

A highly selective colorimetric chemosensor for detecting the respective amounts of iron(II) and iron(III) ions in water

Zuo-Qin Liang,^a Cai-Xia Wang,^a Jia-Xiang Yang,^{*abc} Hong-Wen Gao,^b Yu-Peng Tian,^a Xu-Tang Tao^c and Min-Hua Jiang^c

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A novel colorimetric chemosensor containing terpyridine was synthesized. It showed high selectivity and sensitivity for Fe(II) and Fe(III) ions in neutral aqueous solution in the presence of other metal ions such as Cd²⁺, Cr³⁺, Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Pb²⁺, Na⁺, Ca²⁺, Mg²⁺, K⁺ and Ag⁺. Upon the addition of Fe²⁺ or Fe³⁺, the sensor displayed a unique new peak around 567 nm in its absorption spectra, and the color of the solution changed from light yellow to light magenta. In particular, the respective amounts of Fe(II) and Fe(III) ions in the solution can be detected using the light-absorption ratio variation approach (LARVA).

Introduction

The development of chemosensors for metal ions occurred early,¹ but the design of fluorescent and chromogenic chemosensors for the detection of low concentrations of metal ions is still an active area of research.² This is because chemosensors not only possess simplicity and high sensitivity, but are capable of specific recognition of particular ions in the presence of related ones.³ Fe ion is the most abundant transition-metal ion in humans and other mammals, and it plays important roles in various biological systems.⁴ It has been studied with methods⁵ such as atomic absorption spectrometry, spectrophotometry, and so on. These methods can only detect the total amount of Fe(II + III) or a certain valence iron. In recent years, Meier *et al.* and Kimura *et al.* both described a terpyridine-based chemosensor to recognize Fe(II).⁶ Nevertheless, their sensors were not selective for a special metal ion. The properties of a sensor in aqueous solution are very important for compounds intended for application in living systems.⁷ Lately we have developed a sensor for anionic surfactants in water, which has been applied to the analysis of water samples with satisfactory results,⁸ but most of the studies have been concerned with non-aqueous solutions of ions.⁹ In addition, colorimetric sensors are useful to develop simple-to-use, naked eye diagnostic tools.¹⁰ Therefore, our target is to design a highly selective colorimetric sensor in aqueous solution, which can discriminate between Fe(II) and Fe(III).

Terpyridine ligands themselves have generally not been used for sensors, due to possessing an excellent ability to coordinate with a large variety of transition metal ions with high binding constants.¹¹ But we found that iron terpyridine complexes generally show a band in the visible region in absorption

spectra. Here, we report on the synthesis and the sensing application of 3-{4-[2-(4-dibutylaminophenyl)vinyl]phenyl}-1-(4-[2,2':6',2'']terpyridin-4'-yl-benzyl)-3H-imidazol-1-ium bromide (TBIB) ($\epsilon_{275\text{ nm}} = 3.80 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{318\text{ nm}} = 1.50 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{366\text{ nm}} = 1.46 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in aqueous solution. The terpyridine ligand showed high sensitivity and selectivity for Fe²⁺ and Fe³⁺ over other cations in aqueous solution. In its absorption spectra, a new band appeared at 567 nm only in the presence of Fe²⁺ or Fe³⁺, and the color of the solution changed from light yellow to light magenta (Fig. 1). In addition, we can determine the respective amounts of Fe²⁺ and Fe³⁺ in the solution using the light-absorption ratio variation approach (LARVA).¹²

Results and discussion

The chromophore of the chemosensor was based on a donor- π -acceptor system. This could display a strong color development as well as great absorbance. This feature could make it possible for the chemosensor to be a colorimetric one. The amino group conjugated to the phenyl ring was the electron donor and the two butyl groups introduced were to enhance the electron-donating ability of the nitrogen atom. The imidazolium salt was the electron acceptor, and made TBIB possess some solubility in aqueous solution. The synthetic strategy and the structure of the resulting product are depicted in Scheme 1. 4-(4-(1H-Imidazol-1-yl)styryl)-N,N-

