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Preparation of anthracene-based tetra-perimidine hexafluorophosphate and selective recognition for chromium(III) ion

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Abstract

A novel anthracene-based tetra-perimidine hexafluorophosphate, 9,10-di{bi[2'-(*N*-ethylperimidinyl)ethyl]aminomethyl}anthracene PF₆⁻ (**3**) was prepared, and its structure was determined through X-ray analysis, ¹H and ¹³C NMR. There are two soft (*N*-ethylperimidinylCH₂CH₂)₂NCH₂- moieties on 9,10-locations of anthracene in the cationic part of **3**. Compound **3** was used as a chemosensor to research the recognition ability for Cr³⁺ by fluorescence and UV titrations, IR, ¹H NMR and HRMS. The results indicate that **3** is an effective chemosensor for Cr³⁺.

Keywords:

Tetra-perimidine; Chemosensor; Chromium(III) ion.

Introduction

Fluorescence chemosensor is an attractive and efficient tool toward the detection of metal ions in environmental and biological science because of its high sensitivity, selectivity and simple instrument [1-5]. Among metal ions, the detection of chromium(III) ion occupies an important position. Chromium(III) ion is an essential microelement for humans and animals, and it plays an important role in glucose

metabolism and lipid metabolism in the body [6,7]. The deficiency of chromium(III) ion in the human body will lead to various diseases, including diabetes, autoimmune and cardiovascular disease [8]. On the other hand, excessive chromium(III) ion is toxic to human, and it can cause cancer through oxidizing DNA and some proteins [9-11]. Therefore, the detection of chromium(III) ion has the vital practical significance for human health.

In recent years, some fluorescence chemosensors for detection of chromium(III) ion have been developed [12-20]. Generally, the chemosensors with fluorescence enhancement are more efficient than those of fluorescence turn-off chemosensors [21-26]. But the paramagnetic nature of chromium(III) ion can cause fluorescence quenching of the fluorophore via the enhancement of spin-orbit coupling [27-32]. So far, only a few successful examples of fluorescence enhancement sensors for Cr^{3+} were reported [33-37]. Thus, developing new and effective fluorescence turn-on chemosensors for Cr^{3+} is necessary.

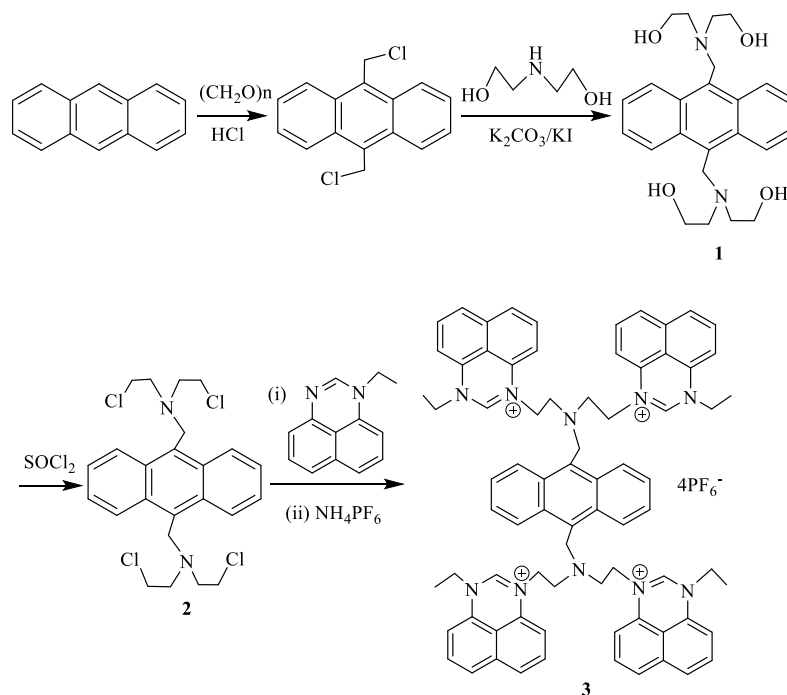
In the process of our research, tetradentate compound bearing fluorophore aroused our interest. In this paper, we designed and synthesized a novel anthracene-based tetra-perimidine hexafluorophosphate, 9,10-di{bi[2'-(*N*-ethylperimidinyl)ethyl]aminomethyl}anthracene PF_6^- (**3**), and its structure was determined by CCD XRD, ^1H and ^{13}C NMR. Particularly, compound **3** was used as a chemosensor to research the recognition ability for Cr^{3+} through fluorescence and ultraviolet methods, IR, ^1H NMR and HRMS. The results indicate that **3** is an effective chemosensor for Cr^{3+} .

