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Journal Name

ARTICLE

Dimethyl yellow-based colorimetric chemosensors for "naked eye" detection of Cr^{3+} in aqueous media *via* test papers†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Three colorimetric chemosensors were designed and synthesized by incorporating the dimethyl yellow dye and multidentate chelating moieties into the preorganized dipodal receptors. The novel sensors display high selectivity for Cr^{3+} over a wide range of tested metal ions in a rapid visual output manner. Uv-vis titrations with Cr^{3+} revealed the appearance of a new intense absorption band centered at about 515-530 nm which was accompanied by a dramatic change in color from light yellow to magenta, with the association constant being about $2.0\text{-}3.0\times10^{5}$ M^{-1}. Further binding model studies by mass spectroscopy, Job' s plot, and linear fitting of the UV-vis titration curve demonstrated that the receptors formed 4:4, 1:2, and 4:4 binding modes with Cr^{3+}, respectively. The easy-to-prepare test papers indicating the potential application for detecting Cr^{3+} in natural aqueous environments without any spectroscopic instrumentation.

1. Introduction

Design of receptors for Chromium (III) is an area of intense research activity, because they are potentially attractive for use in such areas as metabolism of carbohydrates, fats, proteins and nucleic acids by activating certain enzymes and stabilizing proteins and nucleic acids.[1] Meanwhile, Cr^{3+} is an environmental pollutant that has caused concern in industry and agriculture. Depending on the environment, Cr^{3+} can be transformed to its oxidation form Cr^{6+}, which is an extremely toxic and carcinogenic species.[2] Recently, synthetic strategies for constructing functional Cr^{3+} receptors with various structures and novel binding properties have been well established.[1f, 3, 6] In particular, considerable attention has been drawn to design different binding models for the optical imaging with fluorescent sensors for Cr^{3+} in living cells. However, the development of simple, sensitive, rapid and low-cost methods for the detection and amplification of Cr^{3+} binding events to produce a measurable "naked eye" output in aqueous solutions has been a formidable challenge that has yet to be achieved.[4] Additionally, to our best knowledge, all these reported sensors often display poor binding selectivity for Cr^{3+} over other heavy and transition-metal (HTM) ions.

Many chemical systems have been utilized for HTM ions detection based on various recognition mechanisms, such as intermolecular charge transfer (ICT), chelation-induced enhanced fluorescence (CHEF), photo-induced electron transfer (PET), metal-to-ligand charge-transfer transition (MLCT) and fluorescence resonance energy transfer (FRET).[5, 1f] Notably, the mechanism of CHEF is an active area of research. Ligands bearing multidentate chelating units, which can potentially coordinate to the metal ion and contribute to the metal-chelation effect, have been important in the applications of ionophore design.[6] As a continuation of our research work on the di- or tripodal receptors, by incorporating chromophores onto the di- or tripodands,[7] we herein report the syntheses and Cr^{3+} binding properties of new dimethyl yellow-based colorimetric chemosensors for "naked eye" detection of Cr^{3+} over a wide range of tested metal ions in aqueous media. The multidentate chelating units were identified as the cation receiving moieties, while the dimethyl yellow dye was served as the chromophore unit (Scheme 1, **DYN1-3**). The two necessary factors were introduced as trigger sites to achieve efficient metal interactions and a consequently good signal response. Interestingly, the highly sensitive chromophore of dimethyl yellow provide an opportunity to "naked eye" detection of HTM ions in a rapid and sensitive test paper manner.[8] Das *et al* have first reported a dimethyl yellow-based dual responsive test paper sensor for naked eye detection of Hg^{2+}/Cr^{3+} in neutral water.[9] The successful applications of the dimethyl yellow group encouraged us finding a higher selectivity Cr^{3+} receptor to extend the excellent research. To the best of our knowledge, **DYNs** was the first Cr^{3+} molecular chemosensors with high selectivity and sensitivity afforded an interesting naked eye output manner in aqueous media *via* test papers. The cheap and effective new sensors will prove advantageous in helping to monitor of heavy metal pollution in undeveloped regions.

2. Experimental

2.1 General experimental

Materials unless otherwise stated, were obtained from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x
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NMR spectra were measured using a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in DMSO-d_6, or $CDCl_3$, TMS as internal standard). Mass spectrometric (MS) data were obtained using API/MS mass spectrometry, GCT CA156 MS spectrometry and LCQ-TOF MS spectrometry. Melting points (m. p.) were determined using a MP100. Optical absorption spectra were measured using a TU-1900 UV-vis spectrophotometer at room temperature. Elemental analyses (EA) were performed using a HXS-4AD analyzer. ICP-AES spectra were measured using a PE-AA800 (graphite furnace atomic absorption). All density functional theory (DFT) calculations were performed in Virtual Laboratory for Computational Chemistry, CNIC, CAS. Frontier molecular orbitals have been performed at the Becke3LYP (B3LYP) level of the density functional theory.

