H NMR (300 MHz, CDCl₃, TMS): δ 8.31 (s, 2H, -CH=N), 7.98–8.02 (dd, J = 3.3 Hz, J = 3.3 Hz, 2H, quinoxaline, 7.66-7.69 (dd, J = 3.5 Hz,J = 3.3 Hz, 2H, quinoxaline), 7.23 (d, J = 8.4 Hz, 4H, benzene), 6.90 (t, J = 6.5 Hz, 4H, benzene), 6.64-6.73 (m, 4H, pyrrole), 3.83(s, 6H, -OCH₃), 3.74 (s, 2H, -NH);¹³C NMR (75 MHz, CDCl₃, TMS): δ 158.24, 147.70, 144.40, 143.44, 140.44, 133.10, 129.98, 128.73, 122.22, 117.03, 114.61, 114.20, 77.24, 58.53, 55.67; IR (KBr, cm⁻¹): v 3477-3414 (m), 1616 (s), 1503 (s), 1244 (s), 1185 (s), 1034 (s), 912 (s), 743 (s); 616 (s); FAB-MS (m/z): 527, (M + H)⁺; Anal. calcd for C₃₂H₂₆N₆O₂, C, 72.99; H, 4.98; N, 15.96. Found: C, 72.86; H, 5.08; N, 15.79.

N,*N*'-((5,5'-(Quinoxaline-2,3-diyl)bis(1*H*-pyrrole-5,2-diyl))bis-(methanylylidene))dianiline (5). As for 4 except that aniline (21 mg, 0.22 mmol) was used in place of 4-methoxyaniline. Yellow powder (35 mg, 75%). ¹H NMR (300 MHz, CDCl₃, TMS): δ 8.31 (s, 2H, -CH=N), 7.99–8.02 (t, *J* = 4.0 Hz, 2H, quinoxaline), 7.67– 7.70 (dd, *J* = 3.3 Hz, *J* = 3.3 Hz, 2H, quinoxaline), 7.39 (t, *J* = 7.7 Hz, 4H, benzene), 7.13–7.25 (m, 4H, benzene), 6.91 (d, *J* = 2.7 Hz, 2H, benzene), 6.68–6.78 (m, 4H, pyrrole), 3.66 (s, 2H, -NH); IR (KBr, cm⁻¹): *v* 3429–3063 (m), 1655 (s), 1491 (s), 1423 (s), 1342 (s),



4a R=OMe

Scheme 1 Synthesis of Schiff bases 4 and 5. (i) 1H-pyrrole, CH_2Cl_2 , pyridine, -80 °C, 24%; (ii) 1,2-diaminobenzene, AcOH, reflux in the dark, 94%; (iii) POCl₃, DMF, 0 °C for 10 min/1,2-dichloroethene, reflux for 2 h, 79%; (iv) CH₃OH, 4-methoxyaniline, 97%, (or aniline, 75%); (v) Cu(AcO)₂, CH₃OH, CH₂Cl₂, reflux, 1 h, 97%.

1271 (s), 1193 (s), 1142 (s), 1043 (s), 911 (s), 766 (s), 693 (s); FAB-MS (m/z): 467, (M + H)⁺; Anal. calcd for C₂₉H₂₂N₆, C, 77.23; H, 4.75; N, 18.01. Found: C, 77.02; H, 4.68; N, 18.23.

Complex 4-Cu (4a). Compound **4** (53 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (10 mL), then the solution of $(CH_3CO_2)_2Cu \cdot H_2O$ (20 mg, 0.1 mmol) in dry methanol (5 mL) was added. The color of the solution turned from yellow to dark red. The mixture was refluxed for 1 h. After cooling to room temperature, the mixture was evaporated to dryness. The residue was subjected to chromatography over silica gel (eluent, CH_2Cl_2), and recrystallized from CH_2Cl_2 – CH_3OH , (57 mg, 97%). IR (KBr, cm⁻¹): *v* 3437 (br), 2924 (s), 1609 (s), 1583 (s), 1505 (s), 1487 (s), 1413 (s), 1330 (s), 1243 (s), 1205 (s), 1174 (s), 1030 (s), 828 (s), 783 (s), 555 (s). FAB-MS (*m/z*): 590, (M + H)⁺; Anal. calcd for $C_{32}H_{24}N_6O_2Cu$, C, 65.35; H, 4.11; N, 14.29. Found: C, 65.32; H, 3.99; N, 14.30.

