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5-(*N*-Ethylcarbazol-3-yl)thiophene-2-carbaldehyde (ECTC): a novel fluorescent sensor for ferric ion

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Abstract: 5-(*N*-Ethylcarbazol-3-yl)thiophene-2-carbaldehyde (ECTC), was synthesized by Suzuki coupling reaction and characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis. This compound strongly quenches fluorescence of Fe^{3+} ion, whereas almost no quenching is observed in the presence of other metal ions including Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+} and Co^{2+}. Under optimized conditions, the fluorescence intensity of ECTC is quenched in a linear fashion by Fe^{3+} ion in a wide range of 0.1 μᴍ–10 μᴍ with the limit of detection below 0.1 μᴍ.

Keywords: carbazole derivative; ferric ion; fluorescent sensor; Suzuki coupling.

Introduction

The development of chemosensors for highly selective detection of metal ions has attracted considerable attention in recent years owing to their important roles in biological, environmental and chemical domains [1–4]. As one of the most essential trace elements in living organism, Fe^{3+} plays a major role in a wide range of biological processes such as oxygen metabolism, electron transport, and DNA synthesis. The variation of Fe^{3+} concentrations can produce a significant influence on physiological function of organism [5]. Moreover, iron(III) is an important limiting element for phytoplankton in water environment [6]. Thus, it is very important to establish efficient detecting and monitoring methods with high sensitivity and selectivity for the detection of Fe^{3+} in biological and environmental systems. To date, a series of fluorescent sensors for the detection of Fe^{3+} have been developed [7–11]. Some of these sensors suffer from complicated structure, laborious synthesis, and poor selectivity, which restricts their applications in environmental monitoring and biological assays [12–15]. Moreover, the detection limits of these sensors are mainly in the range of 10^{-3}–10^{-6} ᴍ [16–19] and it is difficult to detect low concentration of Fe^{3+} in solution. Interestingly, I^{-} can be used as an assistance reagent to detect Fe^{3+} at 10^{-6} ᴍ or even at lower concentration [20]. In this indirect approach, Fe^{3+} reacts with excess I^{-} to produce I_3^{-} that quenches the fluorescence of sensor molecules. Nevertheless, these systems containing the extra reagent are complicated. Therefore, it is a great challenge to find a fluorescent sensors for Fe^{3+} with simple structure and low detection limit.

Carbazole is the key structural moiety of many electroluminescent materials due to its excellent fluorescent properties [21, 22]. However, the reports about fluorescent sensors based on carbazole to detect and sense metal ions are relatively rare [23]. Herein, we designed and synthesized a novel fluorescent compound, 5-(*N*-ethylcarbazol-3-yl)thiophene-2-carbaldehyde (ECTC) *via* Suzuki coupling reaction. Upon addition of Fe^{3+} ions to the solution of ECTC, a significant fluorescence quenching is observed, whereas almost no quenching is observed in the presence of other tested metal ions (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+} and Co^{2+}). Hence, ECTC could act as a fluorescent sensor to detect and recognize Fe^{3+} ion in solution.

Results and discussion

ECTC was synthesized according to the synthetic route outlined in Scheme 1. Bromination of 9-ethylcarbazole [24] with *N*-bromosuccinimide followed by the Suzuki reaction with 5-formyl-2-thiopheneboronic acid provided the desired compound ECTC with good yield. Its structure was characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis.

First, the spectroscopic properties of compound ECTC were investigated. As shown in Figure 1, the maximum UV absorption peak is around 240 nm, which can be attributed to π-π* transitions of carbazole and thiophene

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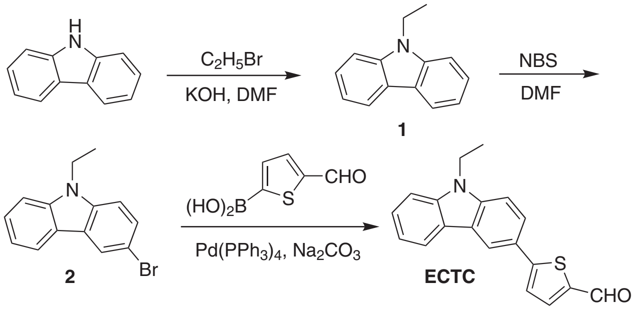

Scheme 1

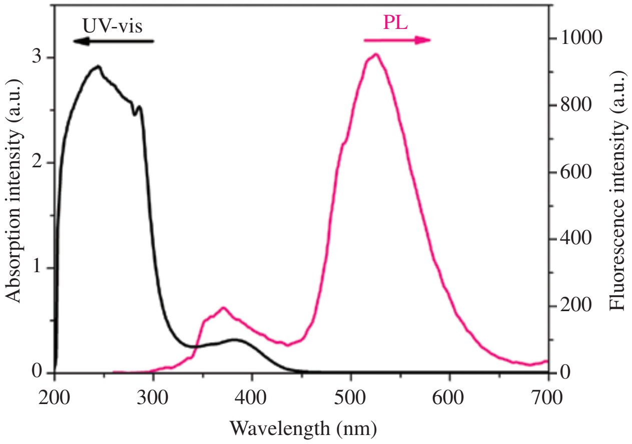

Figure 1 The UV–vis absorption and fluorescence emission spectra of ECTC (10 μм) in dichloromethane.

