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Improved colorimetric dual-emission and endued piezofluorochromism by inserting a phenyl between 9-anthryl and terpyridine



PIĞMËNTS

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ABSTRACT

Tridentate terpyridine is a functional building unit, and 9-anthylterpyridine has been used as ratiometric fluorescent sensor for Cd(II) and secondary sensor for pyrophosphate detection. Here we have inserted a phenyl unit between 9-anthryl and terpyridine to synthesize a new terpyridine derivative, 4-(9-anthryl)phenyl terpyridine (ATP) to investigate the effect of structure change on optical properties. The results show that ATP not only remains the selectively colorimetric fluorescence sensing to Cd^{2+} but also the interval of two emission bands from ATP and ATP–Cd(II) complex can be enlarged significantly to 185 nm. Unlike 9-anthylterpyridine–Cd(II) complex, ATP–Cd(II) complex could be decomplexed by most polyvalent anions. Moreover, the insertion of a phenyl ring can render ATP –Cd(II) complex remarkable piezofluorochromism with grinding-induced spectral shift of 54 nm. Xray diffraction and differential scanning calorimetry experiments confirm the phase transformation between crystalline and amorphous states upon external stimuli is responsible for reversible PFC behavior.

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1. Introduction

Pyridine, 2,2'-bipyridine, and 2,2':6,2"-terpyridine are all functional building blocks, and the conjugated molecules containing them have aroused widespread concern and great interest for their distinguished photophysical and electrochemical properties [1-15]. Especially, 2,2':6,2"-terpyridine has become an indispensable unit in supramolecular and material chemistry due to its tridentate ligand feature, synthetic accessibility, and excellent ability to bind with both low and high-oxidation state metal ions [16-21]. Up to now, there have been a variety of reports on the synthesis, optical and optoelectronic properties of terpyridine-containing derivatives and their metal complexes, and some of them exhibited interesting applications in fluorescence sensors, non-linear optics, and light-emitting devices [6,22]. Recently, Jiao et al. synthesized an fluorescent terpyridine derivative with anthryl as the chromophore exhibiting ratiometric fluorescent sensing to Cd(II) (an non-essential toxic elements in the human body) and PPi (pyrophosphate $P_2O_7^{4-}$, an essential anion for normal cell function) [23]. Compared to intensity-based fluorescent sensors (Off–On process), ratiometric fluorescent sensors show an obvious advantage because they can eliminate most or all ambiguities by self-calibration through two emission bands [24].

We have been interested in anthracene-based conjugated molecules and found that the subtle manipulation of the conjugated skeletons and peripheral groups could endow anthracenebased conjugated molecules with unique and tunable optical and optoelectronic properties [25–30]. Here we have synthesized a new terpyridine derivative with 9-phenylanthryl as the luminogen moiety, 4-(9-anthryl)phenyl terpyridine (ATP), to investigate the effect of the insertion of phenyl unit between anthryl and terpyridine on optical properties. It was found that the insertion of phenyl ring could not only widen the interval of dual emission from ATP and ATP–Cd(II) complex but also enlarge the response range to polyvalent anions. Moreover, the insertion of phenyl unit endues ATP–Cd(II) complex with remarkable piezofluorochromism [31].



2. Experimental section

2.1. Materials

Acetonitrile (MeCN) and tetrahydrofuran (THF) were distilled (over metallic sodium) before use. 9-Bromoanthracene, 4formylboronic acid, 2-acetylpyridine, tetrakis-(triphenylphosphine)-palladium and others were all commercial available analytical-grade chemicals and were used as received, unless otherwise claimed.

2.2. Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker–AC500 (500 MHz) spectrometer with CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard. The elemental analysis was performed on Perkin–Elmer 2400. UV–vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Emission spectra were measured with a Hitachi F-4600 spectrophotometer. The peak wavelength of the lowest energy absorption band was used as the excitation wavelength for the PL measurement. The fluorescence quantum yield (Φ) was determined at room temperature by the dilution method using rhodamine B in methanol as the reference. [32] Powder wide angle X-ray diffraction (PWXD) measurements were performed on a Powder X-ray Diffractometry (INCA Energy, Oxford Instruments), operating at 3 kW. Differential scanning calorimetry (DSC) experiments were carried out on a Netzsch DSC204F1 at a heating rate of 10 °C/min.