Results and Discussion

Synthesis and characterization of **3**

As displayed in Scheme 1, paraformaldehyde reacted with anthracene to give 9,10-di(chloromethyl)anthracene, which reacted further with $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ to give compound **1** [38]. Compound **1** was treated with SOCl_2 to generate compound **2**, and it reacted with 1-ethylperimidine in the presence of KI to afford

9,10-di{bi[2'-(*N*-ethylperimidinyl)ethyl]aminomethyl}anthracene iodide. Then 9,10-di{bi[2'-(*N*-ethylperimidinyl)ethyl]aminomethyl}anthracene PF₆⁻ (**3**) was obtained via anion exchange reaction with NH₄PF₆. Compound **3** was stable to heat, moisture and air, and it has good solubility in CH₂Cl₂, DMSO and CH₃CN, but it has poor solubility in non-polar solvent. In the ¹H NMR spectrum of **3**, the proton signals of *NCHN* in benzoquinazoline was at δ = 8.69 ppm [39].



Scheme 1: Synthetic route of compound **3**.

Structure of compound **3**

In Figure 1, the cationic part of **3** contained two soft (*N*-ethylperimidinylCH₂CH₂)₂NCH₂- moieties on 9,10-locations of anthracene, and the dihedral angle between two perimidine rings in each unit was 18.1(4)°. Two of the four perimidine rings were parallel to anthracene ring, in which intramolecular π - π interactions [40] were observed (the distance of face-to-face between perimidine ring and anthracene ring being 3.566(1) Å, and the distance of center-to-center being 3.664(4) Å). The bond distances of C(3)-N(1) and C(3)-N(2) were 1.310(5) and 1.315(5) Å, and the angles of N(2)-C(3)-N(1) and N(4)-C(18)-N(5) were 125.2(3)°

and $124.3(4)^\circ$ [39]. 1D polymeric chain of **3** was generated through intermolecular π - π interactions from perimidine rings as shown in Figure S1a (the distance of face-to-face being $3.558(4)$ Å, and the distance of center-to-center being $3.566(1)$ Å). Besides, 2D supramolecular layer was formed via 1D supramolecular chains through two types of C-H \cdots F hydrogen bonds (C(3)-H(3A) \cdots F(2) and C(17)-H(17A) \cdots F(2)) (Figure S1b in Supporting Information).

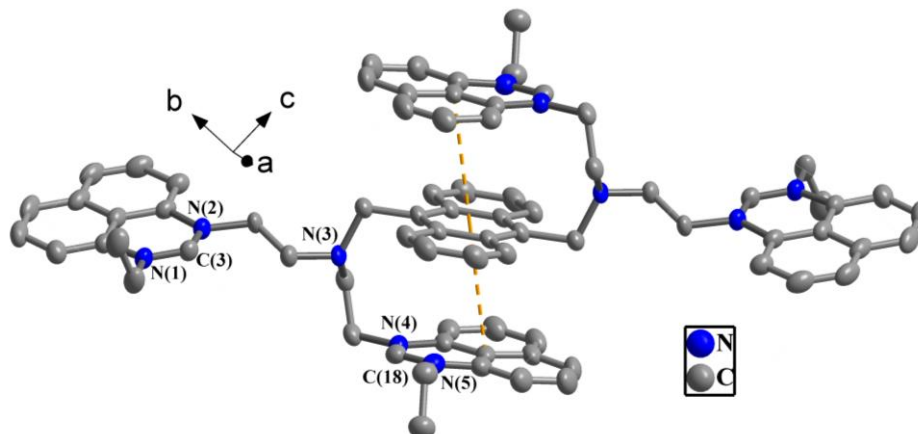


Figure 1: Perspective view of **3**. Selected bond angles ($^\circ$) and lengths (Å): N(2)-C(3)-N(1) $125.2(3)$, N(5)-C(18)-N(4) $124.3(4)$; C(3)-N(1) $1.310(5)$, C(3)-N(2) $1.315(5)$.