X-ray crystallography

The crystallographic data for **4** and **4a** are summarized in Table 1. Intensities were both collected at 293 K, on a Bruker AXS SMART APEX II CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The collected frames were processed

Table 1 Crystallographic data for compound 4 and 4a

Compound	4	4a
Empirical formula	C ₃₂ H ₂₆ N ₆ O ₂ ·CH ₃ OH	$C_{32}H_{24}CuN_6O_2$
Formula weight	558.63	588.11
Colour and habit	yellow needle	red block
Crystal size/mm	$0.34 \times 0.32 \times 0.28$	$0.32 \times 0.31 \times 0.24$
Crystal system	Monoclinic	Triclinic
Space group	$P2_{1}/c$	$P\bar{1}$
T/K	293(2)	293(2)
a/Å	22.061(5)	8.6290(18)
b/Å	7.7536(18)	16.338(4)
c/Å	17.062(4)	20.422(4)
α (°)	90	67.414(3)
$\hat{\boldsymbol{\beta}}(^{\circ})$	100.265(4)	80.191(4)
γ (°)	90	85.300(4)
$V/Å^3$	2871.9(12)	2619.1(10)
Fm	1176	1212.0
Z	4	4
$Dcalc/g cm^{-1}$	1.292	1.491
Absorption coefficient/mm ⁻¹	0.085	0.877
Reflections collected	15950	15909
Independent reflections	5649 [R(int) = 0.0269]	10636 [R(int) = 0.0226]
θ range/#9702:	2.43 to 26.00	2.03 to 26.50
Limiting indices	-27 < = h < = 27.	-10 < = h < = 10.
	-6 < = k < = 9.	-20 < = k < = 20.
	-21 < = l < = 21	-25 < = l < = 21
Final R indices $(I > 2\sigma(I))$	$R_1 = 0.0450$, w $R_2 = 0.1138$	$R_1 = 0.0439$, w $R_2 = 0.1013$
<i>R</i> indices (all data)	$R_1 = 0.0728$ w $R_2 = 0.1302$	$R_1 = 0.0821$ w $R_2 = 0.1151$
Goodness-of-fit on F^2	1.030	1.023

with the software SAINT³⁰ and an absorption correction was applied (SADABS)³¹ to the collected reflections.

The space groups of each crystal were determined from the systematic absences and Laue symmetry checks and confirmed by successful refinement of the structures.

The structures of both compounds were solved by direct methods (SHELXTL-97)³² and refined against F^2 by full-matrix least-squares analyses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated in their idealized positions and allowed to ride on their respective parent carbon atoms.³³ Full details of the crystallographic analyses are given in Supporting Information as CIF files.[†]

CCDC reference numbers 781633 (4) and 781632 (4a).

Results and discussion

Synthesis and characterization of compounds

The new fluorescent sensor 4 (or 5) was synthesized by refluxing the methanol solution of 2,3-bis(5-formylpyrrol-2-yl)quinoxaline (3) and 4-methoxyaniline (or aniline) for 2 h. The products were obtained as a yellow powder in high yield and characterized by IR, ¹H NMR, ¹³C NMR, FAB-MS and elemental analysis.

In order to determine the complex model, single crystals of **4** and **4a** suitable for X-ray analysis were obtained from their dichloromethane-methanol-petroleum solution by slow evaporation at room temperature. Perspective drawings of compounds **4** and **4a** are shown in Fig. 2 and 3, respectively.

In Fig. 2, compound 4 has two identical arms on the opposite side. Two arms twist small angles with the quinoxaline plane, one angle 33.2° , the other angle 11.6° . Each arm adopts a unique

