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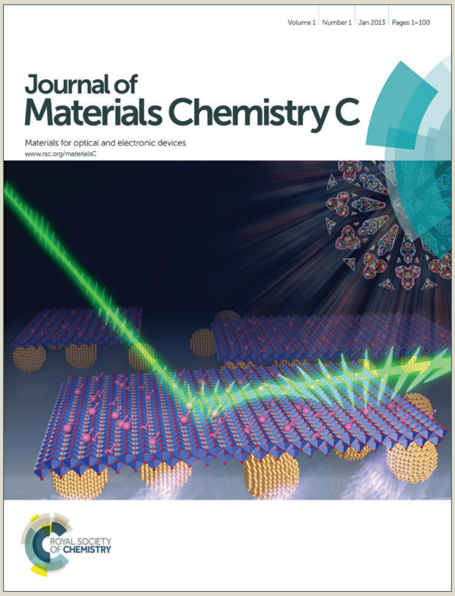

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ARTICLE

A charged iridophosphor for time-resolved luminescent CO_2 gas identification

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A phosphorescent CO_2 gas probe based on an iridium(III) complex with 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline ligand has been developed. Its phosphorescence is quenched by the addition of CH_3COO^-. Then, after bubbling CO_2 into the detecting solution, the quenched phosphorescence can be recovered. This phosphorescent CO_2 probe exhibits higher photostability and reduced photobleaching than some of the reported organic fluorescent probes. Time-resolved photoluminescence experiment has been performed for CO_2 gas detection, which can effectively remove the background fluorescence and improve the sensitivity and signal-to-noise ratio of the sensor in complicated media.

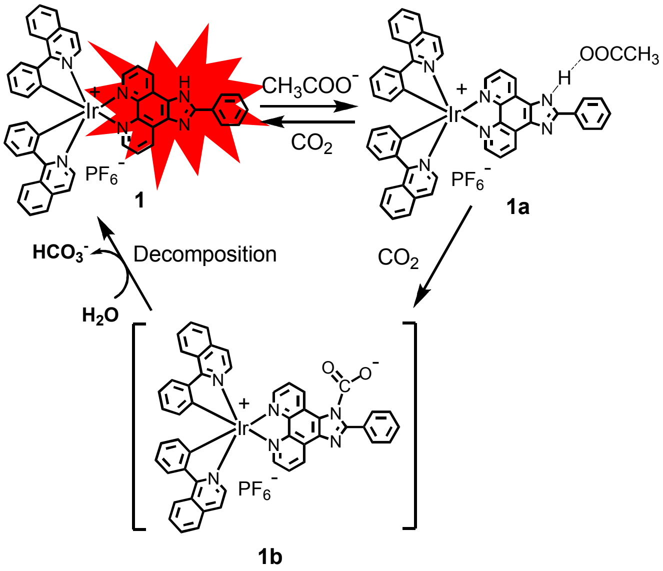
Introduction

Carbon dioxide gas identification is of great importance in various fields, such as public health, food packaging, agricultural production and medicine.[1] Quantification of environmental release of CO_2 also needs significant attention because of its pivotal role in controlling global climate change. Many analytical methodologies have been developed for CO_2 detection, including infrared spectroscopic, electrochemical and gas chromatography-mass spectrometry (GC-MS) techniques.[2] However, these methods are generally complicated, time-consuming, and require expensive and bulky equipment, and some of them cannot tolerate the interference of carbon monoxide.[3] Compared with other traditional methods, the optical CO_2 sensors have attracted considerable interest due to their low cost, simple construction, quick response, high tolerance to interfering agents, and high visibility to the naked eyes.[4]

Recently, optical sensors have proved to be useful for the studies of many analytes because of their inherent ease of manufacture and use and relatively high chemical and mechanical stability. It is not uncommon to make use of the acidic properties of CO_2 to design such optical sensors, but there are only few fluorescent pH indicators in the literature that can meet the requirements of pK_a, photostability and brightness simultaneously.[5] Up to now, several alternative detection approaches have been developed. By bubbling CO_2 into an amine solution, it can generate carbamate ionic liquid, which is accompanied by an increase in viscosity, and such change can be detected with the help of aggregation-induced emission (AIE).[6] Recently, an optical CO_2 sensor that utilizes tetrapropyl benzobis(imidazolium) salt has been reported for both fluorescence and colorimetric detection.[7a]

