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Synthesis and binding properties of a new fluorescent molecular clip based on 2-ethyl cyanoacrylate

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A new fluorescent molecular clip based on 2-ethyl cyanoacrylate has been synthesised and its binding properties investigated by fluorescence spectroscopy to show that it can selectively bind Fe^{3+} with fluorescence quenching.

Keywords: molecular clip, 2-ethyl cyanoacrylate, fluorescence quenching, Fe^{3+}

The design and synthesis of novel receptors with different molecular cavities is one of the major challenges in hostguest chemistry. 2-Ethyl cyanoacrylate is useful as an inhibitor of *Pyricularia oryzae*, *Rhizoctonia solani*, *Botrytis cinerea* and *Gibberella zeae*.[1] It possesses good symmetry within the aromatic walls and shows good binding properties for aromatic guests, especially, for dihydroxybenzene, by hydrogen bonding, it–it stacking interactions and a so-called cavity-effect.[2–4]

We have found derivatives of 2-ethyl cyanoacrylate form new molecular clips. We now report the synthesis of one and develop its function as a selective fluorescent chemsensor for Fe^{3+}. We have designed the new molecular clip (**4**) which has a large π-system that can be used as the signalling subunit in the two sidewalls and two carbonyl oxygen atoms of the pyrazole ring and nitrogen atoms in the cavity be can used as the potential binding sites. We now report the synthesis of **4** and a binding study with different metal ions.

The synthesis of the title clip molecule **4** is shown in Scheme 1. The structure and conformation of compound **4** were further elucidated by single crystal X-ray diffraction, as shown in Fig. 1.

The crystals of **4** were obtained by slow evaporation of its solution in ethyl acetate/petroleum ether (3:1, v/v) mixtures. The crystal structure of **4** clearly reveals that it has a well-defined geometry due to the rigidity that the fused rings confer on the molecule. The structure shows a planar chlorobenzene ring (N1, N2, C4, C5, C3) approximately perpendicular to the pyrazole ring (N1, N2, C4, C5, C3) with a dihedral angle of 33.3 °, the dihedral angle between the chlorobenzene and the other pyrazole rings (N5, N6, C21, C22, C23) is 59.9 °, the dihedral angle between the pyrazole rings is 84.7 °. The molecular conformation is stabilised by N---H...O hydrogen bonding. The chlorobenzene ring and pyrazole rings in the cavity give **4** great potential to bind metal ions.

The binding properties of **4** with various metal ions were investigated by fluorescent spectroscopy titration experiments.

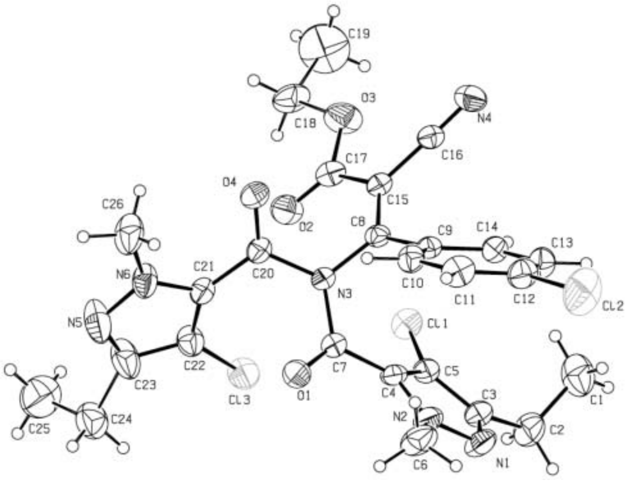
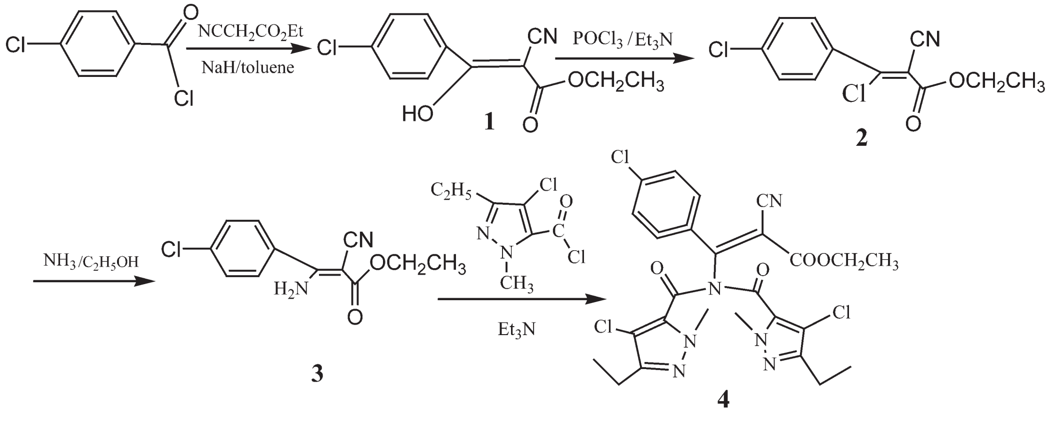