Recognition of Cr^{3+} using **3** as a chemosensor

Compound **3** was employed as a host to study the detection ability for some cations through fluorescence and ultraviolet titrations in $\text{CH}_3\text{CN}/\text{DMSO}$ ($v:v = 9:1$) at room temperature. The triple emission band at 402 nm, 423 nm and 447 nm of free compound **3** (5.0×10^{-6} mol/L) was observed (Figure 2), which were ascribed to the emission of anthracene. When adding 30.0 equiv. of K^+ , Na^+ , Li^+ , Ag^+ , NH_4^+ , Zn^{2+} , Cd^{2+} , Ca^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} , Co^{2+} , Al^{3+} , Hg^+ and Hg^{2+} , the intensity of the emission band did not change obviously. However, the significant enhancement in the region of 388-500 nm was observed after adding the same amount of Cr^{3+} .

To further investigate the recognition of Cr^{3+} by **3**, the fluorescence titrations were carried out (Figure 3). The fluorescence intensity of **3** in the region of 388-500 nm increased gradually upon the titration of Cr^{3+} into the solution of **3** (5.0×10^{-6} mol/L),

and continued titrating to the end (the emission intensity stayed the same). In the inset of Figure 3, when the ratio of $C_{Cr^{3+}}$ with C_3 was lower than 0.8, the fluorescence intensity enhances sharply. With $C_{Cr^{3+}}$ enhancing, the rate of fluorescence enhancement slowed down. The emission intensity of **3** continuously enhanced till the value of $C_{Cr^{3+}}/C_3$ exceeded 40. The limit of detection (LOD) value has also been calculated, which was 2.33×10^{-7} mol/L (Figure S5 in Supporting Information). The LOD values of some reported literatures ranged from 9.40×10^{-7} mol/L to 5.55×10^{-6} mol/L [41-43]. The association constant K_{SV} was calculated as 1.12×10^4 M⁻¹ for **3**·Cr³⁺ by eq. (1) (R = 0.998) (Figure S2) [44].

$$F/F_0 = 1 + K_{SV}C_{Cr^{3+}} \quad (1)$$

The fluorescence intensity of **3** with or without Cr³⁺ were represented by F and F_0 . K_{SV} was the association constant. $C_{Cr^{3+}}$ was the concentration of Cr³⁺.

In the ultraviolet titration experiments, the absorption band in the region of 245-265 nm increased gradually upon the titration of Cr³⁺ into the solution of **3** (5.0×10^{-6} mol/L) in CH₃CN/DMSO (v:v = 9:1) at 25 °C (Figure S4). To evaluate the stability of **3**·Cr³⁺, the K value (stability constant) for **3**·Cr³⁺ was computed as 8.23×10^4 M⁻¹ by eq. (2) (R = 0.999) (Figure S6 in Supporting Information) [45-48].

$$A_0/(A_0 - A) = [\epsilon_r/(\epsilon_r - \epsilon_c)](1/KC_3 + 1) \quad (2)$$

The absorbance of **3** without Cr³⁺ was represented by A_0 . The discrepancy of absorbance between the absence and existence of Cr³⁺ was represented by $(A_0 - A)$. The molar extinction coefficients of Cr³⁺ and **3**·Cr³⁺ was represented by ϵ_r and ϵ_c .

A 1:1 binding pattern between **3** and Cr³⁺ was established with Job's plot method. In the insets of Figure S4, the maximum point appeared at χ of **3** being 0.5. Then, 30.0 equiv. of Cr³⁺ was added into a series of solutions of **3**, which were mixed in advance with 30.0 equivalents of K⁺, Na⁺, Li⁺, Ag⁺, NH₄⁺, Zn²⁺, Cd²⁺, Ca²⁺, Ni²⁺, Pb²⁺, Cu²⁺, Co²⁺, Al³⁺, Hg⁺ and Hg²⁺. As shown in Figure S7, the emission intensities of these mixed solutions were similar to the solution with **3** and Cr³⁺ only. This experimental result indicated **3** can bind with Cr³⁺ selectively from many kinds of cations.