Although excellent CO_2 detection has been realized by exploiting fluorescent sensors,[7] the interference of background fluorescence is always a thorny problem, which might come from some organic dyes in the solvents. Phosphorescent heavy-metal complexes typically with long emission lifetimes (in the microsecond to millisecond range) offer an effective way to solve this problem by using time-resolved photoluminescence technique (TRPT).[8] Besides, their excellent photophysical properties, such as evident Stokes shifts and high photostability, etc, make them a good candidate for sensing purpose.[9] Because of these, many chemical sensors based on heavy-metal complexes, such as iridium(III), ruthenium(II) and platinum(II) complexes, have been reported for targeting small molecules, anions, and metal ions.[10] Among these, iridium(III) complexes are regarded as one of the most promising phosphorescent materials due to their high photoluminescence quantum yields and excellent color tunability. Utilization of these iridium(III) dyes in chemosensing systems has been well highlighted in the literature.[11] As far as we know, research on phosphorescent probes for CO_2 gas detection is still quite rare.[12]

The -NH unit on 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline can interact with CH_3COO^- to form strong hydrogen bond, leading to a quenching effect on the luminophore.[13] It is well known that CO_2 can readily react with the amine (-NH) group.[14] So, we expect that CO_2 could react with the -NH group to destroy the hydrogen bond of ($N\text{-}H\cdots OOCCH_3$), resulting in recovery of phosphorescence. In this work, a phosphorescent CO_2 sensor **1** in which 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline is used as an ancillary ligand in a cyclometalated iridium(III) species has been designed and synthesized (Scheme 1). After bubbling CO_2 gas into the solution, the phosphorescence quenched by CH_3COO^- can be recovered. This phosphorescent CO_2 probe displays higher photostability and reduced photobleaching over some of the reported organic probes. More importantly, the time-resolved photoluminescence technique demonstrates that **1** can be used to detect CO_2 in the presence of strong background fluorescence, which improves the sensitivity and signal-to-noise ratio of the sensor in complicated media.



Scheme 1 A proposed detection mechanism of CO_2 gas by complex **1**.

Results and discussion

Synthetic procedures

The 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline and 1-phenylisoquinoline ligands were synthesized following the literature reports.[15] Complex **1** was prepared in two steps: firstly, the chloro-bridged iridium(III) precursor $[Ir(piq)_2Cl]_2$ (piq = 1-phenylisoquinoline) was prepared according to the published method.[9] Then, complex **1** was synthesized through the bridge-splitting reaction of $[Ir(piq)_2Cl]_2$ and subsequent complexation with 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline. The desired complex was characterized by ^{1}H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry.

Photophysical properties

The UV-vis absorption spectrum of **1** in CH_3CN displays an intense band at 281 nm ($\varepsilon = 3.2 \times 10^4$ M^{-1} cm^{-1}), which is attributed to the spin-allowed ligand-centered transition (^{1}LC). Weaker broad bands at 382 nm ($\varepsilon = 4.75 \times 10^3$ M^{-1} cm^{-1}) and 444 nm ($\varepsilon = 2.4 \times 10^3$ M^{-1} cm^{-1}) are attributed to the singlet metal-to-ligand charge-transfer transition (^{1}MLCT), triplet metal-to-ligand charge-transfer transition (^{3}MLCT) and the spin-forbidden ligand-centered transition (^{3}LC) (Fig. 1). The photoluminescence (PL) spectra of **1** in different solutions (CH_2Cl_2, EtOH, CH_3OH, CH_3CN and THF) are shown in Fig. 1. The PL maximum of **1** is located at ~596 nm which is rather independent of the solvent changes, suggesting that the emission mainly comes from the LC excited state.