2.2 General procedures for spectroscopy

Stock solutions (2×10^{-2} M) of the CH_3CN perchlorate salts of K^+, Na^+, Co^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Fe^{2+}, Ag^+, Pb^{2+}, Hg^{2+}, Al^{3+}, and Cr^{3+} were prepared and diluted to the appropriate concentration. Stock solutions of **DYN1-4** (1 mM) were also prepared in distilled CH_3CN solution. Test solutions were prepared by placing 40 μL of host stock solution into a quartz cell of 1 cm optical path length including 2 mL CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) solution, and then adding an appropriate aliquot of each metal stock solution with a micro-syringe. All the spectroscopic measurements were performed at least in triplicate and averaged.

For Cr^{3+}-bound **DYN1**, ESI-TOF spectra were measured using a LCQ-TOF MS spectrometry. The reaction mixtures of Cr^{3+} perchlorate and **DYN1** in a 5:1 molar ratio in 30 mL mixed solvents of dichloromethane and methanol (9:1, v/v) were stirred at room temperature for 24 h, then filtered and concentrated to 3 mL. Addition of diethyl ether gave the product as a purple solid. The crude product was redissolved in dichloromethane for the ESI-TOF spectra. **DYN2**-Cr^{3+} and **DYN3**-Cr^{3+} are slightly soluble in DMSO, but the solubility is too low to allow for ESI-TOF measurements.

2.3 Synthesis and characterization

Compound 1. 5-aminoisophthalic acid (3.788 g, 20.9 mmol) was dissolved in dilute hydrochloric acid (15 mL concentrated hydrochloric acid was dissolved in 150 mL water), after cooling to 0 ℃, formed a brown suspension. Sodium nitrite (1.617 g, 23 mmol) was added into the brown suspension in water (10 mL). The mixture was stirred for 30 minutes, and obtained a brown diazonium salt in aqueous solution. N,N-dimethylaniline (2.534 g, 20.9 mmol) was dissolved in potassium hydroxide (2.225 g, 39.75 mmol), the mixture was added dropwise to the above diazonium salt that was stirred to form orange turbid liquid, continued stirring for 24 h. The purple precipitated formed was filtered, and dried *in vacuo*. Yield: 5.32 g (85%). m.p. 291-293℃; Anal calc. for $C_{16}H_{15}N_3O_4$: C 61.34, H 4.82, N 13.41, O 20.43%. Found: C 61.37, H 4. 85, N 13.39, O 20.39%; ^{1}H NMR (101 MHz, DMSO-d_6) δ: 8.47 (s, $2H_{Ar}$), 8.47 (s, $1H_{Ar}$), 6.87 (d, $2H_{Ar}$, J = 4 Hz), 7.87 (d, $2H_{Ar}$, J = 4 Hz), 3.09 (s, $6H_{CH_3}$); ^{13}C NMR (400 MHz, DMSO-d_6) δ: 168.9, 152.6, 151.6, 142.2, 132.7, 130.5, 128.3, 123.9, 114.6, 42.7; MS m/z: 314.11 $[M + H]^+$.

Compound 2. Compound **1** (4 g, 12.7 mmol) suspended in methanol (200 mL), was added slowly to a solution of thionyl chloride (20 mL) at 0 ℃ and the mixture was allowed to reflux for 24 h. After cooling to room temperature, sodium carbonate solution was added to adjust pH to 7~8. After the removal of the solvent of methanol, the mixture was extracted with ethyl acetate (300 mL). The removal of ethyl acetate under vacuum gave a yellow solid, which was purified by silica gel column chromatography using CH_2Cl_2/CH_3OH (50 : 1) as eluent to afford compound **2** as an orange solid. Yield: 3.58 g (89.5%). m.p. 237-239 ℃; Anal calc. for $C_{18}H_{19}N_3O_4$: C 63.33, H 5.61, N 12.31, O 18.75%. Found: C 63.35, H 5.63, N 12.30, O 18.72%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.48 (s, $1H_{Ar}$), 8.47 (s, $2H_{Ar}$), 7.87 (d, $2H_{Ar}$, J = 4 Hz), 6.86 (d, $2H_{Ar}$, J = 4 Hz), 3.94 (s, $6H_{CH_3}$), 3.10 (s, $6H_{CH_3}$); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 166.1, 152.3, 151.7, 142.5, 132.7, 130.3, 128.1, 122.3, 115.5, 53.6, 41.6; MS m/z: 342.14 $[M + H]^+$.