In order to understand whether the anions of these metal salts have effects on the binding of **3** to Cr³⁺, other chromium(III) salts (CrCl₃, CrBr₃, Cr₂(SO₄)₃, Cr(NO₃)₃,

Cr(OAc)₃) were tested. As displayed in Figure S8, when 30.0 equiv. of other chromium(III) salts were added, similar fluorescence intensities were detected. Reversible binding experiment was also carried out (Figure S9 in Supporting Information). 30.0 equivalent of EDTA was added to a solution of Cr³⁺ (15.0 × 10⁻⁵ M) and **3** (5.0 × 10⁻⁶ M), and it led in the reduction of fluorescent intensity at 390-500 nm. This fluorescent intensity was analogous to that of free **3**, which displayed that the free **3** was regenerated. When Cr³⁺ was added again, the fluorescent intensity increased. The experimental result showed that **3** had good reversible and regenerative capacity.

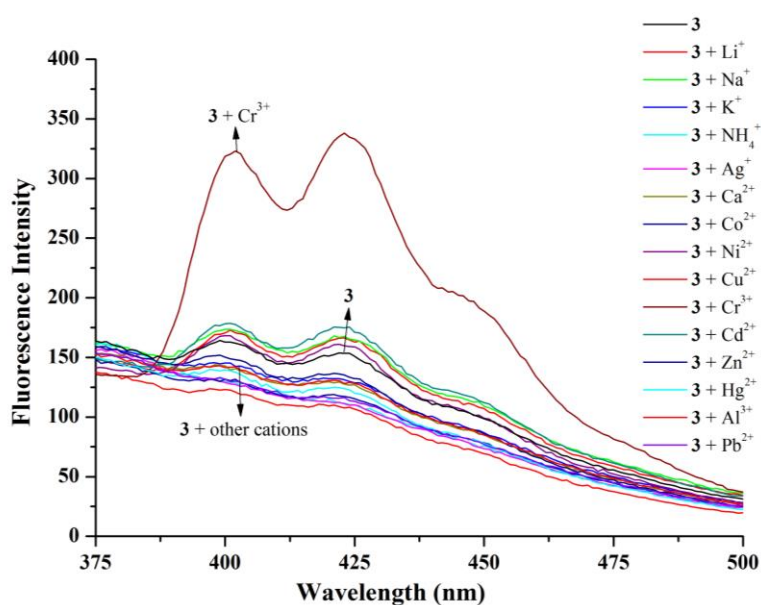


Figure 2: Fluorescent spectra of **3** (5.0 × 10⁻⁶ M) upon adding salts (30.0 equiv) of K⁺, Na⁺, Li⁺, Ag⁺, NH₄⁺, Zn²⁺, Cd²⁺, Ca²⁺, Ni²⁺, Pb²⁺, Cu²⁺, Co²⁺, Al³⁺, Cr³⁺, Hg⁺ and Hg²⁺ (15.0 × 10⁻⁵ mol/L) in CH₃CN/DMSO (v:v = 9:1) at room temperature (λ_{ex} = 258 nm).