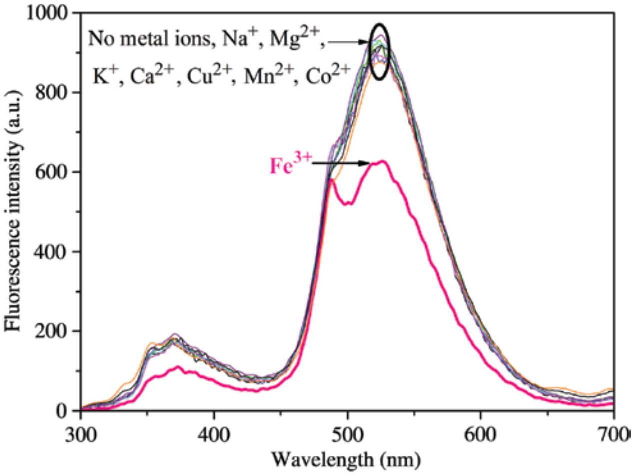

Figure 2 The effect of various metal ions on fluorescence of ECTC in ethanol.
Concentrations: [ECTC] = 1×10^{-5} м, [metal ion] = 1×10^{-5} м; λ_{ex} = 240 nm.

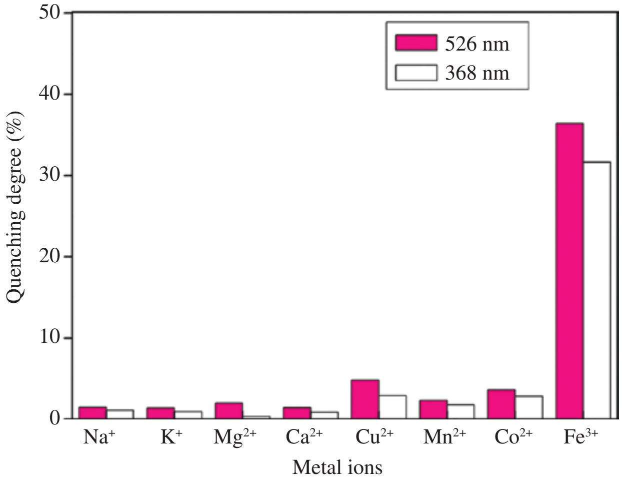

Figure 3 The quenching degrees of fluorescence of ECTC in ethanol at 368 nm and 526 nm in the presence of various metal ions.
Conditions: [ECTC] = 1×10^{-5} м, [metal ion] = 1×10^{-5} м, λ_{ex} = 240 nm.

systems. The maximum fluorescent emission appears at 526 nm.

Second, some common metal ions, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+} and Fe^{3+}, were used to evaluate the metal ion binding properties of ECTC in ethanol. As shown in Figure 2, the fluorescence spectrum of ECTC shows a strong emission owing to the characteristic emission of the carbazole skeleton. Upon addition of Fe^{3+} ions to the solution of ECTC, a significant fluorescence quenching is observed. By contrast, changes in the fluorescence profile of ECTC in the presence of other tested metal ions are negligible. These results demonstrate that ECTC could be a potential fluorescent probe for the selective determination of Fe^{3+}.

In order to describe the quenching effect for each tested metal ion more accurately, the degrees of fluorescence quenching η were measured at two wavelengths and the results are shown in Figure 3. The quenching degree η is calculated from the formula: $\eta = (I_0 - I)/I_0$. Therein, I_0 and I are the fluorescence intensities of ECTC in ethanol in the absence and presence of a particular metal ion, respectively. The η value for Fe^{3+} is 36.4% at 526 nm. By contrast, the η values for Cu^{2+} and Co^{2+} are 4.8% and 3.6% at 526 nm, respectively. The η values of other ions are below 2% at 526 nm. These quantitative results indicate that the presence of these metal ions in solution would hardly disturb the detection of Fe^{3+} in some complex system.

The effect of concentration of Fe^{3+} on quenching was then investigated and the results are shown in Figure 4. As can be seen, quenching increases with increase in concentration of Fe^{3+} and upon addition of 50 equiv of Fe^{3+} ion to 10 μм of ECTC, almost complete quenching is observed. The fluorescent intensity of each solution at 526 nm was chosen as the reference to investigate the quantitative relationship between

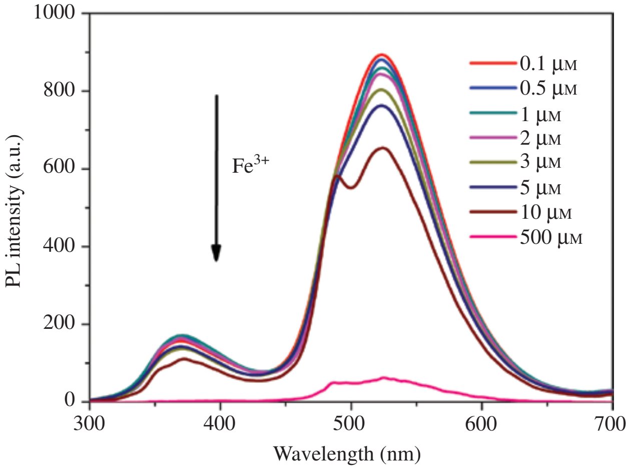

Figure 4 The fluorescence emission spectra of ECTC as functions of different concentrations of Fe^{3+}; [ECTC] = 1 × 10^{-5} м, λ_{ex} = 240 nm.