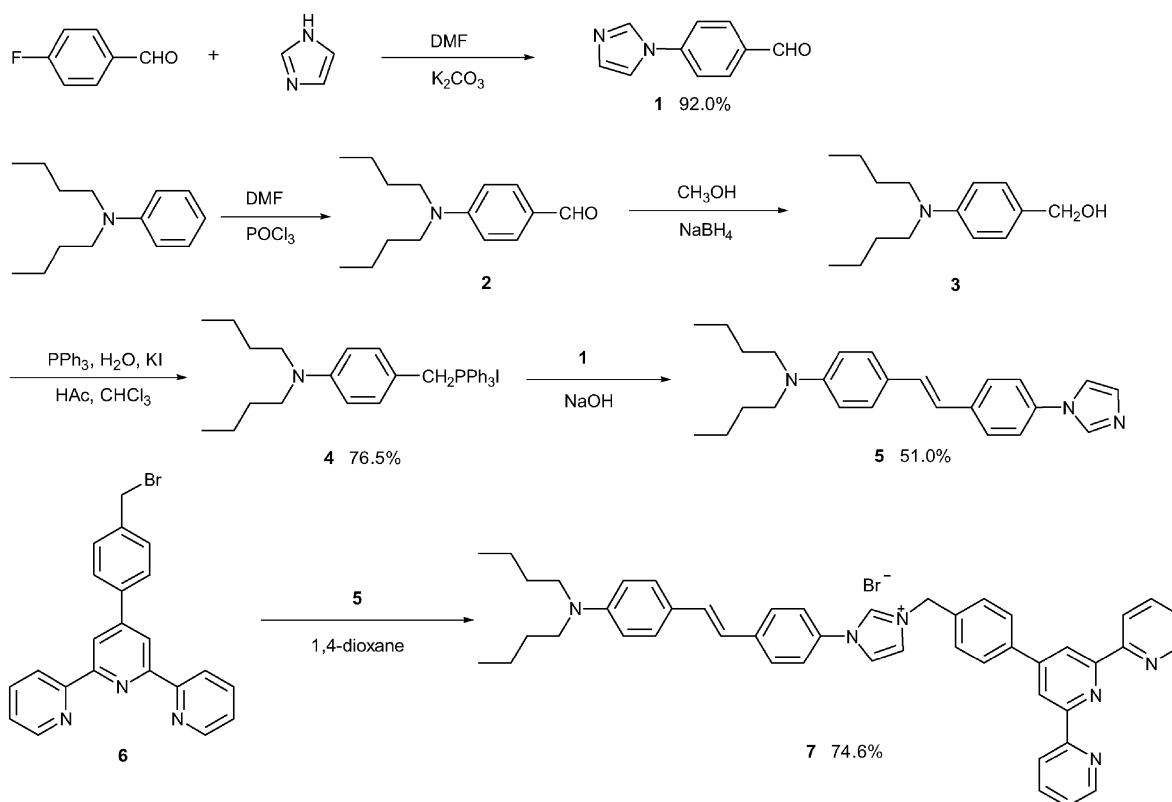


Fig. 1 Color changes observed for TBIB in water upon addition of cations. From left to right: 1: none; 2: Co²⁺; 3: Ni²⁺; 4: Ag⁺; 5: Fe²⁺ or Fe³⁺. Upon the respective addition of Na⁺, Ca²⁺, Mg²⁺, K⁺, Cd²⁺, Cr³⁺, Cu²⁺, Pb²⁺, Zn²⁺, the color is similar to 3.

^a Department of Chemistry, Anhui University, Hefei 230039, People's Republic of China. E-mail: jxyang@ahu.edu.cn

^b Key Laboratory of Yangtze Water Environment of Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, People's Republic of China

^c State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China



Scheme 1 Synthesis of TBIB (7).

dibutylbenzamine **5** was prepared from 4-imidazol-1-ylbenzaldehyde **1** and phosphonium salt **4** by the Wittig reaction. 4'-(4''-Bromomethylphenyl)-2,2':6',2''-terpyridine **6** was prepared according to the literature.⁸ Finally, **5** and **6** in 1,4-dioxane were stirred at 100 °C for three days to give the final product **7** (TBIB).

The influence of pH on the absorbance of TBIB was determined in aqueous solution as shown in Fig. 2. The absorbance of TBIB at 567 nm remained unaffected by varying pH. The ratios of absorbance at 318 nm and 366 nm were almost a constant minimal value in the pH range 6.28 to 4.46, and then rapidly increased from pH 4.46 to pH 2.20. This change may be caused by the protonation of the pyridyl nitrogen.

