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A Simple Fluorescent Ion-Pair Binding Host that Acts as an "If-Then" Logic Gate

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A donor-acceptor-type carbazole pyridine derivative behaves as an "if-then" fluorescent molecular logic gate using chemical inputs in the form of copper(II) cations and nitrate anions.

Introduction

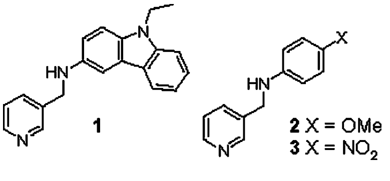
The field of molecular electronics has been of enduring interest over the past 20 years or so.[1,2] Ever since the first report of a photonic molecular AND gate by de Silva in 1993[3] there has been particular interest in molecular analogues of logic gates that respond to chemical stimuli by means of fluorescence or other photophysical output.[1,4–8] There are now examples of molecular systems that can carry out a wide range of logic functions such as AND, NOR, XOR, NAND, INHIBIT, half-addition, demultiplexing etc.[9–16] Among the common logic operations, however, there are relatively few reports of simple molecules that can perform a two-input material conditional ("if-then") logic function. The truth table for the material conditional operation is given in Table 1.[17] The operation requires the molecular logic gate to be in the "on" state both in the absence of any input and in the presence of both inputs. One input must switch the gate "off" while the other must switch it back "on" again. The material conditional gate thus gives an output either in the absence of any input, or in the presence of one particular activating input. The requirement of a sequence of "on", "off" and "on" again in response to zero, one and two chemical inputs, respectively makes the material conditional logic operation more challenging to achieve in a chemical system than gates requiring simple "on-off" operations, although logic gates have been prepared that depend on ion-pair binding.[18–20] We now report a simple receptor capable of binding both Cu^{2+} and NO_3^- anions that exhibits material conditional logical fluoresence output.

Table 1. Truth Table for the material conditional logic operation.[17]

Input(1) Cu^{2+}	Input(1) NO_3^-	Output emission at 490 nm
0	0	1
1	0	0
0	1	1
1	1	1

Results and Discussion

Compound **1** is readily prepared by condensation of pyridine-3-carboxaldehyde with 9-ethyl-9*H*-carbazol-3-ylamine followed by reduction with $NaBH_4$ and its ruthenium(II) complexes have been shown to photophysically sense anions.[21] The ligand is designed such that photoexcitation of the carbazole chromophore results in intra-ligand charge transfer (ILCT) to the pyridyl acceptor. This charge transfer should be influenced by the binding of the pyridyl functionality to metal ions and by hydrogen bonding of the amine groups to anions. The UV/Vis spectrum of the ligand in acetonitrile solution shows a band at 377 nm assigned to the ILCT process. The same band is observed in model compounds **2** and **3**.[21] Compound **1** (Scheme 1) also exhibits a broad emission maximum at 430 nm in its fluorescence spectrum. The assignment of this absorption band as an ILCT process was confirmed by time-dependent DFT calculations which suggested that the first three excited states of the ligand contribute to a broad band at about 350 nm (cf. 377 nm observed in MeCN) and involve charge transfer



Scheme 1. Structures of ligands **1**–**3**.

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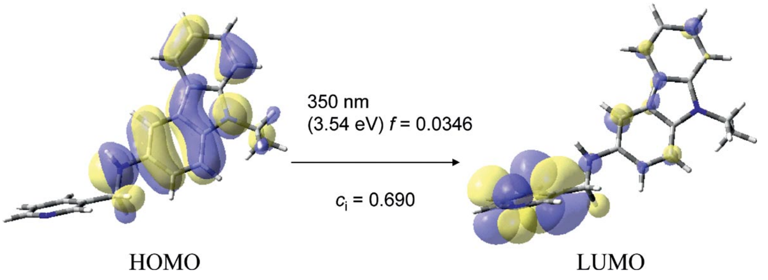

Figure 1. Electronic transition to the dominant configuration of the first excited state of **1**.[21]

from the carbazole to the pyridyl group. Figure 1 shows the dominant single particle-hole configuration (c_i = 0.69) of the first excited state.