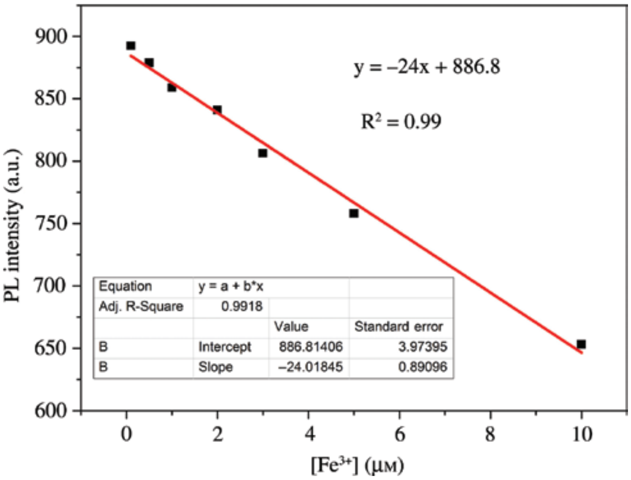

Figure 5 The fluorescence titration of ECTC with Fe^{3+} ion: [ECTC] = 1 × 10^{-5} м, λ_{ex} = 240 nm.

fluorescent intensity and concentration of Fe^{3+} because the other fluorescence emission at 368 nm was lower. As shown in Figure 5, under optimized conditions, the fluorescence intensity of ECTC is linearly quenched (linearly dependent coefficient R-square: 0.99) by Fe^{3+} ions in a wide range of 0.1 μм–10 μм and the limit of detection could be below 0.1 μм.

Finally, we wish to propose a possible quenching mechanism. It can be suggested that similarly to the reaction between Fe^{3+} and I^- [20], the aldehyde group of ECTC is oxidized by Fe^{3+} to a carboxylic acid group. Since the coordinating capability of the carboxylic group is better than that of the aldehyde group, coordination of the oxidized ECTC molecule with $iron^{3+}$ ion is expected to be stronger that of ECTC, which would decrease planarity of the unfused biaromatic system which, in turn, would reduce fluorescence intensity, as observed [25].

Conclusion

A novel fluorescence sensor ECTC was synthesized and characterized. This compound exhibits strong fluorescence quenching in the presence of Fe^{3+} ion, whereas almost no quenching is observed in the presence of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+} and Co^{2+}. Under optimized conditions, the fluorescence intensity of ECTC is quenched by Fe^{3+} ion in a linear fashion in a wide range of 0.1 μм–10 μм. Compound ECTC could be an efficient fluorescent probe for the selective determination of Fe^{3+}.

Experimental

9-Ethylcarbazole (1) and 3-bromo-9-ethylcarbazole (2)

These compounds were prepared as previously described [24].

Synthesis of 5-(*N*-ethylcarbazol-3-yl)thiophene-2-carbaldehyde (ECTC)

Tetrakis(triphenylphosphine)palladium (0.18 g, 0.16 mmol) and aqueous sodium carbonate solution (7 mL, 1 м) were added to a solution of 3-bromo-9-ethylcarbazole (**2**, 0.75 g, 2.74 mmol) and 5-formyl-2-thiopheneboronic acid (0.43 g, 2.74 mmol) in 1,4-dioxane (20 mL) under argon atmosphere. The mixture was stirred for 24 h under heated under reflux, then cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure and the residue dissolved in dichloromethane (30 mL). The solution was washed several times with water, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue of ECTC was subjected to silica gel chromatography eluting with petroleum ether/ethyl acetate (4:1): a yellow solid; yield 0.60 g (72%); ^1H NMR ($CDCl_3$, 400 MHz): δ 9.91 (s, 1H), 8.43 (d, *J* = 1.6 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 7.80 (m, 2H), 7.54 (m, 1H), 7.47 (t, *J* = 6.3 Hz, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 182.7, 159.1, 156.4, 141.2, 140.5, 138.0, 126.5, 124.5, 124.1, 123.5, 122.9, 122.7, 120.7, 119.6, 118.6, 109.1, 109.0, 37.8, 13.9. Anal. Calcd for $C_{19}H_{15}SNO$: C, 74.75; H, 4.91; S, 10.49; N, 4.59. Found: C, 74.81; H, 4.98; S 10.42; N 4.53.

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