configuration in which the benzene ring and the pyrrole parts are in a trans relationship. In Fig. 3, the binding mode of 4 (or 5) towards the metal ion was revealed by X-ray structures of the Cu(II) complex 4a. The structure indicates that this compound forms a 1:1 metal-ligand complex with four N atoms in the two arms twisting together. Selected bond lengths and bond angles of 4a are given in Table 2. There are two independent molecules of 4a in the asymmetric unit. The distances of 1.941(2) and 1.970(2) Å [or 1.951(2) and 1.969(2) Å] for Cu(1)-N_{pyr} [or Cu(2)- N_{pvr} (pyrrole nitrogen) are slightly shorter than that of 2.034(2) and 2.062(2) Å [or 2.029(2) and 2.061(2) Å] for Cu(1)-N_{im} [or Cu(2)–N_{im}]. These slight deviations are as a result of the formation of ionic bonds between the copper and the pyrrole nitrogen atoms. All the distances between Cu and the four N atoms are all shorter than 2.5 Å. Driven by metal-coordination, rotation of the pyrrol fragment by nearly 180° around C-C bond orients the nitrogen atoms N(3) and N(4) [or N(8) and N(10)] of the pyrrol and imino nitrogen atoms N(1) and N(2) [or N(7) and N(9)] in the same direction, thus enabling the molecule to function as a planar quadridentate N₄ chelator. Two benzene planes of the arms in each molecule are almost parallel to each other with the dihedral angles about 4.1° and 3.9° , respectively. In the structures of 4a, the copper atom is bound to four nitrogen atoms, two from the deprotonated pyrroles and two from the adjacent imines, and is almost coplanar to the respective N₄ plane (\sum angles at Cu(1) = 359.90, \sum angles at Cu(2) = 359.74).

Fluorescence titration of 4 and 5 with metal ions

To obtain an insight into the binding properties of 4 and 5 toward metal ions, the changes of the fluorescence properties of 1×10^{-5} mol L⁻¹ of 4 and 5 were investigated upon addition



Fig. 2 ORTEP view of the X-Ray structure of compound 4 with all heavy atoms labeled.



Fig. 3 ORTEP view of the X-Ray structure of compound 4a with all heavy atoms labeled.

of a wide range of 4 equiv. cations including Pb^{2+} , Mg^{2+} , Ca^{2+} , Ni^{2+} , Ba^{2+} , Co^{2+} , Cd^{2+} , Hg^{2+} , Zn^{2+} and Cu^{2+} in THF solution at 293 K. The chemosensory behavior of 4 and 5 is similar, which is depicted in Fig. 4: the THF solution of 4 or 5 displayed a remarkable emission increase when Zn^{2+} or Cd^{2+} ion was added in; when Hg^{2+} or Cu^{2+} was added into the solution of 4 or 5, a significant fluorescent emission quenching was observed;

by contrast, relatively insignificant spectral changes were beheld upon addition of most of the other metal ions. So it can be concluded that **4** and **5** have a high selectivity for recognition of Zn^{2+} , Cd^{2+} , Hg^{2+} and Cu^{2+} . The sensitivity of the fluorescence emission response of **4** and **5** toward Zn^{2+} , Cd^{2+} , Hg^{2+} and Cu^{2+} was subsequently examined under the same conditions with various metal ion concentrations (Fig. 5 to 8).



Fig. 4 Fluorescent emission changes of (a) compound 4 ($1.0 \times 10^{-5} \text{ mol } L^{-1}$), $\lambda_{ex} = 406 \text{ nm or (b) compound 5 } (<math>1.0 \times 10^{-5} \text{ mol } L^{-1}$), $\lambda_{ex} = 398 \text{ nm in THF}$ solution in the presence of 4 equiv. various metal ions.

 Table 2
 Selected bond lengths and bond angles of compound 4a

Compound 4a	Bond length/Å	Compound 4a	Bond angle (°)
Cu(1)–N(1)	2.034(2)	N(1)–Cu(1)–N(2)	99.09(10)
Cu(1) - N(2)	2.062(2)	N(3)-Cu(1)-N(2)	83.98(9)
Cu(1) - N(3)	1.941(2)	N(3)-Cu(1)-N(4)	92.81(9)
Cu(1) - N(4)	1.970(2)	N(4) - Cu(1) - N(1)	84.02(9)
Cu(2)-N(7)	2.061(2)	N(8) - Cu(2) - N(7)	83.77(9)
Cu(2) - N(8)	1.951(2)	N(8) - Cu(2) - N(10)	92.76(9)
Cu(2) - N(9)	2.029(2)	N(9)-Cu(2)-N(7)	99.10(9)
Cu(2)–N(10)	1.969(2)	N(10)-Cu(2)-N(9)	84.11(9)

Fig. 5 shows the titration profiles of 4 on Cd²⁺ and Zn²⁺ addition. When the concentration of Cd²⁺ is increased up to 1.2 equiv, the fluorescence intensity of 4 is increased by 5-fold at 573 nm; when the concentration of Zn²⁺ is increased up to 0.9 equiv, the fluorescence intensity of 4 is increased by 3-fold at 553 nm.