The binding of a range of transition-metal ions with **1** was probed by UV/Vis spectrophotometric titration experiments in acetonitrile solution and fitted using Specfit.[22] This gave the following binding constants for the formation of 1:1 complexes: $Co(NO_3)_2$ 3.98(11), $Cu(BF_4)_2$ 4.44(18), $Cu(CF_3SO_3)$ 4.66(15), $Cu(O_2CMe)_2$, 3.06(6), $Ni(NO_3)_2$ 4.47(11) and $Zn(CF_3SO_3)_2$ 4.50(9). For $CuCl_2$ and $Cu(NO_3)_2$ the best fit was for a 1:1 and 2:1 M/L ratio with β_{11} = 4.36(9) and β_{21} = 7.21(15) for the chloride and β_{11} = 5.76(16) and β_{21} = 10.62(15) for the nitrate. The larger errors reflect the more complicated stoichiometry and it may be that higher species are also present. In general, these values are consistent with typical affinities of monodentate pyridyl ligands for transition metals in acetonitrile, and it is noticeable that the copper(II) nitrate is the most strongly bound, with significant anion dependence on the copper(II) affinity.

Remarkable differences in the ability of the various metal salts to quench the ILCT emission of the ligand were observed, however, the weakly bound copper(II) acetate has essentially no effect on the emission intensity. While structural data on complexes of **1** was not forthcoming, the X-ray crystal structure of the model complex [{Cu(μ-OAc)$_2$-(**3**)}$_2$] (**4**) suggests that the copper acetate complexes exist as metal–metal bonded dimers (Figure 2)[23,24] that would thus be expected to bind weakly to the copper(II) axial site. This diamagnetic structure is thus highly unrepresentative of the likely paramagnetic monomeric complexes arising from the reactions of **1** with other copper(II) salts.

In contrast to copper acetate, addition of ca. four equivalents of copper(II) triflate, tetrafluoroborate and chloride resulted in the quenching of the emission of **1**. The quenching may be due to an LMCT type process involving the vacant copper(II) d orbitals (these orbitals are filled by metal–metal bonding in the analogous acetate compex), analogous to the ruthenium(II) system,[21] direct energy transfer to a copper-centred excited state or oxidative electron transfer to copper(II). Addition of copper(II) nitrate results in the disappearance of the emission of **1** and the growth of a new band at longer wavelength, λ_{max} = 520 nm. Addition of other nitrate salts (Co, Ni) or zinc(II) triflate results in some dimunition of the intensity of the 430 nm emission, but it is still relatively strong even after addition of 10 equiv. of metal salt. Thus it is only copper(II) nitrate in particular that gives a significant emission at 520 nm, Figure 3. Titration of ligand **1** with tetrabutyl ammonium nitrate without addition of copper(II) does not result in any significant change in the fluorescence wavelength or intensity hence the new emission is a unique property of the addition of *both* copper(II) and nitrate anion and suggests the formation of a ternary copper(II)-**1**-nitrate complex. In terms of molecular logic we can designate the Cu^{2+} and NO_3^- ions as chemical inputs. We observe fluoresence in the absence of either input with a maximum at 430 nm. Addition of NO_3^- has no effect on the emission Addition of Cu^{2+} (but not Zn^{2+}, Co^{2+} or Ni^{2+}) results in the quenching of this band. Addition of both inputs together gives emission with a maximum at 520 nm. If we focus on one particular wavelength such as 490 nm where there is significant emission either in the absence of inputs or in the presence of either NO_3^- or both Cu^{II} and NO_3^- then this behaviour corresponds to the material conditional Truth Table given in Table 1.

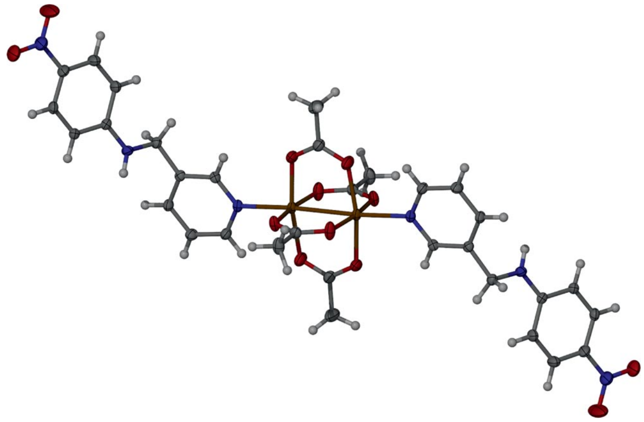

Figure 2. X-ray molecular structure of the model compound **4**.