Compound 3. Compound **2** (3.0 g, 11.7 mmol) was dissolved in methanol (120 mL) containing hydrazine hydrate (13 g). After refluxing for about 18 h, the solvent was removed by evaporation. The orange crystalline solid obtained was used in next step. Yield: 2.78 g (92.7%). m.p. 258-261 ℃; Anal calc. for $C_{16}H_{19}N_7O_2$: C 56.29, H 5.61, N 28.72, O 9.38%. Found: C 56.26, H 5.63, N 28.71, O 9.40%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.99 (s, $2H_{NH}$), 8.29 (s, $2H_{Ar}$), 8.29 (s, $1H_{Ar}$), 7.85 (d, $2H_{Ar}$, J = 4 Hz), 6.87 (d, $2H_{Ar}$, J = 4 Hz), 4.59 (m, $4H_{NH_2}$), 3.09 (s, $6H_{CH3}$); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 162.9, 152.9, 151.1, 141.1, 135.7, 131.3, 122.6, 122.9, 111.2, 44.6; MS m/z: 342.16 $[M + H]^+$.

Compound DYN1-4. A mixture of compound **3** (2 mmol), appropriate aldehyde (4.3 mmol) and acetic acid (5 drops) was heated to reflux in methanol (30 mL) under a nitrogen atmosphere for 12 h. After cool to room temperature, red solid appeared, filter cake was washed by methanol to afford compound **DYN1-4** as an orange solid (80%).

DYN1: m.p. 247-249 ℃; Anal calc. for $C_{28}H_{25}N_9O_2$: C 64.73, H 4.85, N 24.26, O 6.16%. Found: C 64.72, H 4.84, N 24.26, O 6.18%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.41 (s, $2H_{NH}$, J = 4 Hz), 8.66 (d, $2H_{Ar}$), 8.54 (m, $5H_{Ar}$+H_{CH}), 8.04 (d, $2H_{Ar}$, J = 4 Hz), 7.93 (m, $4H_{Ar}$), 7.46 (t, $2H_{Ar}$, J = 12 Hz), 6.90 (d, $2H_{Ar}$, J = 4 Hz), 3.11 (s, $6H_{CH_3}$); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.1, 161.7, 154.2, 151.1, 148.2, 144.6, 137.6, 135.4, 134.1, 127.7, 122.6, 120.7, 117.6, 111.4, 110.2, 66.4; MS m/z: 542.2$[M + Na]^+$.

DYN2: m.p. 271-273 ℃; Anal calc. for $C_{36}H_{29}N_9O_2$: C 69.78, H 4.72, N 20.34, O 5.16%. Found: C 69.71, H 4.73, N 20.37, O 5.19%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.58 (s, $2H_{NH}$), 8.69 (s, $2H_{Ar}$), 8.58 (s, $2H_{Ar}$), 8.57 (s, $1H_{CH}$), 8.48 (d, $2H_{Ar}$, J = 4 Hz), 8.19 (d, $2H_{Ar}$, J = 4 Hz), 8.08 (d, $2H_{Ar}$, J = 4 Hz), 8.05 (d, $2H_{Ar}$, J = 4 Hz), 7.94 (d, $2H_{Ar}$, J = 4 Hz), 7.82 (t, $2H_{Ar}$, J = 16 Hz), 7.67 (t, $2H_{Ar}$, J = 16 Hz), 6.91 (d, $2H_{Ar}$, J = 4 Hz), 3.14 (s, $6H_{CH_3}$); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 165.2, 157.1, 152.7, 144.6, 143.7, 142.1, 137.1, 136.5, 134.1, 132.2, 130.4, 129.6, 128.8, 127.6, 126.4, 126.1, 122.1, 120.4, 112.1, 55.2; MS m/z: 619$[M + Na]^+$.

DYN3: m.p. 249-250 ℃; Anal calc. for $C_{36}H_{29}N_9O_4$: C 66.35, H 4.49, N 19.34, O 9.82%. Found: C 66.31, H 4.48, N 19.32, O 9.89%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.61 (s, $2H_{NH}$), 9.90 (s, $2H_{OH}$), 8.73 (s, $2H_{Ar}$), 8.57 (s, $1H_{Ar}$), 8.56 (s, $2H_{CH}$), 8.39 (d, $2H_{Ar}$, J = 4 Hz), 8.17 (d, $2H_{Ar}$, J = 4 Hz), 7.94 (d, $2H_{Ar}$, J = 4 Hz), 7.48 (m, $4H_{Ar}$), 7.16 (d, $2H_{Ar}$, J = 4 Hz), 6.91 (d, $2H_{Ar}$, J = 4 Hz), 3.12 (s, $6H_{CH_3}$);