Fig. 6 shows the titration profiles of 5 on Cd^{2+} and Zn^{2+} addition. When the concentration of Cd^{2+} is increased up to 1.2 equiv, the fluorescence intensity of 5 is increased by 6-fold at 573 nm; when the concentration of Zn^{2+} is increased up to 1.2 equiv, the fluorescence intensity of **5** is increased by 3-fold at 530 nm.

As shown in Fig. 7 and Fig. 8, a strong decrease of the emission intensity was observed upon addition of Cu^{2+} or Hg^{2+} . After addition of 1.5 equiv. of Cu^{2+} or Hg^{2+} , the fluorescence intensity at 516 nm of 4 were reduced to 51% and 24% of the initial one, respectively. After addition of 2.5 equiv. of Cu^{2+} or Hg^{2+} , the fluorescence intensity at 516 nm of 4 were both reduced by 7%. After addition of 2.4 equiv. of Cu^{2+} or Hg^{2+} , the fluorescence intensity of 5 at 505 nm were reduced to 2%, 3% of the initial one, respectively.

Hence, **4** and **5** can be used as "turn-on" molecular probes toward Cd^{2+} and Zn^{2+} , while "turn-off" molecular probes toward Hg^{2+} and Cu^{2+} .

Fig. 9 shows the Job's plots of receptor **4** and **5** with Zn^{2+} , Cd^{2+} , Hg^{2+} and Cu^{2+} . The total concentration of the host and guest was constant (3.0×10^{-5} mol L⁻¹) in THF, with a continuously variable molar fraction of the guest ([G]/([H]+[G])). When the molar fraction of the guest was 0.50, the difference of fluorescence



Fig. 5 Fluorescence spectra of 4 ($1.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$) upon the addition of various amounts of (a) Cd²⁺ or (b) Zn²⁺ in THF solution, $\lambda_{\text{ex}} = 406 \text{ nm}$. The inset shows the fluorescence intensity as a function of (a) [Cd²⁺] at $\lambda_{\text{max}(\text{em})} = 573 \text{ nm}$ and (b) [Zn²⁺] at $\lambda_{\text{max}(\text{em})} = 553 \text{ nm}$.



Fig. 6 Fluorescence spectra of **5** ($1.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$) upon the addition of various amounts of (a) Cd²⁺ or (b) Zn²⁺ in THF solution, $\lambda_{ex} = 398 \text{ nm}$. The inset shows the fluorescence intensity as a function of (a) [Cd²⁺] at $\lambda_{max(em)} = 573 \text{ nm}$ and (b) [Zn²⁺] at $\lambda_{max(em)} = 530 \text{ nm}$.



Fig. 7 Fluorescence spectra of 4 (1.0×10^{-5} mol L⁻¹) upon the addition of various amounts of (a) Cu²⁺ or (b) Hg²⁺ in THF solution, $\lambda_{ex} = 406$ nm. The inset shows the fluorescence intensity as a function of (a) [Cu²⁺] or (b) [Hg²⁺] at $\lambda_{max (em)} = 516$ nm.



Fig. 8 Fluorescence spectra of 5 ($1.0 \times 10^{-5} \text{ mol } L^{-1}$) upon the addition of various amounts of (a) Cu²⁺ or (b) Hg²⁺ in THF solution, $\lambda_{ex} = 398 \text{ nm}$. The inset shows the fluorescence intensity as a function of (a) [Cu²⁺] or (b) [Hg²⁺] at $\lambda_{max (em)} = 505 \text{ nm}$.



Fig. 9 Job plots of (a) compound **4** or (b) compound **5** with Cd^{2+} , Cu^{2+} , Hg^{2+} and Zn^{2+} . The total concentration of the host and guest is 3.0×10^{-5} mol L^{-1} in THF solution. I_0 : fluorescence intensity of the host; *I*: fluorescence intensity of host in the presence of the guest.