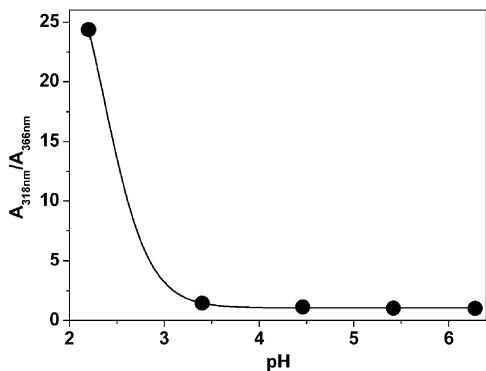


Fig. 2 Influence of pH on the absorbance of TBIB in aqueous solution.

The selective and sensitive signal response of TBIB toward Fe^{2+} ion and Fe^{3+} ion was preserved in absorption. All titration experiments were performed in aqueous solution around pH 6.0. As shown in Figs. 3 and 4, the addition of low concentration of Fe^{2+} or Fe^{3+} ion to the solution of TBIB led to a sharp new band at 567 nm ($\epsilon_{\text{Fe}(\text{tpy})_2^{2+}} = 1.84 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; $\epsilon_{\text{Fe}(\text{tpy})_2^{3+}} = 1.98 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which was caused by the metal-to-ligand-charge-transfer (MLCT).^{6a} With the increasing concentration of Fe^{2+} ion, the sharp new peak gradually rose until a mole ratio (TBIB/ Fe^{2+}) of 2 : 1 was reached. The relationship between TBIB concentration and the formation of the $\text{Fe}(\text{tpy})_2^{2+}$ complex is shown in the inset in Fig. 3. From the inset we also found the absorption at 567 nm showed a linear increase and a sharp endpoint at TBIB/ Fe^{2+} ratio of 2 : 1 as the concentration of TBIB increased. The two experiments indicate that there is no dissociation from $\text{Fe}(\text{tpy})_2^{2+}$ to $\text{Fe}(\text{tpy})^{2+}$ in the experimental process. The binding mode of the terpyridine unit for Fe^{3+} was similar to that of $\text{Fe}(\text{tpy})_2^{2+}$ as shown in Fig. 4. Interestingly, with the increasing concentration of Fe^{2+} from 0 to 50.0 $\mu\text{g L}^{-1}$ in the solution, the bands of the $\text{Fe}(\text{tpy})_2^{2+}$ at 318 nm and 366 nm rose simultaneously, and the absorbance ratio $A_{318 \text{ nm}}/A_{366 \text{ nm}}$ didn't change. However, the band of the $\text{Fe}(\text{tpy})_2^{3+}$ rose at 318 nm, and descended at 366 nm. As a result, the absorbance ratio $A_{318 \text{ nm}}/A_{366 \text{ nm}}$ of the $\text{Fe}(\text{tpy})_2^{3+}$ solutions increased rapidly with the increase of Fe^{3+} concentration. Based on these characteristics, the LARVA has been applied to the determination of Fe^{3+} , and its main equations are given as eqns (2) and (3).¹² The symbol ΔA_r is the difference of absorbance ratios between the ML_n and L

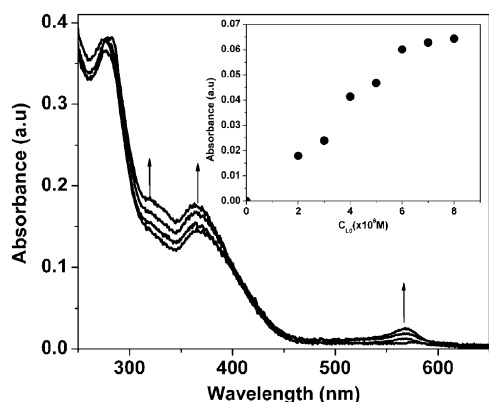


Fig. 3 Changes in absorption spectra of TBIB (1×10^{-5} M) on the addition of Fe^{2+} in aqueous solution (pH = 6.0). The Fe^{2+} concentration is 0, 20.0, 30.0, 50.0 $\mu\text{g L}^{-1}$, respectively. The inset shows the relationship between TBIB concentration and the absorbance of $\text{Fe}(\text{tpy})_2^{2+}$ solution at 567 nm. The concentration of Fe^{2+} is 3.5×10^{-6} M in the solution. The concentration of TBIB is 0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0×10^{-6} M, respectively.