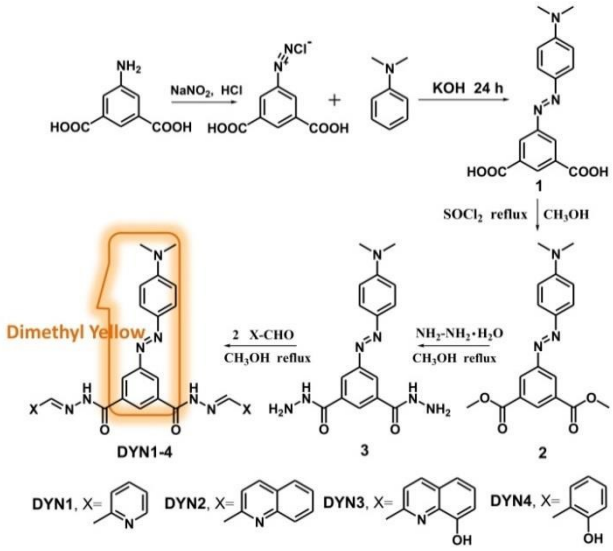
^{13}C NMR (101 MHz, DMSO-d_6) δ: 163.7, 158.2, 156.4, 148.9, 144.3, 142.5, 139.2, 136.0, 132.6, 132.2, 131.2, 128.9, 127.8, 127.4, 126.6, 124.7, 121.2, 116.8, 109.8, 57.1; MS m/z: 652.3[M + H]$^+$, 674.5[M + Na]$^+$.

DYN4: m.p. 275-277 ℃; Anal calc. for $C_{30}H_{27}N_7O_4$: C 65.56, H 4.95, N 17.84, O 11.65%. Found: C 65.52, H 4.98, N 17.81, O 11.69%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.30 (s, 2H$_{OH}$), 11.28 (s, 2H$_{NH}$), 8.69 (s, 2H$_{Ar}$), 8.34 (s, 1H$_{Ar}$), 8.00 (s, 2H$_{CH}$), 7.99 (d, 2H$_{Ar}$, J = 4 Hz), 7.70 (t, 2H$_{Ar}$), 7.58 (d, 2H$_{Ar}$, J = 4 Hz), 7.32 (t, 2H$_{Ar}$), 6.87 (d, 2H$_{Ar}$, J = 4 Hz), 4.37 (s, 6H$_{CH3}$); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 166.2, 157.2, 156.5, 144.9, 143.1, 142.6, 138.0, 133.7, 132.6, 132.4, 130.2, 127.9, 127.1, 126.3, 122.1, 112.7, 115.8, 60.9; MS m/z: 550.3[M + H]$^+$, 572.2[M + Na]$^+$.

3. Results and discussion

3.1 Synthesis and characterization

The design and synthesis of **DYN1-4** was accomplished by a new synthetic strategy, as shown in Scheme 1. The key intermediate molecule **1** was obtained by diazotization reaction of 5-aminoisophthalic acid with N,N-dimethylaniline in the basic solution environment. Compound **2** was prepared by esterification reaction. The presence of excess of thionyl chloride is crucial for obtaining a good yield in this reaction. Compound **3** was synthesized by reaction of compound **2** with hydrazine hydrate in methanol under reflux overnight. This is the common method of preparing **3** which is the precursor amine for the synthesis of ligand **DYN1-4** in a Schiff-base reaction with 2-pyridinecarboxaldehyde, quinoline-2-carbaldehyde, 8-hydroxyquinoline-2-carbaldehyde and 2-hydroxybenzaldehyde, respectively. A general procedure using glacial acetic acid as the catalyst for this nucleophilic substitution reaction was reported previously and found to be most effective in the syntheses listed here. The chemical structures of these dyes **DYN1-4** were characterized by Nuclear Magnetic Resonance (NMR), MS and EA.



Scheme 1. Synthetic routes for the preparation of **DYN1-4.**

3.2 Spectroscopic properties of DYN1

The absorption response of **DYN1** (2×10^{-5} M) towards the perchlorate salts of Cr^{3+}, Al^{3+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Ag^+, Cd^{2+}, Pb^{2+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, Na^+, and K^+ ($c = 2\times10^{-4}$ M) were carried out in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) solution. **DYN1** exhibited mainly two strong characteristic absorption bands (Fig. 1a). The first band located at 253-360 nm can be assigned to the moderate energy (π→π* and n→π*) transition of the aromatic rings, while the second band at 360-525 nm is due to the low energy (π→π*) transition involving the π-electrons of the azo group. The results of DFT calculations for **DYN1-4** reveal that the electronic density in the HOMO and LUMO is all localized mainly on –N=N– moiety (Fig. S17, ESI†). Therefore, it is reasonable that the only low-energy absorption band of **DYN1** at 360-525 nm can be assigned to ICT. The electron-donating chromophore -NMe_2 and the acceptor multidentate chelating units appended electron-withdrawing amide create a "push-pull" interaction which provides a strong nature of ICT.[10] This results in the formation of a strong absorption band at 425 nm, giving naked eye light yellow color. But the addition of Cr^{3+} to the receptor solution and the strong interaction between the receptor **DYN1** and Cr^{3+} could enhance π delocalization, which was expected to reduce the energy of the π→π* transition and therefore accounts for the appearance of a new absorption band near 516 nm resulting in the formation of a strong magenta color (Fig. 1a). With increasing the concentration of Cr^{3+} ions in the receptor solution, the absorption peak at 425 nm gradually decreases and the peak at 516 nm rises and after addition of 1.5 equiv. of Cr^{3+}, it reaches a saturation level. The absorbance increases 48 fold at 516 nm, which is also responsible for the generation of magenta color after addition of Cr^{3+} into the solution of the receptor. The detection limit of **DYN1** toward Cr^{3+} was obtained as 4.4 μM (Fig. S3, ESI†), which is sufficiently low for the detection of the Cr^{3+} found in many chemical systems.