Table 3 Association constants K_{ass} of receptors 4 and 5 with guest cations

Cation	Receptor 4		Receptor 5	
Hg(II)	K_{ass} (M ⁻¹)	R	K_{ass} (M ⁻¹)	R
	2.7 × 10 ⁶	0.9855	1.7 × 10 ⁵	0.9950
Cu(II)	5.2×10^{4}	0.9550	3.4×10^4	0.9873
Cd(II)	$1.4 \times 10^{\circ}$	0.9884	2.8×10^{7}	0.9994
Zn(II)	5.1×10^{6}	0.9768	2.0×10^{6}	0.9809

intensity between the host and the guest reached a maximum, which demonstrated that both receptors **4** and **5** formed a 1:1 complex with Zn^{2+} , Cd^{2+} , Hg^{2+} or Cu^{2+} , respectively.³⁴ The association constants (Kass) of **4** and **5** with guest cations are shown in Table 3.

As shown in Fig. 10, both compounds 4 and 5 have a low level fluorescence intensities, but after addition of 1.5 equiv. Cd²⁺



Fig. 10 Fluorescence intensity changes of 4 or $5 (1.0 \times 10^{-5} \text{ mol } L^{-1})$ upon the addition of 1.5 equiv. Cd^{2+} or Zn^{2+} and 4 equiv. Hg^{2+} or Cu^{2+} in THF solution.

or Zn^{2+} ion, the intensity increases to about 3 or 5-fold. Then adding 4 equiv. Hg^{2+} or Cu^{2+} to the above Cd^{2+} or Zn^{2+} solution induced an evident fluorescent change from significant enhancing to nearly quenching, which displayed a pronounced ON/OFFtype signalling behaviour. The quenching effects of Hg^{2+} or Cu^{2+} do abolish the ratiometric effect on binding of Cd^{2+} and Zn^{2+} . This character can be employed as an ion switch. When Cd^{2+} or Zn^{2+} is added into 4 or 5, the power switches on, and then when Hg^{2+} or Cu^{2+} is added into the system, the power switches off.

A strong CHEQ effect (Chelation Enhancement of the Quenching) 4 and 5 toward Cu(II) and Hg(II) can be observed in Fig. 7 and Fig. 8. This CHEQ effect can be attributed to an energy/electron transfer quenching of the p* emissive state though low-lying metal-centred unfilled d-orbitals for Cu(II), and to an intersystem crossing mechanism due to the heavy atom effect for Hg(II).^{35,36}

Zn(II) and Cd(II) coordinated to ligands **4** or **5** are generally emissive species, causing a CHEF effect (Chelation Enhancement of the Fluorescence Emission).³⁵ The stronger the involvement of the nitrogen atoms in the complexation, the stronger the effect on the fluorescence of the ligand. This can be explained by assuming that the deprotonation and complexation of the pyrrole with Zn(II) and Cd(II) block its lone pair of electrons from transferring to the DPQ moiety *via* PET (photo-induced electron transfer).³⁶

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

For the complex of 1:1 stoichiometry, according to the following relation:¹⁸

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

Where *X* represents the absorbance intensity, $c_{\rm H}$ and $c_{\rm G}$ are the corresponding concentration of the host and guest. The association constants obtained by a non-linear least-square analysis (the inset of the Fig. 5 to 8) of *X vs.* $c_{\rm H}$ and $c_{\rm G}$ are listed in Table 3. The data show that both receptors 4 and 5 have an excellent sensitivity for Zn(II), Cd(II), Hg(II) and Cu(II).

Conclusions

In summary, a new class of fluorescent probes, **4** and **5** derived from DPQ, have been synthesized and characterized. The analyses of fluorescence properties of these compounds reveal that these species display sensitive response of fluorescence toward Zn(II), Cd(II), Hg(II) and Cu(II) ions. The emission intensity increases with gradual addition of Zn(II) or Cd(II) and quenches when Hg(II) or Cu(II) is added to the system. Our findings will help to improve the direct detection of these ions in the environment. Further modification³⁷ and investigation³⁸⁻⁴² of these compounds and analogs on DNA, protein, and tumor cells is planned in due course.

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Notes and references

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