solutions. C_{M0} is the initial concentration of M. Both p' and q' are constants when the reaction and measurement conditions are selected. The symbols $A_{\lambda 1}$, $A_{\lambda 2}$, $A_{\lambda 1}^L$ and $A_{\lambda 2}^L$

$$\Delta A_r^{-1} = p' C_{M0}^{-1} + q' \quad (1)$$

where

$$\Delta A_r = A_r - A_{r0} = \frac{A_{\lambda 2}}{A_{\lambda 1}} - \frac{A_{\lambda 2}^L}{A_{\lambda 1}^L} \quad (2)$$

are the absorbances of ML_n and L solutions, respectively measured at wavelengths λ_1 and λ_2 against water. However, if C_{M0} is low enough, eqn (1) may be simplified into:

$$\Delta A_r = p C_{M0} + q \quad (3)$$

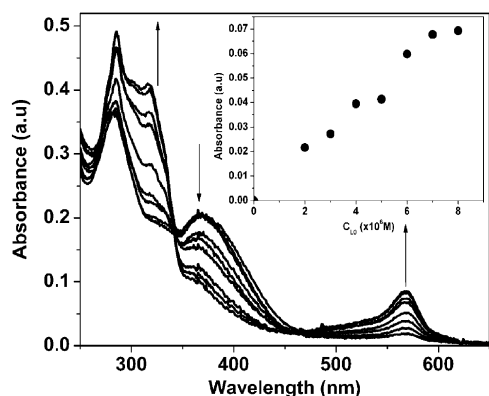


Fig. 4 Changes in absorption spectra of TBIB (1×10^{-5} M) on the addition of Fe^{3+} in aqueous solution (pH = 6.0). The Fe^{3+} concentration is 20.0, 30.0, 50.0, 70.0, 100.0, 150.0, 200.0, 250.0, 300.0 $\mu\text{g L}^{-1}$, respectively. The inset shows the relationship between TBIB concentration and the absorbance of $\text{Fe}(\text{tpy})_2^{3+}$ solution at 567 nm. The concentration of Fe^{3+} is 3.5×10^{-6} M in the solution. The concentration of TBIB is 0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0×10^{-6} M, respectively.

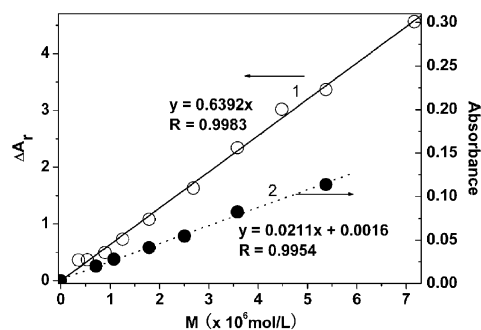


Fig. 5 Standard curves for the determination of Fe^{3+} (1) and the total amount of Fe^{2+} and Fe^{3+} (2).

where p is the sensitivity factor and the inverse reverse ratio of C_{L0} , 12d and q is the linear regression intercept, which often approaches 0. The less L is added, the higher the analytical sensitivity obtained. However, too low a value of L can cause a considerable error of measurement because of the instrument background noise. From the absorption spectra of the TBIB–Fe(III) reaction as shown in Fig. 4, 318 and 366 nm were selected as the work wavelengths. Thus, ΔA_r may be calculated by the relation:

$$\Delta A_r = \frac{A_{318 \text{ nm}}}{A_{366 \text{ nm}}} - \frac{A_{318 \text{ nm}}^0}{A_{366 \text{ nm}}^0} \quad (4)$$

where $A_{318 \text{ nm}}$ and $A_{366 \text{ nm}}$ are the absorbances of $\text{Fe}(\text{tpy})_2^{3+}$ solution measured at 318 nm and 366 nm against water. $A_{318 \text{ nm}}^0$ and $A_{366 \text{ nm}}^0$ are the absorbances of $\text{Fe}(\text{tpy})_2^{2+}$ solution or the TBIB solution measured at 318 nm and 366 nm against water. The linear regression curves from a series of standard Fe(II, III) solutions are shown in Fig. 5, where curve 1 is used for the determination of the amount of Fe^{3+} and curve 2 for the detection of the total amount of Fe^{2+} and Fe^{3+} by using the absorbances of $\text{Fe}(\text{tpy})_2^{2+}$ and $\text{Fe}(\text{tpy})_2^{3+}$ at 567 nm.