Under the same conditions, no significant absorption variation of **DYN1** (20 μM) was observed in the presence of other tested metal

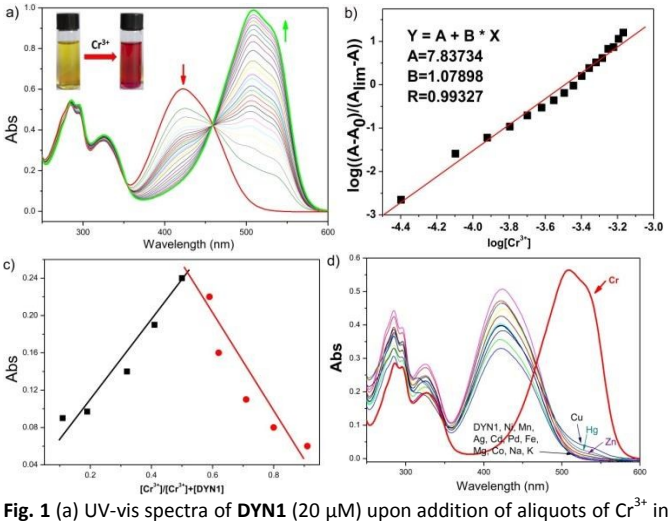


Fig. 1 (a) UV-vis spectra of **DYN1** (20 μM) upon addition of aliquots of Cr^{3+} in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) solution. (b) Hill plot of **DYN1** binding with Cr^{3+} associated with absorbance change at 516 nm. (c) Job's plot diagram of **DYN1** for Cr^{3+}. (d) UV-vis spectra of **DYN1** (20 μM) in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) upon titration with 2.0 equiv. of each of the guest metal ions. The absorbance measurements were recorded at 516 nm.

salts of perchlorate (Fig. 1d). Furthermore, the competition experiments revealed that **DYN1** retained the excellent Cr^{3+} specificity in the presence of a variety of other metal ions found in environmental and biological settings. This means that the absorbance enhancement induced by Cr^{3+} was slightly affected by these metal ions (Fig. S1, ESI†). These results suggest that **DYN1** could respond to Cr^{3+} with high selectivity in an absorption output manner.

Binding analysis using the method of the linear fitting of the UV-vis titration curve (Fig. 1b) and the continues variations (Job's plot, Fig. 1c) established that a 1:1 **DYN1**-Cr^{3+} complex was responsible for the observed absorption enhancement, and the association constant for Cr^{3+} binding to **DYN1** was calculated as 2.69 ± 0.10×10^5 M^{-1}.[11] This higher value of molar absorption coefficient clearly indicates that **DYN1** is highly sensitive towards Cr^{3+} with a naked-eye color change from light yellow to magenta (Fig. 1a). The presence of a sharp isosbestic point at 462 nm indicated the formation of the stable complex with a certain stoichiometric ratio between **DYN1** and Cr^{3+} resulting in a new ICT band that appeared at 516 nm.

The binding model was further supported by the ESI-TOF spectra. In the case of the solution of **DYN1** in the presence of a sufficient amount of $Cr(ClO_4)_3$, an exact comparison of the most interesting experimental peak (which is observed at m/z 1241.26, 96%) with the simulation results obtained on the basis of natural isotopic abundances reveals that this species can be reasonably assigned to $[Cr_4(\mathbf{DYN1})_4(ClO_4)_2\text{-}8H]^{2+}$, thus demonstrating the formation of M_4L_4 species in the solution (Fig. 2 and Fig. S18, ESI†). In this occurrence, **DYN1** could be acting as a hexacoordinate chelator, and the carbonyl O, imine N and pyridine N atoms from the distinct ligands are the most likely binding sites for Cr^{3+}. This result confirming that the Cr^{3+} is strongly coordinated by the hexadentate chelators in a macrocycle coordination geometry, demonstrating that the M_4L_4 species was the only one complexation species (Scheme 2).