In order to probe the reversibility of the quenching process we undertook the addition of tetrabutylammonium nitrate (input 2) to a solution of ligand **1** in the presence of four equivalents of copper(II) triflate (input 1). Under these circumstances the system is in a quenched "0" state. The nitrate addition, however, results in the immediate growth of the 520 nm emission converting the system from an "off" to an "on" state. The quenching by copper(II) triflate is fully reversible; addition of cyclam (a strong complexing

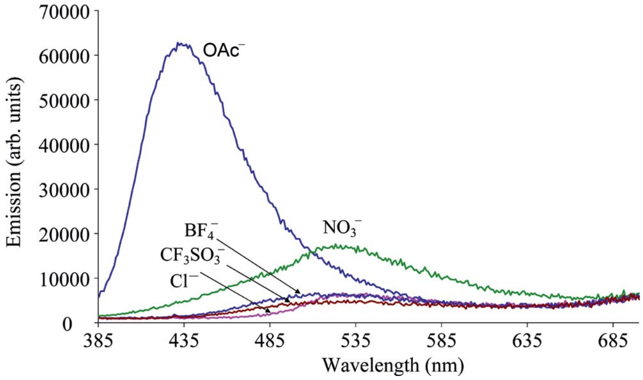

Figure 3. Fluorescence emission spectrum of **1** (1.03×10^{-4} M) in the presence of 10 mol-equiv. of CuX_2 in CH_3CN (X = OAc, Cl, NO_3, BF_4 and CF_3SO_3).

agent for copper(II)[25]) results in recovery of the free ligand emission at 430 nm as the cyclam sequesters the copper(II) and liberates free **1**. Similarly, addition of cyclam to the copper(II)-**1**-NO_3^- mixture with emission centred on 520 nm, also results is displacement of free **1** and recovery of the emission at 430 nm (Figure 4).

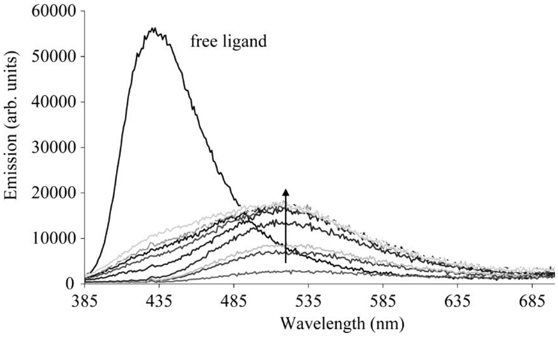

Figure 4. Fluorescence emission spectrum of **1** (1.03×10^{-4} M, MeCN solution) in the presence of four equivalents of Cu-$(CF_3SO_3)_2$ upon addition of increasing amounts of NBu_4NO_3 up to 10 mol-equiv.

The precise assignment of the anion-induced emission at 520 nm is the subject of current work, however it is likely that simultaneous coordination of nitrate to the metal centre and hydrogen bonding to the ligand amine group[26,27] play a significant role.

Conclusions

In conclusion we have demonstrated that a simple fluorophore-receptor ligand is capable of behaving as a photonic analogue of a material conditional ("if-then") two-input logic gate. The system responds highly selectively and reversibly to a particular metal ion, Cu^{2+}, and a particular anion, NO_3^-.

Experimental Section

Crystal Data for 4: $C_{32}H_{34}Cu_2N_6O_{12}$, M = 821.73, blue-green plate, $0.32\times0.31\times0.28$ mm³, monoclinic, space group $P2_1/c$ (No. 14), a = 15.1171(6), b = 13.9050(6), c = 8.4424(4) Å, β = 99.282(2)°, V = 1751.38(13) Å³, Z = 2, D_c = 1.558 g/cm³, $F(000)$ = 844, Smart 1 K, Mo-K_α radiation, λ = 0.71073 Å, T = 393(2) K, $2\theta_{max}$ = 60.0°, 15872 reflections collected, 5101 unique (R_{int} = 0.0306). Final $GooF$ = 1.022, $R1$ = 0.0355, $wR2$ = 0.0897, R indices based on 4125 reflections with $I > 2\sigma(I)$, 235 parameters, 0 restraints; Lp and absorption corrections applied, μ = 1.285 mm⁻¹.

CCDC-719771 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fluorescence titration experiments were carried out using a Jobin–Yvon Horiba Fluorolog 3–22 Tau-3 spectrofluorimeter with a right angle illumination method at room temperature and were corrected for the spectral response of the instrument. A specific concentration of host (as indicated in Figure captions) was made up in a single quartz cuvette, with a path length of 1 cm, in acetonitrile (3.0 mL). The anions, as their tetrabutylammonium salts, were made up to 300 µL, 10 times the concentration of the host, in acetonitrile. 15 µL aliquots of the guest were added to the cuvette, the sample was excited at 375 nm, and spectra were recorded after each addition.

Acknowledgments

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