2.3. Piezochromic and stimuli-recovering experiments

Grinding experiment: Pristine ATP–Cd(II) solid was put on a glass plate and then ground with a metal spatula at room temperature. *Solvent-fuming experiment*: The ground sample was above the dichloromethane level and was exposed to the vapor for 30 s at room temperature. *Annealing experiment*: the ground sample was put into an oven with the temperature 200 °C for 3 min. After external stimuli, the fluorescence images and emission spectra were recorded at room temperature.

2.4. Synthesis

2.4.1. 9-(4-Formylphenyl)anthracene

In a 100 mL round bottom flask, 9-bromoanthracene (1 g, 4 mmol) and 4-formylboronic acid (0.78 g, 5.2 mmol), and 2 M K₂CO₃ were dissolved in THF (50 mL), and water (20 mL) at N₂ atmosphere. Then tetrakis-(triphenylphosphine)-palladium (0.17 g, 0.15 mmol) was added into the mixture and the mixture was refluxed for 72 h. After that, the water was added to the mixture and the organic phase extracted with dichloromethane was dried over MgSO₄. The crude product was used to the next reaction step without further purification. ¹H NMR (500 MHz, CDCl₃) δ 10.19 (s, 1H), 8.55 (s, 1H), 8.13 (d, 2H), 8.04 (d, 2H), 7.64 (d, 2H), 7.58 (d, 2H), 7.49 (m, 2H), 7.38 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 192.4, 142.2, 138.6, 137.3, 132.5, 131.7, 130.1, 128.9, 127.7, 126.5, 126.2, 125.6 ppm.

2.4.2. 4'-(4-(Anthracen-9-yl)phenyl)-2,2':6',2"-terpyridine (ATP)

In a 250 mL round bottom flask, 2-acetylpyridine (1.22 g, 10.0 mmol), NH₃ (aqueous) (15 mL, 12.6 mmol), KOH (0.78 g, 12.0 mmol) was respectively added to a solution of 9-(4-for-mylphenyl)anthracene (1.04 g, 5.0 mmol) in EtOH (25 mL). The solution was refluxed for 24 h. After cooling down to room temperature, the solution was evaporated to dryness under reduced pressure to give the crude product. The crude product was purified

by column chromatography (silica gel ethyl acetate/methylene chloride/EtOH = 2/4/1, v/v/v). A pure white solid with a yield of 28% (0.68 g) was obtained. ¹H NMR (500 MHz, CDCl₃) δ 8.92 (s, 2H), 8.74 (d, 2H), 8.70 (d, 2H), 8.54 (s, 1H), 8.14 (d, 2H), 8.08 (d, 2H), 7.91 (m, 2H), 7.73 (d, 2H), 7.60 (d, 2H), 7.49 (m, 2H), 7.40 (m, 4H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 156.32, 156.11, 150.17, 149.21, 139.71, 137.85, 136.88, 136.32, 131.91, 131.40, 130.19, 128.38, 128.00, 127.41, 126.70, 125.54, 125.17, 123.85, 121.37, 119.06 ppm.

2.4.3. Synthesis of ATP–Cd(II) complex

In a 100 mL round bottom flask, ATP (97 mg, 0.2 mmol), and Cd(NO₃)₂·4H₂O (61.6 mg, 0.2 mmol) was added to CH₃CN (14 mL) and the mixture was stirred for 2 h at room temperature. The solution was concentrated, a slight yellow solid ATP–Cd(II) complex (98%) was obtained. ¹H NMR (500 MHz, CDCl₃) δ 9.05 (d, 2H), 8.6 (s, 3H), 8.44 (d, 2H), 8.17 (m, 2H), 8.12 (d, 2H), 8.04 (d, 2H), 7.74 (d, 4H), 7.69 (d, 2H),7.53 (m, 2H), 7.42 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 154.89, 151.38, 150.19, 148.24, 142.13, 140.17, 135.56, 135.04, 132.80, 131.37, 130.02, 128.63, 127.47, 127.20, 126.67, 126.17, 125.89, 125.30, 121.90, 120.51 ppm.

3. Results and discussion

3.1. Synthesis and characterization of ATP and its Cd(II) complex

4-(9-Anthryl)phenyl terpyridine (ATP) was synthesized from the Suzuki coupling of 9-bromoanthracene and (4-formylphenyl) boronic acid, followed by the addition of 2-acetylpyridine, KOH and NH₃·H₂O in EtOH under reflux (Scheme 1). Detailed synthetic procedures and characterization data are provided in the Experimental section. The ATP–Cd(II) complex has been obtained in quantitative yield by reacting ATP with Cd(NO₃)₂·4H₂O in CH₃CN as detailed in the Experimental section. ATP and the ATP–Cd(II) complex were characterized by NMR and elemental analysis.