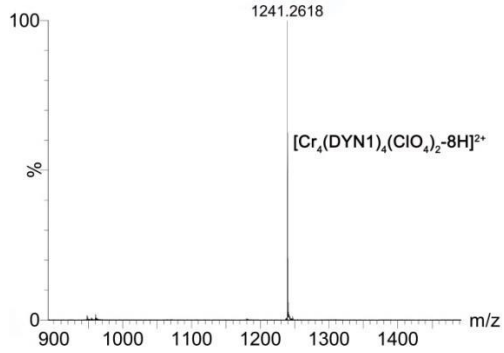
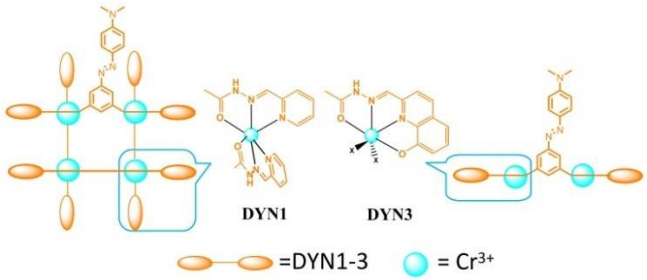


Fig. 2 ESI-TOF spectra of the M_4L_4 macrocycle coordination geometry formed in the mixed solvents of dichloromethane and methanol.



Scheme 2. Possible binding mode of **DYN1-3** with Cr^{3+} (X is the coordinating anion or solvent).

3.3 Spectroscopic properties of DYN3

To further investigate the coordination effect of such dimethyl yellow-based chemosensor, the receptor **DYN3** was designed and synthesized in multiple steps (Scheme 1). The terminal groups of pyridine were replaced by 8-hydroxyquinoline only. With the additional binding site of the hydroxy O atoms, **DYN3** was anticipated to act as an octadentate ligand. **DYN3** also exhibited two characteristic absorption bands centered at ca. 310 and 425 nm. The absorbance spectra exhibited an obviously red shift take place (from 423 nm to 526 nm) upon treatment with 2.6 equivalents of $Cr(ClO_4)_3$ (Fig. 3a). Meanwhile, the color of **DYN3** changes from light yellow to red after addition of Cr^{3+}. The detection limit of **DYN3** toward Cr^{3+} was obtained as 6.4 μM (Fig. S6, ESI†). The individual profile of the absorbance of the band at 526 nm (increasing) demonstrated the 1:2 stoichiometry for **DYN3** and Cr^{3+}, with the association constant being calculated as 2.12 ± 0.10×10^5 M^{-1} (Fig. 3b). **DYN3** also showed good selectivity for Cr^{3+} over other metal ions, and the photophysical spectrum for response of **DYN3** to Cr^{3+} were similar to that for **DYN1** (Fig. 3d and Fig. S4, ESI†). The 1:2 binding mode was further supported by a Job's plot of the **DYN3**–Cr^{3+} absorbance spectra, with the inflection point at about 0.63 (Fig. 3c). In accordance with the coordination number of 6 for Cr^{3+}, the most likely binding sites for Cr^{3+} are the conjugated moiety including carbonyl O, imino N, and quinoline N and O atoms of -OH. The other two coordination sites of Cr^{3+} may be taken by solvents and/or the counter-anions, resulting in a 1:2 stoichiometry with Cr^{3+} (Scheme. 2).

3.4 Spectroscopic properties of DYN2 and DYN4

To further investigate the selectivity of the different ionophores and effect of the -OH group on the sensitivity of the chemosensors (**DYN1** and **DYN3**) toward Cr^{3+}, **DYN2** and **DYN4** were

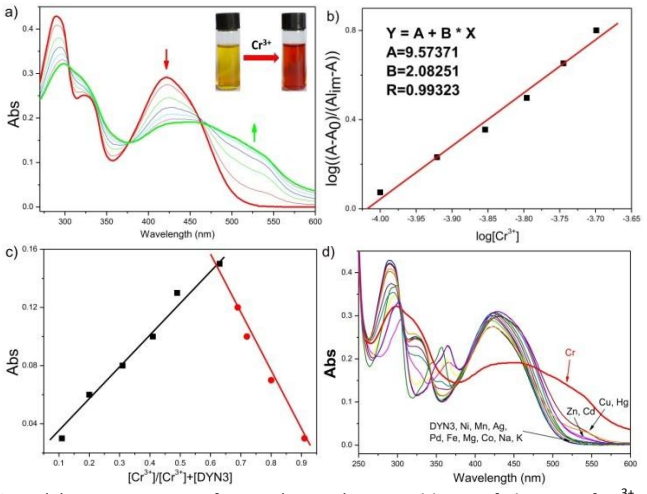


Fig. 3 (a) UV-vis spectra of **DYN3** (20 μM) upon addition of aliquots of Cr^{3+} in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) solution. (b) Hill plot of **DYN3** binding with Cr^{3+} associated with absorbance change at 526 nm. (c) Job's plot diagram of **DYN3** for Cr^{3+}. (d) UV-vis spectra of **DYN3** (20 μM) in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) upon titration with 3.0 equiv. of each of the guest metal ions. The absorbance measurements were recorded at 526 nm.

