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A novel dibenzimidazole-based fluorescent organic molecule as a turn-off fluorescent probe for Cr³⁺ ion with high sensitivity and quick response

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ABSTRACT

Due to the toxicity and ubiquity of chromium contamination, fluorometric detection of chromium ions (Cr^{3+}) has attracted much attention. Here, a new fluorescent probe 4PBI-Cz based on novel dibenzimidazole group was designed and synthesized to identify chromium ions. The photophysical and electrochemical properties of 4PBI-Cz were characterized in detail. In view of the strong complexation property, the fluorescence of 4PBI-Cz exhibit gradually turn-off phenomenon with the addition of chromium ions. In particular, the response time of the probe with chromium ions was less than 1 s, faster than most of the reported fluorescence probes. Moreover, the detection limit for chromium ions is only 3.5 nM, which can be attributed to the high sensibility of dibenzimidazole to the ions. This research indicates that the new proposed dibenzimidazole group is an exciting recognition receptor for designing quick response and ultrasensitive fluorescent probes for the determination of Cr^{3+} .

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1. Introduction

Chromium is recognized as one of the eight micronutrients that are indispensable to the human body [1]. From a medical point of view, chromium can effectively regulate blood sugar and has a good preventive effect on cardiovascular diseases caused by high cholesterol [2,3]. In addition, chromium-based stainless steel plays an important role in people's lives. However, excessive levels of chromium in the body inevitably cause irreparable damage to the digestive system, and improper discharge of the plant using chromium and its compounds will also cause dreaded heavy metal contamination [4–6]. Therefore, it is very necessary and desirable to find a method that can quickly, sensitively and selectively identify chromium ions in the environment and test samples.

With the gradual advancement of detection technology, there are many methods for detecting metal ions, such as atomic absorption spectroscopy (AAS) and so on. However, the application of mentioned traditional analytical methods are limited because of the high cost of the instrument, the complexity of the operation, and the time-consuming sample preparation [7-10]. Therefore, the emergence of fluorescence method with the advantages of simple operation, low cost, high selectivity, high sensitivity and rapid response attracted the focus of researchers [11–14]. At present, no specific recognition group to be complexed with Cr^{3+} [15–17], which results in few articles about the fluorescence probe for detecting chromium ion [18-21]. The most important thing is that in this few articles, more research is based on different materials to detect hexavalent chromium ions. For example, Wang et al. synthesized a colorimetric fluorescent material based on metalorganometallic framework to detect hexavalent chromium with a detection limit of 0.21 uM [22]. Chen et al. proposed a method for simultaneously identifying trivalent chromium and hexavalent chromium by using chlorophyll fluorescence of moss [23]. Based on the doped carbon point, Zhang et al. developed a fluorescence method for hexavalent chromium ions whose detection limit is 5 nM and can be used in actual water samples [24]. Therefore, it is still worthwhile to develop a novel fluorescent probe that can be utilized to detect Cr³⁺.







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In this work, a new group, dibenzimidazole, was proposed to design novel probe to detection of Cr³⁺. The 4PBI-Cz was synthesized by the palladium-catalyzed Suzuki reaction from the dibenzimidazole and carbazole core. The fluorescence and absorption spectra of the probes related to the concentration of chromium ions were studied. When Cr³⁺ ions were added, the fluorescence intensity of the probe was significantly quenched and had a linear relationship with the chromium ion concentration ranging from 0 to 200 nM. Moreover, after adding chromium ions, the absorption peak of the probe at 315 nm gradually disappeared, and a new absorption peak appeared at 280 nm. Importantly, the response time of the probe to Cr^{3+} is less than 1 s, which means that it can be used for the immediate detection of chromium ions. Meanwhile, the probe also exhibited high sensitivity to chromium ions with the detection limits as low as 3.5 nM. These results demonstrated that this new fluorescent probe base on dibenzimidazole group has the advantages of high sensitivity and fast response property, which would open up opportunities for design more probe used for the detection of chromium ions.

