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Copper(II)-directed static excimer formation of an anthracene-based highly selective fluorescent receptor

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ABSTRACT

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Keywords: Excimer Anthracene PET Copper Disassociation A novel "turn-on" fluorescent receptor methylanthracenylimine benzoate (MAB) with anthracene as the fluorophore and methyl 3-aminobenzoate as a metal ion chelating center has been designed and synthesized. The ability of the prepared receptor to detect metal ions has been evaluated by the changes in its emission intensity. MAB demonstrates high selectivity and sensitivity for Cu^{2+} among the nineteen metal ions examined in MeCN. The interaction of MAB with Cu^{2+} causes a significant enhancement in emission intensity due to the combination of a unique anthracenyl static excimer formation, the restricted C=N isomerization and the suppression of highly efficient photoinduced electron transfer (PET) process. The disassociation of the excimer species to monomers is directed by temperature, Cu^{2+} concentration and solvent fraction. Furthermore, the considerable 'off-on' fluorescence response or the conversion of the excimer species to monomers concomitantly led to the apparent colour changes, which could also be identified easily by the naked eye using a UV lamp.

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Copper is the third most abundant element, after iron and zinc, among the heavy metal ions in the human body and, thus, draws considerable interest for its determination.¹⁻⁴ Cu²⁺ ions induce the activation of dioxygen, which is essential to all living organisms and is an important cofactor for many metalloenzymes. Copper also plays roles in iron absorption, in redox processes, and various enzyme activities.⁵⁻⁷ Although copper is an essential trace element for living organisms, it is dangerous at high concentration levels.⁸⁻¹⁰ Several methods including inductively coupled plasma-atomic emission spectrometry,¹¹ inductively coupled plasma-mass spectroscopy,¹² atomic absorption/emission spectroscopy,¹³ and voltammetry¹⁴ have been utilized for measuring Cu^{2+} levels. Most of these methods differ in efficiency and show disadvantages such as low selectivity, low sensitivity needing expensive instruments for detection of Cu²⁺ and delayed responses to Cu²⁺, and are not suitable for on-line monitoring. In contrast, fluorescence detection is a more practical and favorable method in medicine, biology, and environmental chemistry.¹⁵⁻¹⁷ Most Cu²⁺ sensors work as fluorescence quenchers upon binding with Cu^{2+} due to its inherent paramagnetic nature, via energy/electron transfer or spin-orbital coupling.¹⁸⁻²¹ There are a limited number of examples reported wherein enhancement in the fluorescence intensity has been observed upon complexation with Cu²⁺ ions.²²⁻²⁵

Recently, changes in the photophysical properties of molecules on complexation have attracted significant attention in recognition processes. These changes may result from variations in several processes such as excimer/exciplex formation or destruction and electron transfer.²⁶⁻²⁸ To detect different analytes, excimer/exciplex formation or destruction is usually advantageous. Some chemosensors manipulate the changes in the

intensity ratio of excimer to monomer emission as an essential parameter because this ratio depends on the stoichiometry between guest and host. The possible interferences from the environment can be excluded by built-in verification of two emission bands in ratiometric sensing.²⁹⁻³¹

Anthracene acting as a fluorophore has been utilized effectively since its emission property varies according to its local environment.³²⁻³⁴ Excellent monomer and excimer emission changes occur at remarkably different wavelengths based on the distance between two anthracene moieties. Excimer emissions are characteristically observed with a broad fluorescence band with the maxima at lower energy in comparison to monomer emissions, and this band can be taken into account to examine the molecular recognition process in more detail.³⁵⁻³⁸ Although hostdirected intramolecular excimer formation in anthracenecontaining compounds as a result π - π interactions between the anthracene units is well documented, 39-41 there are a few examples which form intermolecular excimer species.42,43 Considering such unique physical properties of anthracene, we have designed a simple but highly effective methyl anthracenylimine benzoate (MAB) derivative, which has the ability to form self-assembled anthracenyl excimer species with a specific metal ion.

MAB was readily synthesized by the route outlined in Scheme 1. Methyl 3-aminobenzoate was prepared starting from benzoic acid. Fischer esterification of benzoic acid afforded methyl benzoate in quantitative yield. The nitration of methyl benzoate with a mixture of HNO_3/H_2SO_4 provided methyl 3-nitrobenzoate in good yield. Reduction of methyl 3-nitrobenzoate with Fe powder/AcOH gave methyl 3-aminobenzoate, the condensation reaction of which with 9-anthracene carboxaldehyde provided

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MAB in 82% yield. The structures of the intermediates and final product were verified by ¹H NMR, ¹³C NMR and FT-IR spectroscopy and HRMS (Supporting Information).