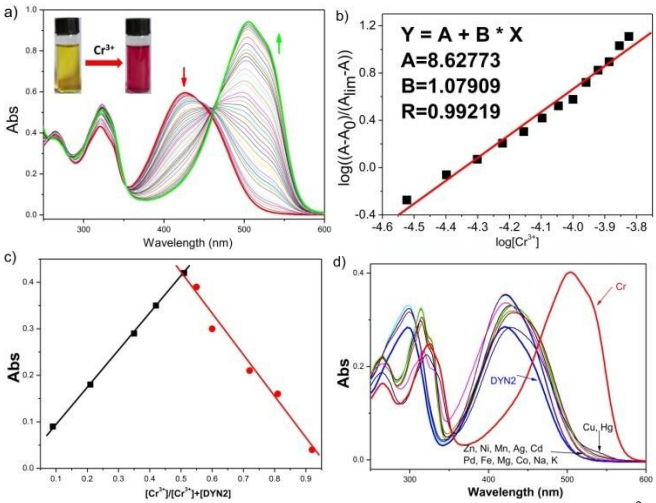


Fig. 4 (a) UV-vis spectra of **DYN2** (20 μM) upon addition of aliquots of Cr^{3+} in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) solution. (b) Hill plot of **DYN2** binding with Cr^{3+} associated with absorbance change at 516 nm. (c) Job's plot diagram of **DYN2** for Cr^{3+}. (d) UV-vis spectra of **DYN2** (20 μM) in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) upon titration with 2.0 equiv. of each of the guest metal ions. The absorbance measurements were recorded at 516 nm.

designed and synthesized in multiple steps (Scheme 1). **DYN2** has the similar structure as that of **DYN1**. Indeed, receptor **DYN2** exhibited the entirely same photophysical spectrum response as that of **DYN1**. Job's plot and the linear fitting of the absorbance titration curve established that a 1:1 **DYN2**-Cr^{3+} complex was responsible for the observed absorbance spectral change (Fig. 4 and Fig. S7, ESI†), and the association constant for Cr^{3+} binding to **DYN2** was calculated as 2.89 ± 0.10×10^5 M^{-1} at 516 nm. **DYN4** exhibited similar absorption bands centered at ca. 300 and 423 nm as that of **DYN1-3**. However, the addition of Cr^{3+} did not cause any significant red shift absorbance changes, even when 10 equivalents of Cr^{3+} were added. In contrast, there were drastic absorbance changes upon the addition of Zn^{2+}, Hg^{2+}, Fe^{3+}, and Pb^{2+} to the CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) solution of **DYN4**. It is indicated that the presence of –OH group in the ionophore moiety of the **DYN4** is a disadvantage for its selectivity toward Cr^{3+}, and thus the selectivity of the Cr^{3+}-specific ionophore can be subtly controlled (Fig. 5). From this vantage point, it should be noted that the terminal group portions play an important role in binding Cr^{3+} by a possible multi-site coordination complexation mode, leading to the observed red shift of the azo band.

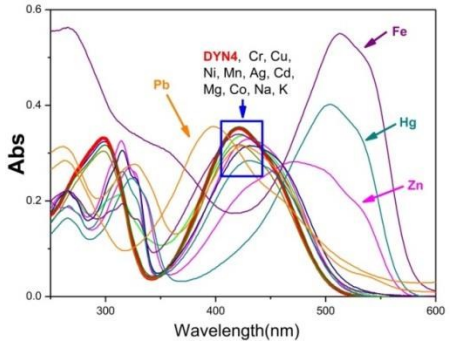


Fig. 5 UV-vis spectra of **DYN4** (20 μM) in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) upon titration with 10.0 equiv. of each of the guest metal ions.

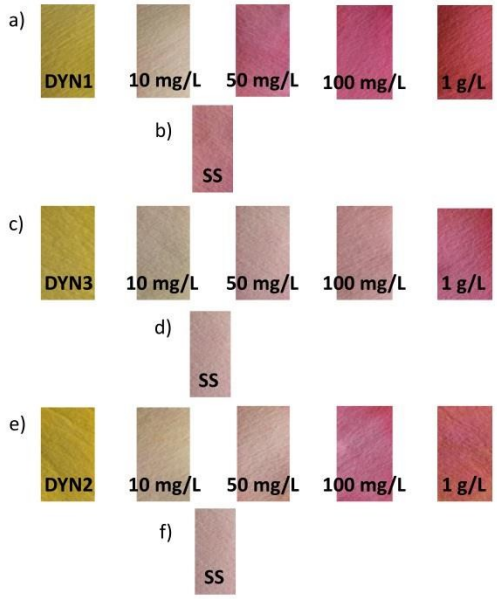


Fig. 6 Colour changes of the test papers for detecting Cr^{3+} in aqueous solution with different Cr^{3+} concentrations. **SS** is the sewage sample.