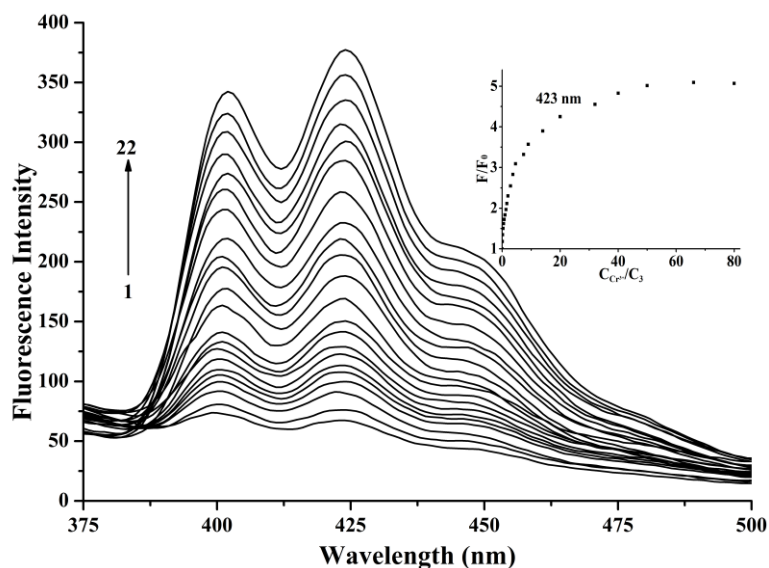


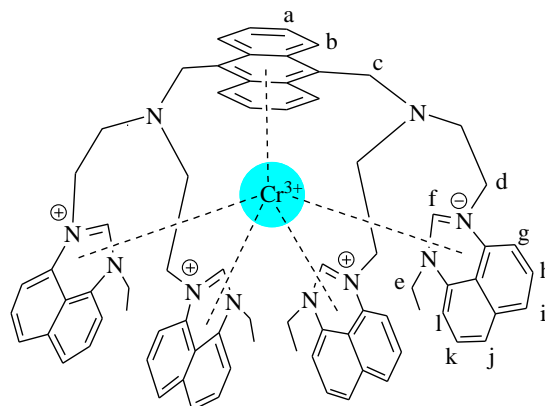
Figure 3: Fluorescent titration spectra of **3** (5.0×10^{-6} M) upon adding Cr^{3+} with different concentrations. $C_{\text{Cr}^{3+}}$ for curves 1-22 (from bottom to top) were 0, 0.04, 0.08, 0.16, 0.24, 0.35, 0.49, 0.67, 0.80, 1.0, 1.45, 1.85, 2.30, 3.70, 4.50, 7.0, 10.0, 16.0, 20.0, 25.0, 33.0, 40.0×10^{-5} mol/L ($\lambda_{\text{ex}} = 258$ nm).

Interactions of **3** with Cr^{3+}

From structural characteristics of **3**, the nitrogen atoms and π systems were most likely binding sites for Cr^{3+} . In order to obtain more information to figure out the binding pattern between **3** and Cr^{3+} , ^1H NMR titration was done in $\text{DMSO-}d_6$. The variations of spectra were depicted in Figure 4. The proton peaks for *Ha* and *Hb* on anthracene ring moved to downfield by 0.02 ppm and 0.03 ppm when $C_3/C_{\text{Cr}^{3+}}$ was 1:1 (Figure 4(iv)), and the signals of *Hc*, *Hd* and *He* on CH_2 moved to downfield by 0.03 ppm, and the proton signals of *Hf-HI* on perimidine rings moved to downfield by 0.02-0.07 ppm. From these results of ^1H NMR titrations, we can know that compound **3** captured Cr^{3+} by four perimidine rings via $\pi \cdots \text{Cr}^{3+}$ interactions (Scheme 2). Moreover, the proton signals kept unchanged when $C_3/C_{\text{Cr}^{3+}}$ exceeded 1:1 (Figure 4(v)), which illustrated that **3** and Cr^{3+} had a 1:1 binding pattern. In HRMS of $\mathbf{3} \cdot \text{Cr}^{3+}$ (Figure S9 in Supporting Information), the observation of m/z (587.1) provided strong evidence for a 1:1 binding pattern between **3** and Cr^{3+} . This further indicated that **3** and Cr^{3+} had a 1:1 complexation. In the infrared spectra (Figure S10 in Supporting Information), the benzene ring (C-C) peak at 1170 cm^{-1} for free compound **3** turned into 1185 cm^{-1} for $\mathbf{3} \cdot \text{Cr}^{3+}$. Also, the (C=N) peak at 1664 cm^{-1} for free compound **3**

changed into 1672 cm^{-1} for $3\cdot\text{Cr}^{3+}$.

According to the above experimental results and structure of **3**, $\pi\cdots\text{Cr}^{3+}$ interactions was turned out to be the main binding force between **3** and Cr^{3+} .



Scheme 2: Interactions of **3** with Cr^{3+} .