Scheme 1. Synthetic route to MAB

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The sensing ability of MAB toward a wide range of metal ions $(L_{1}^{+}, Na^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^{+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+} and Fe^{3+})$ was investigated by fluorescence spectroscopy (λ_{ex} = 388 nm) in MeCN at 20 °C (Figure 1). In the absence of any metal ion, MAB shows a very weak emission at 439 nm in MeCN due to the highly efficient PET (photoinduced electron transfer) process between the methyl 3-aminobenzoate receptor moiety and the anthracene fluorophore. Among the nineteen metal ions, only Cu²⁺ was found to give a distinct spectral change. The addition of Cu^{2+} (5.0 equiv) induces two new emission bands, a weak monomer emission band centred at 471 nm and a strong excimer emission band centred at 594 nm, indicating strong complex formation with Cu²⁺ ions. Under similar conditions, the other tested metal ions had very little effect on the emission. The value of the sensing index (I_{594}/I_{439}) for **MAB** to Cu²⁺ is 14.8 whereas it is less than 0.4 for the other metal ions (Figure 1b). Therefore, MAB shows high selectivity toward Cu²⁺ over other competing metal ions.



Figure 1. (a) Changes in the emission spectra of **MAB** (10.0 μ M) upon addition of various metal ions (50.0 μ M) in MeCN ($\lambda_{ex} = 388$ nm) at 20 °C, (b) histogram of the sensing indexes (I_{594}/I_{439}) for **MAB** to various metal ions.

The fluorogenic binding affinity of **MAB** with Cu^{2+} ions has been examined by fluorescence titration experiments (Figure 2a). On binding of **MAB** to Cu^{2+} ions, the anthracene units come together and form a static excimer, as indicated by an increase in the excimer emission intensity at 594 nm. The increasing concentration of Cu^{2+} induces a slight disassociation to the monomeric form, which has an explicitly different emission wavelength at 471 nm compared to that of the excimer. The intensity of the excimer emission band reaches a maximum with 2.0 equivalents of Cu^{2+} . After this point, no significant change in the spectrum was observed. This observation demonstrates that the disassociation of the excimer species to monomers is slightly dependent on the Cu^{2+} concentration, which is consistent with intermolecular excimer formation (Figure 2b).^{44,45}



Figure 2. (a) Emission titration spectra of **MAB** (10.0 μ M) with Cu²⁺ (1.0 mM) in MeCN at 20 °C, (b) change in the excimer intensities at 594 nm and the monomer intensities at 471 nm during the titration of **MAB** with Cu²⁺.

Generation of a dynamic or static excimer is associated with the distance between two fluorophores.⁴⁶ A practical method to discriminate a dynamic and static excimer is by examination of the excitation spectrum. The results indicate that the excitation spectra of the **MAB**-Cu²⁺ complex at 471 nm (monomer) differ from that at 594 nm (excimer) (Figure 3). Thus, the excitation spectra suggest that the chemical species corresponding to the emissions observed at 471 and 594 nm are of a different chemical origin. This observation is also clear evidence for the generation of an intermolecular anthracenyl static excimer of **MAB** upon Cu²⁺ ion binding. The UV-vis spectra of **MAB** show a new absorption band at 503 nm upon the addition of Cu²⁺. This result also indicates that the anthracene moiety of **MAB**-Cu²⁺ forms a favourable intermolecular π - π stacked dimer between two anthracene moieties in the ground state.



Figure 3. Excitation spectra (normalized) of the MAB-Cu²⁺ complex monitored at 471 and 594 nm at 20 °C.

In order to gain an insight into the disassociation of the excimer species to monomers, changes in the fluorescence spectra of the MAB-Cu²⁺ complex were monitored against temperature (Figure 4). For this purpose, the fluorescence spectra of a solution of the MAB-Cu²⁺ complex at the corresponding temperature were recorded until no significant changes in the spectra were observed. The results clearly show that the excimer emission intensity at 594 nm decreases significantly as the temperature increases, whereas the monomer emission band at 471 nm increased ratiometrically with the formation of an isoemissive point at 557 nm. Correspondingly, a decrease in the excimer/monomer intensity ratio (I_E/I_M) was observed. In Figure 4b, excimer and monomer emission intensities are plotted as a function of temperature. As the temperature increases, the monomer emission is strongly promoted with regard to the excimer emission, as reflected by the lines, from which average intensity changes of 20.62/°C for decreasing excimer intensity and 17.13/°C for increasing monomer intensity are obtained. This observation explicitly suggests that a 1:2 (metal:ligand stoichiometry) complex disassociates yielding a new 1:1 species in solution when the temperature increases in accordance with the following equilibrium.47

$$\left[\operatorname{Cu}(\mathbf{MAB})_2\right]^{2+} + \operatorname{Cu}^{2+} \rightleftharpoons 2\left[\operatorname{Cu}(\mathbf{MAB})\right]^{2+}$$