2. Experimental

2.1. General information

All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. ¹H NMR and ¹³C NMR spectra were measured on a BRUKER AMX 500-MHz instrument with tetramethylsilane as the internal standard. TGA was recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409 PC) under a dry nitrogen gas flow at a heating rate of 10 °C min⁻¹. Glass-transition temperature was recorded by DSC at a heating rate of 10 °C min⁻¹ with a thermal analysis instrument (DSC 2910 modulated calorimeter). The film surface morphology was measured with AFM (Bruker, Dimension Edge). Absorption spectra were recorded with a UV-vis spectrophotometer (Agilent 8453) and PL spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). Cyclic voltammetry was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in CH_2Cl_2 solutions (10^{-3} M) at a scan rate of 100 mV s^{-1} with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected as the internal standard. The solutions were bubbled with argon for 10 min before measurements.

2.2. Quantum chemical calculations

The geometrical and electronic properties of PPO-Cz and PPO-3Cz were performed with the Gaussian 09 program package. The calculation was optimized at the B3LYP/6-31G(d) level of theory. The molecular orbitals were visualized using Gauss View.

2.3. Synthesis

All reagents were used as purchased without further purification. The DMF and DMSO were purified according to standard procedures and distilled under nitrogen. The intermediate 2-(3bromo-5-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole was prepared according to the literature procedure [25].

2.3.1. 2,7-Dibromo-9-phenyl-9H-carbazole

2,7-dibromo-9H-carbazole (3.25 g, 10.0 mmol), 1-iodobenzene (2.45 g, 12.0 mmol), K₂CO₃ (4.17 g, 30 mmol), Cul (0.38 g,

2.0 mmol), 1,10-Phenanthroline hydrate (0.40 g, 2.0 mmol) and DMF (30.0 mL) were added to a 100 mL flask. The mixture was heated to 160 °C under nitrogen for 24 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and water. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The crude residue was purified by column chromatography with dichloromethane and petroleum ether as eluent to afford 3.80 g of white solid, in 92.9% yield. ¹H NMR (500 MHz, CDCl₃, δ): 7.94 (d, *J* = 8.2 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.54-7.47 (m, 5H), 7.40 (t, *J* = 8.2 Hz, 2H).

2.3.2. 2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-1-phenyl-1H-benzo[d] imidazole

2-(3-bromo-5-(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-1phenyl-1H-benzo[d]imidazole (5.41 g, 10.0 mmol), bis(pinacolato) diboron (3.05 g, 12.0 mmol), K₂CO₃ (4.17 g, 30 mmol), Pd(dppf)Cl₂ (1.46 g, 2 mmol) and DMSO (30.0 mL) were added to a 100 mL flask. The mixture was heated to 80 °C under nitrogen for 24 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and water. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The crude residue was purified by column chromatography with dichloromethane and petroleum ether as eluent to afford 3.25 g of white solid, in 55% yield. ¹H NMR (500 MHz, CDCl₃, δ): 8.20 (s, 2H), 7.88 (d, J = 7.9 Hz, 2H), 7.50 (s, 1H), 7.41 (t, J = 7.2 Hz, 6H), 7.33 (dd, J = 14.6, 7.3 Hz, 3H), 7.25 (d, J = 5.4 Hz, 3H), 7.16 (d, I = 7.2 Hz, 4H), 1.27 (s, 12H). ¹³C NMR (500 MHz, CDCl₃, δ): 137.2, 129.8, 128.7, 127.4, 119.7, 110.5, 84.0, 24.8. MS (MALDI-TOF) [m/z]: calcd for C₃₈H₃₃BN₄O₂, 588.51; found, 588.43. Anal. Calcd. for C₃₈H₃₃BN₄O₂: C, 77.55; H, 5.65; N 9.52. Found: C, 77.45; H, 5.70; N 9.56.

2.3.3. 2,7-bis(3,5-bis(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl)-9-phenyl-9H-carbazole (4PBI-Cz)