3.2. The responses of ATP to metal ions

Tridentate terpyridine derivatives with the suitably arranged ring nitrogen and the synthetic accessibility could be used to detect metal cations in solution due to their good abilities to coordinate with both low and high-oxidation state metal ions. Here we have chosen a variety of available metal ions (salts nitrate), including Cd²⁺, Zn²⁺, Li⁺, Na⁺, Sr²⁺, K⁺, Ba²⁺, Al³⁺, Mn²⁺, Cr³⁺, Co²⁺, Cu²⁺, La³⁺, Nd³⁺, and Ce³⁺, to add into the acetonitrile (MeCN) solution of ATP to investigate the fluorescence response behaviors. As shown in Fig. 1, ATP solution itself emits blue with the fluorescence quantum yield (Φ) of 0.72. When Li⁺, Na⁺, Sr²⁺, K⁺, Ba²⁺, Al³⁺, Cu²⁺, La³⁺, Nd³⁺, and Ce³⁺are added into the solution, the fluorescence color of ATP solution hardly change, but Zn²⁺, Mn²⁺, Cr³⁺, and Co²⁺ could quench the fluorescence emission of ATP solution. An interesting phenomenon is that the addition of Cd²⁺ could afford a redemitting solution whose Φ is 0.13. These results indicate that ATP solution could complex with Zn^{2+} , Mn^{2+} , Cr^{3+} , Co^{2+} , and Cd^{2+} , and the complexation with Cd^{2+} could be used as the selectively colorimetric fluorescence sensor for Cd²⁺ detection.

Fig. 2a shows the absorption and emission spectra of ATP and ATP– Cd^{2+} solutions. ATP and its Cd(II) complex have similar absorption spectra whose absorptions mainly appear before 400 nm but different emission spectra. ATP solution shows a single-emission band with the peak wavelength of 430 nm, and ATP– Cd^{2+} solution exhibits a dual-emission profile whose two peak wavelengths are at 420 and 605 nm, respectively. The shortwavelength emission band is from the pendent phenylanthracene segment (local emission), and the long-wavelength one could be ascribed to the ATP– Cd^{2+} complex (intramolecular transfer charge



Scheme 1. Synthetic route and structure of new terpyridine-based luminogen (ATP) and its Cd(II) complex (ATP-Cd²⁺).



Fig. 1. The fluorescence colors of MeCN solution of ATP (1.0×10^{-5} M) upon adding 2.0 equiv. of various metal ions.

(ICT) emission). The complexation happen between ATP and Cd^{2+} could be confirmed further by comparing NMR spectra of ATP and ATP– Cd^{2+} in which the chemical shifts of protons were obviously changed upon the addition of Cd^{2+} (Fig. 2a). Since the single crystal of ATP– Cd^{2+} complex suitable to structure analysis is not able to be obtained, the exact complex structure is not clear at present. Considering that the structure characteristics of ATP and absorption spectrum of ATP– Cd^{2+} complex are the very similar to those of 9-anthryl terpyridine– Cd^{2+} complex reported by Li and Yu et al. the ATP– Cd^{2+} complex might also be 2:2 binding stoichiometry of ATP and Cd^{2+} . It is interesting that the peak interval of two emission bands of ATP– Cd^{2+} complex is up to 185 nm, which is significantly larger than that of 9-anthryl terpyridine– Cd^{2+} complex (130 nm).

Therefore, the insertion of phenyl ring between 9-anthryl and terpyridine not only retains the dual emission feature of ATP–Cd(II) complex but also significantly enlarge the interval of two emission bands to afford more obvious ratiometric and colorimetric fluorescence.

The well-separated two emission bands imply that the complex has two emission species, a long-wavelength emission species induced by complexation and a short-wavelength one form phenylanthracene segment. Since the hardly changed absorption spectra upon complexation and the small overlap between the emission band of ATP and the absorption band of ATP–Cd²⁺ complex in solution, the complex species is not a powerful intramolecular energy trap of phenylanthracene emission, which



Fig. 2. Absorption and emission spectra of ATP and ATP-Cd²⁺ in acetonitrile at 1.0×10^{-5} M (a) and ¹H NMR spectra of ATP and ATP-Cd²⁺ in CDCl₃ (b).