The disassociation process reveals an application of the **MAB**- Cu^{2+} complex as a temperature sensor. However, monomeric species do not become excimers as the temperature decreases. Therefore, the system is said to be irreversible in the temperature range tested. Moreover, this conversion results in the apparent color change from orange to green, which could also be identified by the naked eye easily using a UV lamp.

MAB has been designed as a "fluorophore–spacer–receptor" format according to the design principle of a PET process.²⁶ In **MAB**, the methyl 3-aminobenzoate unit is connected by the imine function to the anthracene, which provides azomethine-N and carbonyl-O binding sites to interact with metal ions.^{48,49} The probable mechanism of complexation and PET process is shown in Scheme 2. The remarkable fluorescence enhancement of **MAB** upon addition of Cu²⁺ ions is attributed to the combination of the following factors: the suppression of the highly efficient PET process,³⁵ unique self-assembled excimer formation^{37,38} and the restricted C=N isomerization.⁵⁰



Figure 4. (a) Fluorescence response of a solution obtained from a mixture of **MAB** (10.0 μ M) with Cu²⁺ (2.0 equiv) in MeCN at varying temperatures, (b) plots of the decreasing excimer emission at 594 nm and the increasing monomer emission at 471 nm as the temperature increases during the disassociation of the excimer species to monomers.



Scheme 2. Proposed mechanism and PET process for the interaction of MAB with Cu²⁺.

To understand the binding affinity of **MAB** with Cu²⁺, an absorption titration experiment was performed (Figure 5). Careful analysis of the spectra obtained during the titration experiments with Cu²⁺ discloses that further small spectral changes occur, except for a new absorption band at 503 nm after the addition of 0.5 equivalents of Cu²⁺ (Figure 5, inset). In particular, the absorbance at 503 nm, which is increased until 0.5 equivalents of Cu²⁺ has been added, decreases again slightly until 1.0 equivalent of Cu²⁺ had been added. The titration profile clearly supports the formation of an excimer. The logarithmic association constant ($logK_a$) of the **MAB**-Cu²⁺ complex according to the 1:2 binding model has been determined by the Benesi-Hildebrand method⁵¹ using UV-vis titration data and is found to be 11.24 M⁻² (Figure S1).

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Figure 5. Absorption titration spectra of MAB (0.1 mM) upon addition of an increasing concentration of Cu^{2+} ions (10.0 mM) in MeCN at 20 °C. Inset: Mole-ratio plot for the interaction of MAB with Cu^{2+} ions at 503 nm.

In order to support a 1:2 stoichiometry determined by the mole-ratio method, the method of continuous variations (Job's method) was also performed (Figure 6). As expected, the complex formation between **MAB** and Cu^{2+} is in accordance with the Job plot analysis. The Job's plot with respect to 503 nm shows a maximum absorbance change at about 0.66 which indicates the presence of a 1:2 (M:L) stoichiometry.



Figure 6. Job's plot for **MAB** with Cu^{2+} ions ($\lambda = 503$ nm) in MeCN at 20 °C. The total concentration of [**MAB**]+[Cu^{2+}] is 0.1 mM.



Figure 7. The visual fluorescence response of MAB (0.1 mM) upon addition of various metal ions (5.0 equiv) under a UV lamp at 365 nm.

MAB displays a very weak emission band at 439 nm with a very low quantum yield of $\Phi_{MAB} = 0.0054$, which resulted from the highly efficient PET quenching of the excited state of the anthracene moiety from the methyl iminobenzoate electron-donating receptor moiety. As the Cu²⁺ concentration increases, a considerable enhancement in the anthracene excimer emission intensity at 594 nm is observed with a significant red-shift (155

nm). Upon complexation, the quantum yield of **MAB**-Cu²⁺ reaches $\Phi_{\text{MAB-Cu}} = 0.35$ (ca. 65 fold). Hence, the detection process results in the apparent color change from colorless to orange, which could also be identified by the naked eye easily using a UV lamp (Figure 7).