2,7-dibromo-9-phenyl-9H-carbazole (1.0 g, 2.0 mmol), 2-(3-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-5-(1-phenyl-1Hbenzo[d]imidazol-2-yl)phenyl)-1-phenyl-1H-benzo[d]imidazole (2.95 g, 5.0 mmol), K2CO3 (4.17 g, 12 mmol), Pd(PPh3)4 (0.012 g, 0.01 mmol), Toluene (30.0 mL), EtOH (15.0 mL) and H₂O (5.0 mL) were added to a 100 mL flask. The mixture was heated to 85 °C under nitrogen for 12 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and water. The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The crude residue was purified by column chromatography with dichloromethane and petroleum ether as eluent to afford 1.40 g of white solid, in 60% yield. ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3 \delta)$: 8.03 (d, I = 8.1 Hz, 2H), 7.92 (s, 2H), 7.89 (d, *J* = 7.8 Hz, 4H), 7.84-7.62 (m, 8H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 10H), 7.38-7.24 (m, 21H), 7.11 (s, 2H), 7.00 (d, *J* = 8.1 Hz, 2H). ¹³C NMR (500 MHz, CDCl₃, δ): 144.88, 144.43, 138.94, 133.01, 132.58, 132.28, 132.13, 131.79, 131.78, 131.51, 131.45, 130.75, 130.46, 130.28, 130.07, 126.83, 126.45, 126.05, 125.19, 123.13, 122.65, 122.34, 113.21, 110.61. MS (MALDI-TOF) [*m*/*z*]: calcd for C₈₂H₅₃N₉, 1164.3; found, 1164.2. Anal. calcd for C₈₂H₅₃N₉: C, 84.59; H, 4.59; N 10.83. Found: C, 84.55; H, 4.62; N 10.74.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes toward 4PBI-Cz was illustrated in Scheme 1. 4PBI-Cz was synthesized by the palladium-catalyzed Suzuki reaction from benzimidazole and carbazole. The final product 4PBI-Cz was obtained as a white solid in a yield of 60%. The target



Scheme 1. Synthetic routes toward 4PBI-Cz.

compounds were characterized by ¹H NMR and ¹³C NMR.

a heating rate of 10 °C min⁻¹.

3.2. Thermal properties

The thermal stability of 4PBI-Cz were investigated by thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of $10 \circ C \min^{-1}$. As shown in Fig. 1, the fluorescent probe has high glass transition temperature (Tg) and decomposition temperature (Td, corresponding to 5% weight loss) of 192 and 485 °C, respectively, which can be attributed to the non-planar structure and higher molecular weight of 4PBI-Cz. The excellent thermal stability is beneficial to facilitate the morphological stabilities and the guarantee long-term reliability of the fluorescent sensors. In order to demonstrate the superiority of the fluorescent probe in film forming ability, the solution-processed thin films of 4PBI-Cz were analysed by atomic force microscope (AFM). As shown in Fig. 2, the roughness of the 4PBI-Cz is 0.64 nm and no aggregation is observed, which is beneficial to improving the sensitivity of fluorescent probe and the preparation of fluorescent sensors.

3.3. Theoretical calculations and electrochemical properties

Using tetrabutylammonium hexafluorophosphate (TBAPF6) as the supporting electrolyte, the electrochemical behaviors of 4PBI-Cz was investigated by cyclic voltammetry analyses (CV) in CH_2Cl_2 for anodic sweeping and anhydrous DMF for cathodic scans. As shown in Fig. 3, the compound exhibited distinct oxidation and reduction behaviors, and it was also observed that the initial oxidation potential was 0.80 eV, whereby the highest occupied



Fig. 1. TGA trace of 4PBI-Cz recorded at a heating rate of 10 $^{\circ}$ C min⁻¹; inset: DSC measurement recorded at a heating rate of 10 $^{\circ}$ C min⁻¹.

2.2 m 0.1 m 0.1 m 0.0 m 0.

Height Sensor

1.0 µm

Fig. 2. AFM 3D height image (6 $\ \mu m \times$ 6 $\ \mu m)$ of 4PBI-Cz.



Fig. 3. Cyclic voltammogram of 4PBI-Cz measured at room temperature in CH_2Cl_2 with the scanning rate of 100 mV s⁻¹.

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) values of the compound were calculated as -5.60 eV and -2.16 eV in combination with the previously

obtained energy gap value.