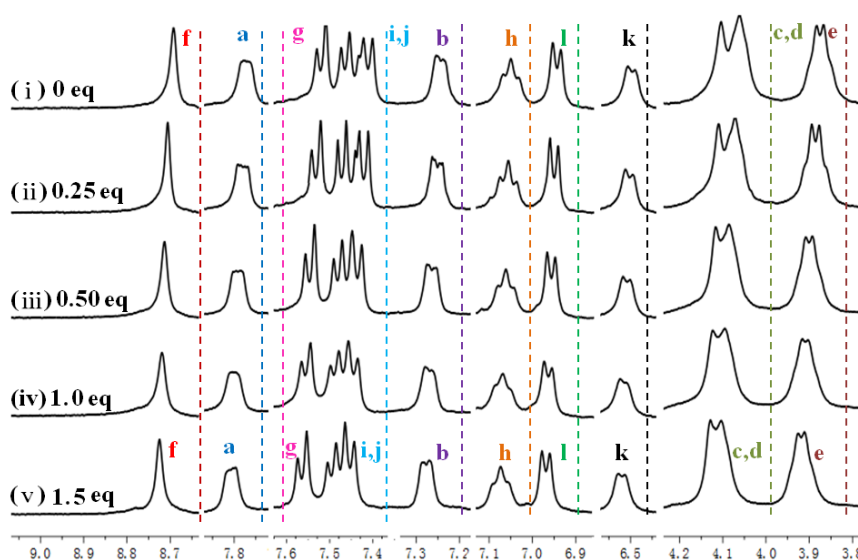


Figure 4: Partial ^1H NMR spectra in $\text{DMSO-}d_6$. (i) Compound **3**; (ii) 0.25 equiv. of Cr^{3+} and **3**; (iii) 0.5 equiv. of Cr^{3+} and **3**; (iv) 1 equiv. of Cr^{3+} and **3**; (v) 1.5 equiv. of Cr^{3+} and **3**.

Conclusion

In summary, a new anthracene-based tetra-perimidine hexafluorophosphate, 9,10-di{bi[2'-(*N*-ethylperimidinyl)ethyl]aminomethyl}anthracene PF_6^- (**3**) was prepared, and its structure was determined through X-ray analysis, ^1H and ^{13}C NMR. Compound **3** was proved to be a chemosensor for Cr^{3+} with high sensitivity an

selectivity, and it can detect Cr^{3+} from other cations effectively by fluorescence enhancement. Therefore, compound **3** can be used as a chemosensor for Cr^{3+} in biological and environmental science because of its potential capacity in fluorescence recognition.

Experimental

Materials and instruments

The solvents and chemicals of preparation and experiment were analytical grade by purchasing commercially. A RF-5301PC fluorescence spectrophotometer (Shimadzu) was used for the report of the fluorescence spectra at room temperature (the excitation and emission slits were both set to 10 nm). UV-vis absorption spectra were recorded using JASCO-V570 spectrometer at room temperature. A Varian spectrometer was employed to collect the data of ^1H NMR and ^{13}C NMR spectra. Perkin-Elmer 2400C Elemental Analyzer was employed for the elemental analyses. Infrared spectra was proceeded to apply A PerkinElmer Spectrum 100 FT-IR spectrophotometer. The mass spectrometer (A VG ZAB-HS) was employed for recording HRMS spectra. The melting points were reported employing a Boetius Block apparatus.

Synthesis of 1-ethylperimidine

A solution of perimidine (1.430 g, 8.5 mmol) in dry THF (50 ml) was added through a dropping funnel to the suspension of NaH (0.479 g, 20.0 mmol) in dry THF (10 mL) at 0 °C, and stirred for 60 min at room temperature. Subsequently, 1.308 g of bromoethane (12.0 mmol) was also added to the reaction mixture at room temperature. The mixture was stirred at 25 °C for 24 h. After filtration, the filtrate was decanted into H_2O (150 ml) and extracted with CHCl_3 (3 × 60 ml). The CHCl_3 layer was rinsed by H_2O (3 × 100 ml) and dried over anhydrous MgSO_4 . 1-Ethylperimidine was given as a yellowgreen solid after removing the solvent. Yield: 0.825 g (49%). M.p.: 198-200 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.49 (t, $J = 7.2$ Hz, 3H, CH_3), 4.28 (q, $J = 7.2$ Hz, 2H, CH_2), 7.31 (d, $J = 8.8$ Hz, 2H, ArH), 7.76 (d, $J = 8.8$ Hz, 2H, ArH), 8.04 (s, 1H, ArH), 8.25 (s, 1H, ArH), 9.73 (s, 1H, NCHN).