To further investigate the selectivity and sensitivity of the described sensory system for metal ions, a series of coloring experiments were performed in water. The addition of other metal ions such as Cd^{2+} , Cr^{3+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , Co^{2+} , Na^+ , Ca^{2+} , Mg^{2+} and K^+ did not produce significant changes in the UV/Vis spectra at 567 nm in aqueous solution. Only upon addition of Ag^+ did the system display a new band (Fig. 6(b)) at 450 nm. Fortunately, in the competition experiments Ag^+ merely showed a little interference. The competition experiments were conducted in the presence of 5×10^{-5} g L^{-1} Fe^{2+} and 2×10^{-4} g L^{-1} Fe^{3+} mixed with Cd^{2+} , Cr^{3+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , Ag^+ , Co^{2+} , Na^+ , Ca^{2+} , Mg^{2+} and K^+ in the TBIB solution. The experimental results are listed in Table 1. The results indicate that the terpyridine ligand has a high selectivity for Fe^{2+} and Fe^{3+} over other metal ions. In the competition experiments, both $\text{Mg}(\text{II})$ and $\text{Ca}(\text{II})$ appear in error over 10% only when their mole concentrations are more than 200 times that of $\text{Fe}(\text{II})$. Besides, $\text{Co}(\text{II})$, $\text{Ag}(\text{I})$ and $\text{Cu}(\text{II})$ caused over 10% of error, resulting from their competition coordination with TBIB. However, their amounts should be less than such addition amounts in physiological studies. We estimated that the errors caused by $\text{Co}(\text{II})$, $\text{Ag}(\text{I})$ and $\text{Cu}(\text{II})$ would be less than 10% in

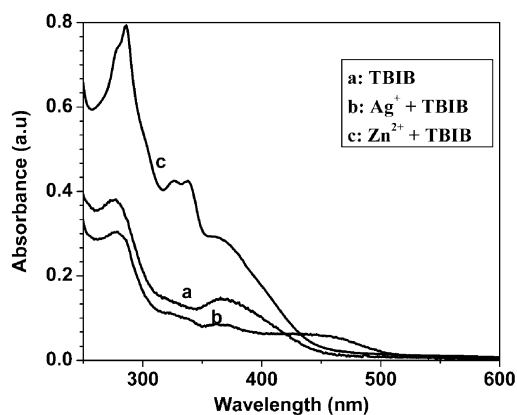


Fig. 6 UV/Vis absorption of TBIB in the presence of Ag^+ and Zn^{2+} in water. $[\text{TBIB}] = 1 \times 10^{-5} \text{ M}$, $[\text{Ag}^+] = 5 \times 10^{-6} \text{ M}$, $[\text{Zn}^{2+}] = 3.67 \times 10^{-6} \text{ M}$.

Table 1 The effect of foreign ions in the solutions and error shown

Ion added	Added, $\mu\text{g}/10 \text{ mL}$	Error ¹ , % ^a	Error ² , % ^a
Fe(II)	0.50	8.62	3.68
Fe(III)	2.00		
Cd(II)	2.00	4.20	-8.60
Cr(III)	4.00	5.04	-4.41
Zn(II)	1.17	-4.86	1.09
Co(II)	2.00	-16.18	7.59
Ni(II)	4.00	6.1	8.95
Mg(II)	44.0	4.02	-14.98
Ca(II)	72.0	3.32	-12.34
Cu(II)	0.700	-8.58	11.6
Pb(II)	38.0	5.79	-1.15
Na(I)	41.4	6.68	-4.20
K(I)	69.7	6.85	-1.11
Ag(I)	1.93	9.15	-10.82

^a Error¹ stands for the metrical error of Fe^{3+} . Error² symbolizes the metrical error of total iron.

physiological studies. Although the sensor has a few deficiencies, it can determine the respective amounts of Fe^{2+} and Fe^{3+} in the solution.

Fe^{2+} and Fe^{3+} ions can be detected at least down to $1.97 \times 10^{-7} \text{ M}$ and $1.67 \times 10^{-7} \text{ M}$, respectively, when TBIB is employed at $1 \times 10^{-5} \text{ M}$ in water. The range makes this system quite sensitive, so the detection of small quantities of Fe^{2+} ion and Fe^{3+} ion is feasible.