To further understand the relationship of the physical properties of the fluorescent probe, density functional theory (DFT) calculations were carried out on their molecular energy levels (Fig. 4). The carbazole core is distinctly twisted by the phenyl benzimidazole (PBI) moieties, leading to a nonplanar structure in 4PBI-Cz. The HOMO and LUMO level of 4PBI-Cz are located at the carbazole units and the benzene ring conjugated moieties. The HOMO and LUMO energy of 4PBI-Cz were calculated to be -5.49 and -1.34 eV, respectively, and the Eg was also calculated to be 4.15 eV. The energy levels of the FMOs can provide the referable information for evaluating the carrier-injecting ability. The symmetrical structure of 4PBI-Cz results in the close HOMO and HOMO -1 as well as LUMO and LUMO +1, which facilitates the intermolecular charge transfer. For further simulating the emission properties, the TD-DFT was also performed to calculated the exciton energy of the emitter. As the result, the calculated singlet and triplet energies are 3.59 and 2.68 eV, respectively.

3.4. Photophysical properties

Fig. 5a shows the UV absorption spectrum of 4PBI-Cz in acetonitrile. The absorption peak at 250 nm is attributed to π - π * transition, while the absorption peak at 325 nm is attributed to n- π * transition. The energy gap value of 4PBI-Cz can be calculated from the initial absorption band to be 3.52 eV. In the state of acetonitrile as the solvent, the photoluminescence spectrum of the compound was presented in Fig. 5b, the spectrum shows that the compound peaks at 420 nm, which is a blue luminescent material. Moreover, Fig. 5c exhibits the phosphorescence spectra at 77 K in toluene, and the triplet energies is 2.58 eV for the compound based on the first phosphorescent emission peak, which is in good agreement with the theoretically calculated values.

To further investigate the photophysical properties, The PL spectrum of the 4PBI-Cz was tested in solvents of different polarities, as shown in Fig. 6 and Table 1, The compound exhibited a significant solvation tendency, showing a pronounced red shift from non-polar n-hexane to high polar DMSO. Meanwhile, this increase of dipole moment from the ground state to the excited state was calculated by Lipper-Mataga calculation. To determine the change in dipole moment upon excitation, Lippert-Mataga equation is used to express the Stokes shift as a function of the solvent polarity parameter $\Delta f(\varepsilon, n)$. The relevant values are calculated by following formulas:

$$hc(v_{a} - v_{f}) = hc(v_{a}^{0} - v_{f}^{0}) - \frac{2(\mu_{e} - \mu_{g})^{2}}{a^{3}}f(\varepsilon, n)$$
(1)

$$f(\varepsilon,n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

$$\tag{2}$$

In Equation (1), *f* refers to the orientational polarizability of the solvent, va-v_f is the Stokes shift when *f* is zero, μ e corresponds to the excited state dipole moment, μ g represents the ground-state dipole moment; *a* is the solvent cavity (Onsager) radius, *e* and n refer to the solvent dielectric and the solvent refractive index, respectively; f(e,n) and *a* can be calculated respectively by Equation (2). Through the investigation of the fitted line in high-polarity solvents, the slope value of the fitted line was acquired as -1324.54 cm⁻¹, and with Equation (1), the dipole moment can be calculated as -1.05×10^{-3} D. It can be seen that the dipole moment is small, suggesting that the absorption and emission spectra are not affected by the polarity of the solvents, which is beneficial to broaden the detection range and application conditions of the probe, and the probe is not easily affected by a small amount of other solvents in the sample during detection.

3.5. Optical response of probe

In order to investigate the response of the probe to chromium ions, the fluorescence and absorption spectra of the probe and fluorescence titration were investigated. On the one hand, as shown in Fig. 7a, with the addition of chromium ions, the absorption peak at 315 nm gradually weakened and a new absorption peak appeared at 280 nm which indicated that probe may be complexed with Cr^{3+} . Moreover, the correlation relationship between the



Fig. 4. Molecular orbital amplitude plot calculated by B3LYP/6-31G(d).



Fig. 5. (a) UV-vis absorption in various solutions. (b) PL features in acetonitrile. (c) The PL spectra at low temperature 77 K. Inset the phosphorescence spectra of 4PBI-Cz after delay.



Fig. 6. Lipperte-Mataga plot of 4PBI-Cz in various solutions.

absorbance of the probe and the concentration of added chromium ions was explored. As shown in Fig. S1, the absorption peak of the probe at 315 nm showed an excellent linear correlation with the Cr3+ concentration when the concentration was within the range of 0–200 nm (R2 = 0.98864). On the other hand, the fluorescence response of probe was also studied. As we can see from Fig. 7b, while with the advancing concentration of Cr^{3+} , the original fluorescence intensity of the probe was clearly annihilated by metal ions on account of the combination of probe and chromium ions.