Synthesis of 9,10-bis(chloromethyl)anthracene

A suspension of paraformaldehyde (6.155 g, 205.0 mmol) and anthracene (17.823 g, 100.0 mmol) in HAc (50 mL) and hydrochloric acid (20 mL) was heated to 100 °C and stirred for 5 h. Then, 200 mL of water was added into the mixture to precipitate a yellow solid. 9,10-Bis(chloromethyl)anthracene was obtained as a yellow powder after filtration and drying treatment. Yield: 22.452 g (82%). M.p.: 246-248 °C. ¹H NMR (400 MHz, CDCl₃): δ 5.62 (s, 4H, CH₂), 7.68 (q, *J* = 1.6 Hz, 4H, ArH), 8.41 (q, *J* = 1.6 Hz, 4H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 130.2 (ArC), 129.7 (ArC), 126.7 (ArC), 124.3 (ArC), 67.1 (CH₂).

Synthesis of 9,10-di[bi(2'-hydroxyethyl)aminomethyl]anthracene (1)

A CH₃CN/CHCl₃ (100 mL, v:v = 1:1) suspension of diethanolamine (9.988 g, 95.0 mmol) and K₂CO₃ (25.015 g, 181.0 mmol) was stirred under refluxing for 1 h, followed by 9,10-bis(chloromethyl)anthracene (8.255 g, 30.0 mmol) and KI (0.914 g, 5.5 mmol) was added. After completion of addition, stirring was performed at 35 °C for 30 h. CH₃CN/CHCl₃ was evaporated in vacuum, and a yellow oil was obtained. A yellow solid of 9,10-di[bi(2'-hydroxyethyl)aminomethyl]anthracene (**1**) was obtained after rinsing by water. Yield: 7.189 g (58%). M.p.: 153-155 °C. ¹³C NMR (100 MHz, CDCl₃): δ 130.9 (ArC), 130.7 (ArC), 125.8 (ArC), 125.1 (ArC), 59.8 (CH₂), 56.1 (CH₂), 51.6 (CH₂). ¹H NMR (400 MHz, CDCl₃): δ 1.96 (s, 4H, OH), 2.77 (t, *J* = 5.3 Hz, 8H, CH₂), 3.43 (t, *J* = 5.3 Hz, 8H, CH₂), 4.74 (s, 4H, CH₂), 7.55 (q, *J* = 3.3 Hz, 4H, ArH), 8.51 (q, *J* = 3.3 Hz, 4H, ArH).

Synthesis of 9,10-di[bi(2'-chloroethyl)aminomethyl]anthracene (2)

Compound **1** (4.105 g, 10.0 mmol) was dissolved in dioxane (50 mL), followed by the solution of SOCl₂ (9.518 g, 80.0 mmol) in dioxane (30 mL) was dropwise added over 1 h with stirring at 30 °C. The mixed solution reacted continually for 3 days at 30 °C. Hydrochloride of 9,10-di[bi(2'-chloroethyl)aminomethyl]anthracene as a yellow solid was given after filtration. This solid was rinsed by 200 mL of NaOH (20%) to wipe off HCl, and then extracted with CHCl₃ (60 mL × 3). The CHCl₃ layer was washed three times with water (20 mL × 3), and dried over anhydrous MgSO₄. A yellow powder of 9,10-di[bi(2'-chloroethyl)aminomethyl]anthracene (**2**) was obtained after

removing CHCl_3 . Yield: 3.670 g (75%). M.p.: 131-133 °C. ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 130.9 (ArC), 130.8 (ArC), 126.0 (ArC), 125.8 (ArC), 55.4 (CH_2), 50.3 (CH_2), 42.7(CH_2). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.92 (t, $J = 6.7$ Hz, 8H, CH_2), 3.52 (q, $J = 6.1$ Hz, 8H, CH_2), 4.74 (s, 4H, CH_2), 7.55 (q, $J = 3.4$ Hz, 4H, ArH), 8.60 (q, $J = 3.4$ Hz, 4H, ArH).