Conclusions

We have made full use of the characteristics of the terpyridine to synthesize a novel sensor for Fe^{2+} and Fe^{3+} ions in aqueous solution. Our sensor system displayed a unique new peak at around 567 nm in the absorption spectra upon the addition of Fe^{2+} or Fe^{3+} , and the color of the solution changed. In particular, the sensor can measure the respective amounts of Fe^{2+} and Fe^{3+} in aqueous solution. To sum up, it showed high selectivity and sensitivity for Fe^{2+} and Fe^{3+} in aqueous solution in the presence of other metal ions. It is a potential Fe^{2+} and Fe^{3+} chemosensor through UV/Vis spectrometry.

Experimental

Syntheses

The resulting compounds were characterized by ^1H and ^{13}C NMR spectrometry using a Bruker Avance 300 MHz or 400 MHz spectrometer. Electrospray mass spectra (ESI-MS) were recorded on an ABI API 4000 mass spectrograph. Melting points were measured with a Mettler Toledo FP62 instrument. Elemental analyses were performed on an Elementar Vario EL-III instrument. IR spectra were recorded on a Nicolet FT-IR-170SX infrared spectrometer. All chemicals were purchased from Aldrich, Acros or Shanghai Reagent Institute and the solvents were purified according to conventional methods before use.

4-Imidazol-1-yl-benzaldehyde 1. 4-Fluorobenzaldehyde (25.0 g, 0.200 mol), imidazole (20.4 g, 0.300 mol) and anhydrous K_2CO_3 (40.0 g) were mixed in DMF (300 mL), and then several drops of catalytic reagent Aliquat 336 were added. The mixture was refluxed for 24 h at 100°C . Half of the solvent was removed under low pressure. After the mixture returned to room temperature, it was poured into ice water and left overnight. After filtration, the light yellow product (31.6 g, yield 92.0%) was obtained. ^1H NMR (CDCl_3 , 400 MHz) δ : 9.20 (1H, s), 8.03 (2H, d, $J = 8.40 \text{ Hz}$), 8.00 (1H, s), 7.59 (2H, d, $J = 8.40 \text{ Hz}$), 7.43 (1H, s), 7.26 (1H, s). IR (KBr, cm^{-1}): 3110, 2846, 2819, 2750, 1690, 1610, 1520, 1310, 1060, 835.

4-(*N,N*-Di-*n*-butylamino)benzaldehyde 2. This compound was prepared according to the literature.¹³

4-Dibutylaminobenzyl alcohol 3. Compound 2 (11.7 g, 50 mmol) was dissolved in methanol (350 mL) in an ice-bath. NaBH_4 (3.80 g, 100 mmol) was added before the temperature was allowed to rise to room temperature. After refluxing for 2 h, the solvent was removed under vacuum. Water was added to the residue, and the product was extracted with CH_2Cl_2 . The organic phase was washed with water and saturated NaCl solution two times, respectively. Then it was dried with anhydrous magnesium sulfate. The solvent was removed to give a yellow product, which did not need to be isolated.

(4-Dibutylaminobenzyl)triphenylphosphonium iodide 4. The mixtures of CHCl_3 (100 mL), H_2O (3.50 mL), PPh_3 (10.7 g, 40.0 mmol), HAc (7.30 g, 0.120 mol), KI (6.70 g, 40.0 mmol), and compound 3 (9.40 g, 40.0 mmol) were stirred and refluxed for 10 h. After the solvent was removed, the toluene was added to the residue. Stirring and refluxing were continued for an hour. It was subsequently cooled in a refrigerator overnight to give a white solid. After filtration, the solid was washed with THF and dried to give compound 4 (18.7 g, yield 76.5%). ^1H NMR (CDCl_3 , 300 MHz) δ : 0.93 (6H, t, $J = 7.20 \text{ Hz}$), 1.30 (4H, m), 1.47 (4H, m), 3.18 (4H, t, $J = 7.65 \text{ Hz}$), 4.95 (4H, d, $J = 12.91 \text{ Hz}$), 6.37 (2H, d, $J = 8.70 \text{ Hz}$), 6.82 (2H, d, $J = 8.70 \text{ Hz}$), 7.68 (12H, m), 7.80 (3H, m).