Fig. 3. Emission spectra of ATP- Cd^{2+} in acetonitrile under different concentration (a) and emission spectra of ATP- Cd^{2+} solids (b).

renders the complex dual emission characteristics. We have examined emission spectra of ATP--Cd²⁺ complex in MeCN under different concentration (Fig. 3a). The total fluorescence intensities decrease with the increase of ATP-Cd²⁺ concentration, but different tendence in intensity change for two emission bands are observed. The emission intensity of complex species increase obviously while the emission intensity of ATP segment decreases sharply with the increase of ATP-Cd²⁺ concentration. Although the emission spectra under higher concentration are not measured due to its poor solubility, this result seems to imply the existence of planar anthracene interactions quenching fluorescence emission, and the interactions of emission species induced by complexation have little effect on fluorescence emission. Meanwhile, we have measured their solid-state emission spectra (Fig. 3b). ATP solid still emits blue with the peak wavelength of 437 nm, but $ATP-Cd^{2+}$ solid is not of both blue and red emissions, just a green emission material. This is probably caused by the different environment and stacking mode of ATP– Cd^{2+} molecules in solution and solid states.

3.3. The fluorescence response of $ATP-Cd^{2+}$ complex to anions

It has been reported that the complex of 9-anthryl terpyridine and Cd^{2+} could be decomplexed by PPi based on the displacement mode, which makes red emission of the complex change into blue emission of ligand 9-anthryl terpyridine [23]. ATP– Cd^{2+} solution has two emission bands located at 422 nm and 610 nm, respectively. When a little excess of PPi is added to the stirred ATP– Cd^{2+} solution, the long-wavelength emission band disappears and only short-wavelength emission band (peak at 430 nm) same as ATP emission remains (Fig. 4a). To this PPi-decomplexed solution, 1.2 equiv of Cd^{2+} is added and the red emission band reappears (Fig. 4a). This suggests that ATP is not only a reversible and recyclable sensor for Cd^{2+} but also its Cd(II) complex is a reversible and recyclable secondary sensor for PPi. The reversible sensing behavior of ATP– Cd^{2+} to PPi is examined over three cycles by the sequential addition of PPi and Cd^{2+} (Fig. 4b). ATP– Cd^{2+} solution emits red, and the addition of PPi affords an blue emission solution. When Cd^{2+} is added to the solution of (ATP– Cd^{2+} + PPi), a red emission solution reappears, and further addition of PPi into the red emission solution of (ATP– Cd^{2+} +PPi + Cd^{2+}) reproduces the blue emission. With the further addition of Cd²⁺, the solution turns dark red, and followed by the addition of PPi, the olive green solution is observed. The deep and dark red fluorescence color in third cycle could be ascribed to the introduction of water dissolving salts Cd^{2+} and PPi.

The complex of 9-anthryl terpyridine and Cd^{2+} could be decomplexed only by PPi, which afforded a selective secondary sensor for PPi [23]. We consider that the insertion of phenyl unit should change the complexing strength of ATP and Cd²⁺, thus ATP–Cd(II) complex might be decomplexed by other anions. Fig. 5 shows the fluorescence images of ATP-Cd(II) solution upon addition of different anions. It is observed that the red emission of ATP-Cd(II) solution is changed into the blue emission when polyvalent anions are added (Fig. 5a), such as PO₄³⁻, SO₄²⁻, S₂O₈²⁻, $C_2O_4^{2-}$, CO_3^{2-} , and $S_2O_3^{2-}$, etc. In contrast, monovalent anions, such as I⁻, Br⁻, Cl⁻, SCN⁻, NO₃⁻, ClO₄⁻, and AcO⁻, etc. hardly cause significant color changes of ATP-Cd(II) solution (Fig. 5b). This implies that the ATP-Cd(II) complex can be decomplexed by PPi and selectively respond to polyvalent anions. The sensing mechanism of ATP-Cd(II) complex towards polyvalent anions should be similar to that of the complex of 9-anthryl terpyridine and Cd^{2+} (displacement mode illustrated in Scheme 1). Fig. 5c-f depicted the fluorescence images of ATP-Cd(II) in acetonitrile upon the cyclic



Fig. 4. Emission spectra (a) and fluorescence images (b) of ATP–Cd²⁺ in acetonitrile $(1.0 \times 10^{-5} \text{ M})$ upon the cyclic addition of PPi and Cd²⁺, respectively.



Fig. 5. (a, b) Fluorescence images of ATP-Cd(II) solution in acetonitrile (1.0 × 10⁻⁵ M) upon addition of different anions (2.0 equiv); (c-f) Fluorescence images upon cyclic addition of polyvalent anions and Cd²⁺ (the condition same as Fig. 4b).

addition of different polyvalent anions and Cd^{2+} . The results confirm that ATP is a reversible and selective colorimetric sensor for Cd^{2+} , and ATP–Cd(II) complex could be used as a reversible secondary sensor for polyvalent anions.