Competitive metal ion interference studies have been carried out for the **MAB**–Cu²⁺ system in MeCN in the presence of background metal ions. **MAB** exhibits significant selectivity towards Cu²⁺ ions as is shown in Figure 8. This indicates that copper ion detection by **MAB** is not influenced by the presence of the other metal ions tested, except for Al³⁺, Fe³⁺ and Fe²⁺, where a slight interference is observed. The detection limit of **MAB**–Cu²⁺ is calculated as 0.53 μ M based on excimer emission from fluorescence titrations. This result shows that **MAB** possesses a high sensitivity in detecting Cu²⁺ ions.



Figure 8. Metal-ion selectivity of MAB (10.0 μ M) in the presence of different metal ions (10.0 μ M) in MeCN at 20 °C.

We have already reported that the disassociation of excimer species of the **MAB**-Cu²⁺ complex in MeCN to monomer species is temperature-dependent. However, we have also observed that a change in the solvent fraction induces the disassociation of excimers to monomer species. As is well known, the emission property is considerably sensitive to the nature of the solvent.⁵² We firstly changed the water fraction in a solution of the MAB-Cu²⁺ complex in MeCN, and surprisingly found that water induces the disassociation of the excimer species to monomers with increasing water content up to 4.8%, with the formation of an isoemissive point at about 571 nm, and after this point, no significant change in the spectra were observed. Figure 9 shows that there is also a blue-shift (13 nm) of the excimer emission at 594 nm and a red-shift (32 nm) of the monomer emission at 508 nm as the water content increases from 0% to 4.8% with respect to that of a water-free example. The fluorescence titrations with other polar solvents such as MeOH, EG (ethylene glycol), n-PrOH and EtOH display similar disassociation behaviours to water with corresponding solvent contents in MeCN of 11.8%, 12.8%, 15.7% and 18.0% at different monomer emission wavelengths of 512, 513, 510 and 508 nm, respectively (Figures S4-7). The solvent-directed dissociation process reveals another application of the MAB-Cu²⁺ complex as a solvent sensor for the determination of the tested solvents, primarily H₂O, in MeCN through the linear increasing monomer intensity. Average intensity changes of 3.43/H2O (µL) for increasing monomer intensity were found. However, only MeCN, CH₂Cl₂ and acetone among the other tested solvents did not show significant disassociation properties (Figure S8). When the dielectric constants of the added solvents such as H₂O, MeOH, EG, n-PrOH and EtOH were compared to the solvent fraction, it was observed that there was no rational relationship between them. Therefore, the introduction of another solvent to a solution of the

MAB-Cu²⁺ complex in MeCN contributed to the conversion of excimer species into monomers according to the solvent type.



Figure 9. (a) Rational changes in both excimer and monomer emission intensities of a solution obtained from a mixture of MAB (5.0 μ M) with Cu²⁺ (2.0 equiv) as a function of water content in MeCN (λ_{ex} = 388 nm) at 20 °C. (b) Changes in the I_E/I_M ratio represented by the excimer intensities at 594 nm and the monomer intensities at 508 nm during the disassociation of excimer species to monomers. Inset: Plot of the decreasing excimer emission at 594 nm and the linear increase of monomer emission at 508 nm as the water content increases.

In summary, a novel anthracene-based, highly selective fluorescent receptor has been synthesized through a simple synthetic route, and its sensing ability for a wide range of metal ions (Li⁺, Na⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Zn²⁺, Cd²⁺, Hg²⁺, Al³⁺ and Pb²⁺) has been explored. MAB exhibits high selectivity and sensitivity for Cu²⁺ in the presence of various metal ions with a significant emission enhancement via unique copper(II)-directed static excimer formation. The basis of the excimer formation has been investigated and found to be static in nature from a survey of the excitation and absorption spectra. The results demonstrate that disassociation of the excimer species to monomers is caused by the temperature and solvent fraction. This dissociation process enables MAB to be used as a temperature and solvent sensor. The Job's plot and mole-ratio curves reveal a 1:2 (M:L) stoichiometry. MAB exhibits a high sensing index value of 14.8 for Cu²⁺ ions. The detection limit is sufficiently low to determine micromolar levels of Cu²⁺ ions. The present study is a good example of a receptor in which the rational conversion of excimer species to monomers can be monitored distinctly.

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Supplementary Material

Supplementary information (experimental procedures, characterization of compounds, and additional data) associated with this article is available. Supplementary data related to this

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- A novel anthracene-based fluorescent "turn on" • receptor (MAB) is reported.
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