It is worth noting that there is a good linear relationship

 Table 1

 Spectral properties of 4PBI-Cz in different solvents.

solvents	$\Delta f(\varepsilon, n)$	4PBI-Cz		
		v _a	v _f	$\Delta v(v_a-v_f)$
n-hexane	0.0012	201 nm, 310 nm	414 nm	8103
toluene	0.013	206 nm, 311 nm	417 nm	8173
CH ₂ Cl ₂	0.218	202 nm, 313 nm	415 nm	7852
THF	0.21	204 nm, 309.5 nm	420 nm	8501
ethanol	0.29	238 nm, 314 nm	419 nm	7981
methanol	0.31	244 nm, 315 nm	419 nm	7879
DMF	0.27	247 nm, 322 nm	418 nm	7132

between the intensity of the probe and the concentration of chromium ions (R2 = 0.99734) as we can see from Fig. 7c. Moreover, the limit of detection can be calculated through the absolute value of the slope in Fig. 7c after measuring the standard deviation of the fluorescence intensity at 405 nm of ten blank samples by the equation (LOD = $3\xi/k$, where ξ is the standard deviation and k is the absolute value of the slope). Hence, the LOD of probe was obtained to be 3.5 nM which is much lower than the highest level of chromium ions in drinking water regulated by WHO. As shown in Fig. 7d, with the addition of Cr^{3+} , the probe responded to it and completed the identification within 1 s, indicating that the probe could be used for the instant identification of chromium ions. The inset is derived from Fig. 7d, which is curve of the fluorescence intensity at 405 nm related to time. In order to explore the combination of chromium ions and probes, the Job's plot experiment was explored. The total concentration of metal ions and the probe was 10 μ M. As shown in Fig. 8, the turning point of the curve was at the probe: chromium ion = 0.5: 0.5. Therefore, it could be



Fig. 7. (a) Normalized absorption spectra of probe in THF at 20 nM upon addition of Cr^{3+} (0–200 nM). (b) Fluorescence response of probe (20 μ M) upon addition of increasing Cr^{3+} concentration in THF solution (0–10 eq). ($\lambda_{ex} = 300$ nm, EX slit = 2.5 nm, EM slit = 2.5 nm). (c) Linear fit between the intensity of probe at 405 nm and the titration concentration of Cr^{3+} ranging from 0 to 200 nM $\lambda_{ex} = 300$ nm, Slits: 2.5 nm/2.5 nm. (d) Fluorescence intensity of probe (20 nM) versus time curve with the addition of 20 nM Cr^{3+} , insert: Time-dependent fitting of fluorescence intensity at 405 nm.



Fig. 8. Job's plot analysis.

estimated that the binding ratio of chromium ions to the probe was 1: 1 (see Fig. 9).

4. Conclusions

In summary, we have designed and synthesized a novel fluorescent probe 4PBI-Cz based on dibenzimidazole for identify chromium ion. 4PBI-Cz exhibits excellent thermal stability with T_d and T_g temperatures of 485 and 192 °C, respectively. The



Fig. 9. Molecular structure and the Cr³⁺-sensing process of 4PBI-Cz.

fluorescent probe exhibited strong blue luminescence with an emission band at 420 nm and further showed sensitive turn-off fluorescence response to Cr^{3+} ion. Importantly, the response time of the probe to chromium ions is as low as 1 s, which is the fastest testing speed ever reported for Cr^{3+} ion. Moreover, the detection limit of chromium ions is 3.5 nM, which is attributed to the excellent coordination ability of benzimidazole units with chromium ions. The results show that the novel fluorescent probe has the advantages of high sensitivity and fast response, and can be used for the detection of Cr^{3+} ion.

Author contributions

Aiyun Zhu and Jie Pan conceived and designed the study. Yan Liu, Feng Chen and Xinxin Ban performed the experiments. Suyu Qiu and Yuhui Luo provided the theoretical calculation. Aiyun Zhu, Jie Pan, Yan Liu, and Feng Chen wrote the paper. Qingzheng Zhu, Jianmin Yu, and Weiwei Liu reviewed and edited the manuscript. All authors read and approved the manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2020.127696.

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