Synthesis of 9,10-di{bi[2'-(N-ethylperimidinyl)ethyl]aminomethyl}anthracene PF_6^- (**3**)

A mixture of 1-ethylperimidine (1.177 g, 6.0 mmol), 9,10-di[bi(2'-chloroethyl)aminomethyl]anthracene (0.389 g, 0.8 mmol) and KI (0.500 g, 3.0 mmol) in 30 mL of DMF/dioxane (v:v = 2:8) was stirred under reflux for 5 days. 9,10-di{bi[2'-(N-ethylperimidinyl)ethyl]aminomethyl}anthracene Γ was generated as a yellow precipitate. The methanol solution (100 mL) of NH_4PF_6 (0.978 g, 6.0 mmol) and 9,10-di{bi[2'-(N-ethylperimidinyl)ethyl]aminomethyl}anthracene Γ was stirred for 3 days. The precipitate was washed with methanol (10 mL \times 2), and 9,10-di{bi[2'-(N-ethylperimidinyl)ethyl]aminomethyl}anthracene PF_6^- (**3**) was obtained by filtration. Yield: 1.158 g (87%). M.p.: 220-222 °C. Calcd for $\text{C}_{76}\text{H}_{76}\text{N}_{10}\text{P}_4\text{F}_{24}$: C, 53.40; H, 4.48; N, 8.19%. Found: C, 53.53; H, 4.26; N, 8.21%. ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 152.2 (NCN), 134.1 (ArC), 130.7 (ArC), 130.6 (ArC), 129.1 (ArC), 128.1 (ArC), 127.6 (ArC), 124.8 (ArC), 124.4 (ArC), 123.4 (ArC), 120.5 (ArC), 107.9 (ArC), 106.8 (ArC), 48.5 (CH_2), 46.7 (CH_2), 46.6 (CH_2), 38.9 (CH_2), 11.9 (CH_2). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.37 (s, 12H, CH_3), 3.18 (s, 8H, CH_2), 3.87 (d, $J = 6.4$ Hz, 8H, CH_2), 4.08 (t, $J = 3.2$ Hz, 12H, CH_2), 6.50 (q, $J = 2.0$ Hz, 4H, ArH), 6.94 (d, $J = 4.4$ Hz, 4H, ArH), 7.05 (s, 4H, ArH), 7.23 (m, 4H, ArH), 7.40 (t, $J = 8.4$ Hz, 8H, ArH), 7.45 (s, 4H, ArH), 7.51 (s, 4H, ArH), 8.69 (s, 4H, NCHN).

Fluorescence titrations

The concentration of **3** is 5.0×10^{-6} M, and the concentrations of guest are 0-40.0 $\times 10^{-5}$ M in the sample solutions. A RF-5301PC fluorescence spectrophotometer (Shimadzu) was employed in the fluorescence titration experiment at room temperature. The excitation wavelength is 258 nm, and the emission and excitation

slits are 10 nm and 5 nm. We recorded the emission spectra from 375 nm to 500 nm. Origin 8.0 was employed for data processing.

UV/vis titrations

In UV/vis titrations, we prepared the sample solutions through employing analogous methods to that of fluorescent titrations. The concentration of **3** is 1.0×10^{-6} M, and the concentration of Cr^{3+} are 0 to 36.0×10^{-6} M. We recorded the absorption spectra from 240 nm to 265 nm. UV titrations were performed on a JASCO-V570 spectrometer at 25 °C. Origin 8.0 was employed for data processing.

Data collection for X-Ray and confirmation of structure

Diffraction data of **3** were collected through employing a Bruker Apex II CCD diffractometer [49]. SHELXS program was employed to solve the structure of **3** [50]. Other crystallographic data were shown in Table S1.

Acknowledgements

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Supporting Information

The supporting crystallographic data. The figures of fluorescence and UV for **3**. The figures of infrared for **3** and **3**/ Cr^{3+} . General considerations, characterization data, and copies of the ^1H NMR and ^{13}C NMR spectra of all compounds.

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Graphical Abstract

A novel anthracene-based tetra-perimidine hexafluorophosphate (**3**) was prepared, characterized. The selective recognition of **3** for Cr^{3+} was studied.