3.4. Piezochromic luminescence of $ATP-Cd^{2+}$ complex

In most, but not all, piezofluorochromic materials, the mainstay is the aggregation-induced emission dyes, and there are only limited organometallic or coordination compounds composed of both metal ions and organic ligands (organic-metal complex) could exhibit piezochromic luminescence. Since the folding or twisted intramolecular conformations and the polytropic intermolecular π - π , metal-metal, or hydrogen-bonding interactions, organic-metal complex might be promising candidates for new PFC materials.

Since steric hindrance of 1,8-hydrogens on anthracene ring, ATP is a highly twisted molecule. However, ATP is highly fluorescent both in solution and solid-state, and does not show PFC behavior. We have carried out the grinding experiment on ATP–Cd(II) complex using a metal spatula on the glass plate to examine the PFC

behavior. The fluorescence images are shown in Fig. 6a. It is observed that the ground ATP–Cd(II) solid emits yellow fluorescence; however, when the ground solid is annealed before the isotropic melt transition or exposed to solvent vapor (fuming above dichloromethane at room temperature), an bluish-green fluorescence same as pristine solid appears. Furthermore, when the fumed or annealed sample is re-ground, the fluorescence color is again changed as the first grinding. This process is reproducible and indicates a reversible PFC behavior.

These naked-eye-visible changes in fluorescence color were recorded on a luminescence spectrophotometer, and the emission spectra are depicted in Fig. 6b. As expected, the recorded emission spectra are comparably consistent with the corresponding fluorescence colors observed (Fig. 6a). The peak emission wavelengths of ground and annealed (or fumed) states are 548 nm and 493 nm, respectively, and from which the grinding-induced spectral shift ($\Delta\lambda_{\rm PFC} = \lambda_{\rm pressed} - \lambda_{\rm annealed}$) is calculated to be 54 nm, a commendable PFC complex material.

To get further information on aggregate structure changes upon grinding the ATP– Cd^{2+} complex solid, powder wide-angle X-ray diffraction (PWXD) and differential scanning calorimetry (DSC)



Fig. 6. Fluorescence images (a) and emission spectra (b) of ATP-Cd²⁺ solid upon grinding, solvent-fuming, re-grinding, and annealing at room temperature under UV light irradiation (365 nm).



Fig. 7. X-ray diffraction patterns at room temperature (a) and DSC curves (b) of ATP-Cd²⁺ solid under pristine and ground states.

experiments were conducted on the ground and as-prepared (pristine) solids. The PWXD pattern of pristine solid shows sharper and intenser reflections, indicative of well-ordered microcrystalline structures (Fig. 7a). In contrast, the ground solid displays broad and featureless diffractogram reflecting notable amorphous features. This indicates that grinding has induced the phase transition of ATP-Cd²⁺ complex solid from crystalline to amorphous states. The formation of amorphous state after grinding could be further confirmed by DSC experiment. As shown in Fig. 7b, no thermal transitions could be detected before 350 °C for the pristine solid. However, there is a clear exothermic peak at 198 °C for the ground solid upon heating, which could be considered as the cold-crystallization temperature (T_{cc}) of amorphized ATP-Cd²⁺ complex, and the its high T_{cc} makes the ground state is very stable at room temperature. Therefore, the transformation between crystalline and amorphous states upon various external stimuli is responsible for the PFC behavior.

4. Conclusions

We have inserted a phenyl ring between anthryl and terpyridine to synthesize a new terpyridine derivative, 4-(9-anthryl)phenyl terpyridine (ATP) to demonstrate the effect of the structure change on optical properties. The insertion of phenyl ring could not only remains the selectively colorimetric fluorescence sensing to Cd²⁻ but also enlarges the interval of two emission bands from ATP and its Cd(II) complex. Unlike 9-anthryl terpyridine, ATP-Cd(II) complex could be decomplexed by not only PPi but also other polyvalent anions such as CO₃²⁻, SO₄²⁻, C₂O₄²⁻, S₂O₈²⁻, PO₄³⁻, etc., implying that the insertion of phenyl unit has weakened the complexing strength of terpyridine and Cd(II). Moreover, the insertion of phenyl ring has rendered ATP-Cd(II) complex new optical property-remarkable and reversible piezofluorochromism based on phase transformation between crystalline and amorphous states upon external stimuli. This work has demonstrated that the subtle manipulation of conjugated backbone could tune and alter the optical properties.

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