Fig. 1

Changes of the fluorescence properties of **4** (in 1×10^{-5} M DMF) solution caused by 15 equiv. of various metal ions (Co^{2+}, Cr^{3+}, Sn^{4+}, Cu^{2+} , Sr^{2+} , Ag^{+}, Ni^{2+}, Pb^{2+}, Fe^{3+}) were measured until their emission intensity was constant. The results show that Fe^{3+} produced significant quenching of the fluorescent emission, whereas the other metals ion that were tested only show a relatively insignificant change (Fig. 2). It can be concluded that **4** has a high selectivity for the recognition of Fe^{3+}.

The sensitivity of the fluorescence emission response of **4** towards Fe^{3+} was also examined under the same conditions with various Fe^{3+} concentrations (Fig. 3). The fluorescence intensity of **4** decreased continually upon addition of Fe^{3+}. When the concentration of Fe^{3+} was increased to 15 equiv, the fluorescence intensity of **4** was reduced to 80% of the initial value. From a Stern–Volmer plot (Fig. 3), the quenching constant was estimated as 5.37×10^{4} M^{-1}.



Scheme 1

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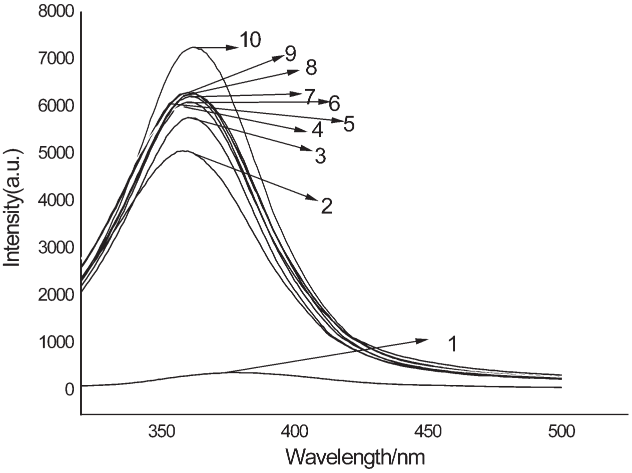

Fig. 2 Fluorescence emission changes of **4** (1×10^{-5} M) in DMF in the presence of 12×10^{-5} M of various metal ions (excitation at 358 nm). (1) Fe^{3+}, (2) host, (3) Sn^{4+}, (4) Cu^{2+}, (5) Sr^{2+}, (6) Ag^{+}, (7)Ni^{2+}, (8)Cr^{3+}, (9) Co^{2+}, (10) Pb^{2+}.

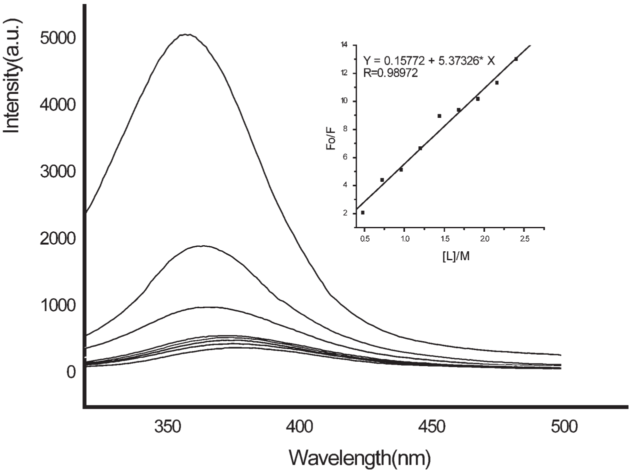

Fig. 3 Fluorescence emission spectra (excitation at 358nm) of **4** (1×10^{-5} M) in DMF in the presence of different concentration of Fe^{3+}. Inset: Stern–Volmer plot of the emission data.