3.5 Test papers for practical applications

For the practical application of **DYN1-3**, test papers were prepared by immersing filter papers (3×0.5 cm^2) in acetonitrile solution of **DYN1-3** (2 mM) and then dried in air. These test kits coated with **DYN1** were exposed to different guest metal ions solutions (1 mM) in CH_3CN:H_2O (1:1, v/v, containing 0.01 M HEPES, pH=7.21) for 2 seconds, the colour change from yellow to red was observed only with the Cr^{3+} in aqueous media whereas there was no colour change observed for other metal ions. Test papers prepared for **DYN2-3** exhibited similar colorimetric changes with Cr^{3+} in aqueous solutions. Colour changes of the test papers can be observed for the aqueous solutions containing Cr^{3+} ion with concentrations varying from 1000 ppm to 10 ppm, and Cr^{3+} can be detected at the lowest concentration limit down to 10 ppm (Fig. 6). To investigate the accuracy of the test papers, the sewage (pH=6.3) was sampled for the comparison. ICP-AES spectra indicated that the concentration of Cr^{3+} from sewage sample is 12.083 mg/L (Fig S19). Colour changes of the test papers can be observed for the sample containing Cr^{3+} with concentrations ranging from 50 ppm to 10 ppm (Fig. 6b, Fig. 6d, and Fig. 6f). Although traditional methods of Cr^{3+} analysis, involving, e.g., ICP-AES and ICP-MS remain important, the easy-to-prepare and easy-to-detect test papers for Cr^{3+} are very interesting. We hope that this kind of cheap and effective new sensor will prove advantageous in helping to monitor of heavy metal pollution in undeveloped regions.

4. Conclusion

In summary, we have designed and synthesized novel dimethyl yellow-based probes **DYN1-3** for Cr^{3+} sensing, which introduced multidentate chelating units as the metal receiving moieties. By introducing suitable terminal coordination groups into the molecules, **DYN1-3** showed highly selective and sensitive colorimetric response to Cr^{3+} in aqueous media with 4:4, 1:2, and 4:4 binding modes,

respectively. The naked eye detectable color changes in absorption (light yellow to magenta) makes **DYN1-3** unique sensors for Cr^{3+}. To the best of our knowledge, **DYNs** was the first Cr^{3+} chemosensor afforded an interesting "naked eye" output manner. For practical applications, we have developed one kind of easy-to-prepare colorimetric test papers for tracing Cr^{3+} in natural water. We anticipate that this approach could open the door for discovering applied Cr^{3+} sensors in water for a variety of chemical and biological applications in the future.

Acknowledgements

This work was supported by the Scientific Research Foundation for Doctors of Science and Technology Department of Liaoning Province (No. 20131063); Key Laboratory of Photochemical Conversion and Optoelectronic Materials，TIPC，CAS.

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TOC for

Dimethyl yellow-based colorimetric chemosensors for "naked eye" detection of Cr^{3+} in aqueous media *via* test papers

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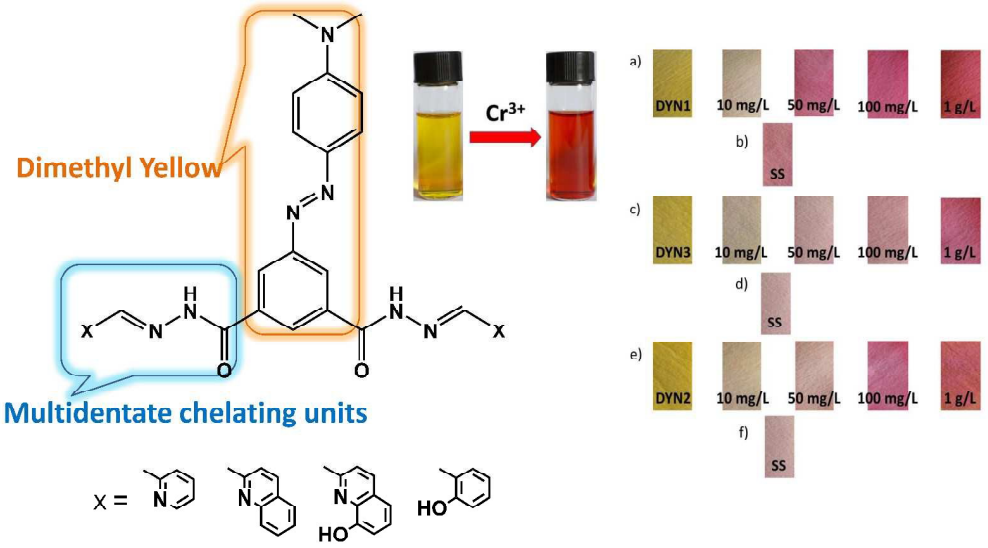

New Dimethyl yellow-based dipodal receptors as colorimetric probes were designed and synthesised for selectively sensing Cr^{3+} in a "naked eye" output manner *via* test papers.