4-(4-(1*H*-Imidazol-1-yl)styryl)-*N,N*-dibutylbenzenamine 5. Compound 4 (7.30 g, 12.0 mmol), compound 1 (1.70 g, 10.0 mmol) and solid NaOH (4.00 g, 100 mmol) were crushed in a mortar for 15 min. The powder was dissolved in CH_2Cl_2 . The organic phase was washed thoroughly with water and

saturated NaCl solution, and then was dried with anhydrous magnesium sulfate. After filtration, the CH_2Cl_2 was removed. The crude product was purified by silica-gel column chromatography with ethyl acetate as the eluent to give the yellow product (1.90 g, yield 51.0%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 0.95 (6H, m), 1.34 (4H, m), 1.50 (4H, m), 3.29 (4 H, m), 6.63 (2H, d, $J = 8.84$ Hz), 6.87 (1H, d, $J = 16.24$ Hz), 7.04 (1H, d, $J = 16.24$ Hz), 7.21 (1H, s), 7.28 (1H, s), 7.32 (2H, d), 7.38 (2H, d, $J = 8.84$ Hz), 7.54 (2H, d, $J = 6.70$ Hz), 7.85 (1H, s).

4'-(4''-Bromomethylphenyl)-2,2':6',2''-terpyridine 6. This compound was prepared according to the literature.⁸

3-{4-[2-(4-Dibutylaminophenyl)vinyl]phenyl}-1-(4-[2,2':6',2'']terpyridin-4'-yl-benzyl)-3H-imidazol-1-ium bromide 7. A mixture of compound **6** (3.40 g, 8.50 mmol) and compound **5** (3.15 g, 8.50 mmol) in 1,4-dioxane (30.0 mL) was stirred at 100 °C for three days, under refluxing. A brown viscous liquid was obtained which was washed with ethyl ether. The crude compound was purified by silica-gel column chromatography with $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4 : 1, v/v) as the eluent to give a pale yellow powder (4.92 g, yield 74.6%). Mp: 273 °C. $^1\text{H NMR}$ (DMSO, 400 MHz) δ : 0.92 (6H, t), 1.34 (4H, m), 1.51 (4H, m), 3.29 (6H, m), 5.63 (2H, s), 6.66 (2H, d, $J = 8.73$ Hz), 7.01 (1H, d, $J = 16.30$ Hz), 7.28 (1H, d, $J = 16.30$ Hz), 7.43 (2H, d, $J = 8.73$ Hz), 7.54 (2H, m), 7.77 (6H, m), 8.02–8.10 (5H, m), 8.39 (1H, s), 8.68 (2H, d, $J = 7.90$ Hz), 8.73 (2H, s), 8.77 (2H, d, $J = 4.46$), 10.06 (1H, s). $^{13}\text{C NMR}$ (DMSO, 150.90 MHz): 13.87, 19.67, 29.06, 49.83, 52.06, 111.40, 118.05, 121.00, 121.52, 121.98, 123.28, 124.61, 126.91, 127.63, 128.15, 129.59, 131.04, 132.48, 135.39, 135.65, 137.52, 138.06, 139.67, 147.91, 148.89, 149.36, 154.88, 155.79. ESI-MS: m/z 695.9, 348.8 and 233.0. Calcd. for $\text{C}_{47}\text{H}_{47}\text{N}_6\text{Br}$: C, 72.76; H, 6.11; N, 10.83. Found: C, 72.66; H, 6.14; N, 10.71%. IR (KBr, cm^{-1}): 2952, 2926, 2874, 2357, 1590, 1522, 1380, 1180, 792.

General instrumentation and reagents for titration experiments

Absorption spectra were recorded with a Model S-4100 spectrophotometer (Scinco Instruments, Korea). A Model BS110S electronic balance (Sartorius Instruments, Beijing) was used to accurately weigh the standard substances. A Model RO DI Water Ultra Purification System (Hi-tech Instruments, Shanghai, China) was used to produce the deionized water. The solution pH was measured with a Model PHS-25 acidity meter (Shanghai Precise Sci. Instrum., China). Standard stock solution of Fe^{2+} was prepared every time by dissolving ammonium iron(II) $((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, A. R., Shanghai Chemical Reagents, China) in deionized water. Standard stock solution of Fe^{3+} was prepared by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ which was purchased from the Institute for Reference Materials of SEPA, Beijing, China. The solutions of other metal ions were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, MgSO_4 ,

CaCl_2 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, NaCl, KCl, AgNO_3 , respectively, dissolved in deionized water.

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