The quenching of the electronically excited state of aromatic hydrocarbons by Fe^{3+} chelates is a known phenomenon that has been the subject of extensive investigations. It has been suggested that two main pathways can account for the efficient radiationless deactivation of the singlet excited state, electron transfer from the excited aromatic chromophore to the metal and/or energy transfer from the excited aromatic chromophore to low-lying metal centred energy states. Such processes could be particularly effective in the complex of **4** with Fe^{3+}, due probably to the fact that the chelated metal cation is held very close to two excited aromatic chromophores. In addition, because the molecular clips **4** has different sidewalls but the same binding properties compared to previously reported molecular clips, we may draw the conclusion that the 2-ethyl cyanoacrylate ring plays a crucial role in the recognition of Fe^{3+}.

In conclusion, a new clip molecule derived from 2-ethyl cyanoacrylate as fluorescent chemosensor has been designed and synthesised. It displays high selectivity for Fe^{3+} revealed by fluorescence quenching.

Experimental

All reagents, obtained from commercial sources, were of AR grade. Melting points were determined with an XT4A micro-melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Mercury Plus-400 spectrometer with TMS as internal reference and $CDCl_3$ as solvent. IR spectra were recorded on a Perkin-Elmer PE-983 IR spectrometer as KBr pellets. MS were obtained with a Finnigan Trace MS instrument using the EI method. Elemental analyses were carried out on a Vario EL III instrument. Fluorescence spectra were determined on a Hitachi F-4500 instrument.

Compounds **1**, **2** and **3**$^{5-6}$ were prepared by the literature method.

Preparation of **4**: To a solution of compound **3** (1.25g, 0.0050 mol) in CH_2Cl_2 (18 mL), 4-chloro-3-ethyl-1- methyl-1H-pyrazole-5-carbonyl chloride (3.11 g, 0.015 mol) was added. Subsequently, Et_3N (1.52 g, 0.015 mol) was added dropwise into the solution under stirring. The reaction mixture was heated to reflux, then stirred for 4 h. Subsequently, it was cooled to room temperature. The reaction solution was filtered off and some white solid was separated. The organic phase was washed with water and then dried over Na_2SO_4. After removal of the solvent, a brown solid was obtained. After column chromatography using ethylacetate/light petroleum (1:6) as eluent, compound **4** (1.1g, 37.16%) was obtained as a white solid. M.p.134.2–134.9 °C (dec.). TLC ($CH_3COOCH_2CH_3$/petroleum ether, 3:1), R_f 0.51. IR (KBr, cm^{-1}): 2226, 1740, 1728, 1685, 1630, 1645. ^{1}H NMR δ: 1.25 (t, 6H, CH_3, J = 7.5Hz), 1.37 (t, 3H, $CO_2CH_2CH_3$, J = 7.0 Hz), 2.66 (q, 4H, CH_2CH_3, J = 7.5 Hz), 3.9 (s, 6H, NCH_3), 4.36 (q, 2H, $CO_2CH_2CH_3$, J = 7.0 Hz), 7.26–7.45 (m, 4H, ArH). MS (EI): *m/z* = 593 [M + H]$^+$. Anal. Calcd for $C_{26}H_{25}Cl_3N_60_4$ (591.87): C, 52.75; H, 4.27; N, 17.98. Found: C, 52.51; H, 4.15; N, 17.67 %.

X-ray diffraction

A white crystal of **4** was mounted on a glass fibre in a random orientation at 298(2) K. The determination of the unit cell and the data collection were performed with MoKa radiation (λ = 0.71073 Å) on a Bruker Smart Apex-CCD diffactometer with a ψ-ω scan mode. The structure was solved by direct methods with the SHELXS-97 programs^{7,8} and expanded by Fourier technique. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at the calculated positions.

Crystal data for **4**: $C_{26}H_{25}Cl_3N_60_4$, M = 591.87, Triclinic, space group P2(1)/c, a = 10.7277(3)Å, b = 16.1476(5)Å, c = 17.3109(5)Å, α = 90 °, β = 107.671(2)°, γ = 90°, V = 2857.21(14) Å^3, Z = 4, Dc = 1.376 Mg m^{-3}, Reflections collected: 18010, independent reflections: 5600 [R_{int} = 0.0453], Final R indices [$I>2σ(I)$]: R^1 = 0.0646, wR^2 = 0.1519. R indices (all data): R^1 = 0.1050, wR^2= 0.1700.

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