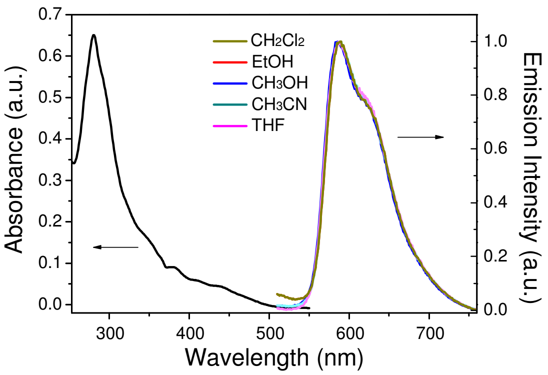


Fig. 1 Absorption spectra of **1** in CH_3CN and PL spectra of **1** in CH_2Cl_2, EtOH, CH_3OH, CH_3CN and THF.

CO_2 detection

We first investigate the photoluminescence changes of **1** with different anions. Upon addition of CH_3COO^- and F^-, the emission of **1** was quenched significantly. It is suggested that the quenching of **1** is due to an electron transfer process from the nitrogen atom of imidazolyl group, which possesses a partial negative charge after the formation of hydrogen bond (Scheme 1), to the excited iridium center. However, there are no obvious spectral variations for **1** upon addition of other anions (such as Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-) (Fig. 2).

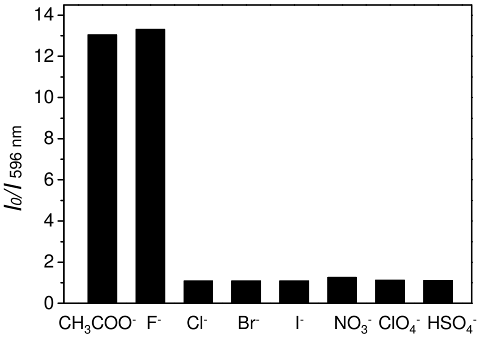


Fig. 2 Photoluminescence responses of complex **1** (10 μM) with the addition of 3.0 equiv. of various anions, Cl^-, Br^-, I^-, NO_3^-, ClO_4^- and HSO_4^- in CH_3CN. The black bars represent the I_0/I ratios at 596 nm after the addition of various anions to the solutions of complex **1**.

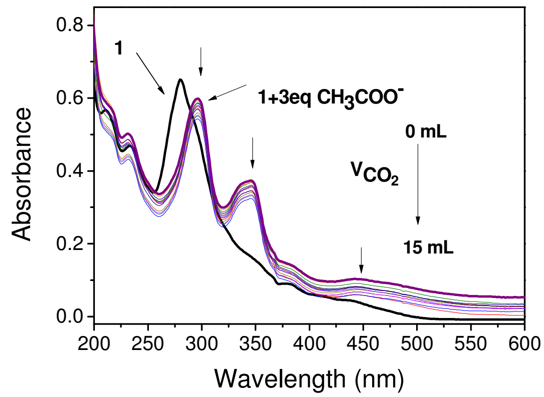


Fig. 3 Changes in the UV-vis spectra of complex **1** in CH_3CN solution (10 µM) containing CH_3COO^- (3 equiv.) with different volumes of CO_2 gas (0–15 mL).

Since CH_3COO^- shows relatively low toxicity to the environment as compared to F^-, it was chosen to interact with complex **1** to quench its luminescence. As shown in Fig. 3, when CH_3COO^- (3 equiv.) was added to the CH_3CN solution of **1** (10 µM), the absorption band at 281 nm was red shifted to 295 nm and a new band appeared at 346 nm, indicating that a strong N-H···$OOCCH_3$ bond has been formed and the phosphorescence emission was quenched significantly (Fig. 4). Next, we expect that bubbling of CO_2 gas into the solution of **1** containing CH_3COO^- would destroy the hydrogen bond by interacting CO_2 with the -NH unit on the imidazolyl group and then recover the luminescence. With the increasing volume of CO_2 (as governed by a mass flow controller) bubbled into the solution, the absorbance at 295 and 346 nm decreased gradually (Fig. 3), which indicated that CO_2 reacted with the lone electron pair in **1**. Furthermore, a dramatic increase in the phosphorescence intensity at 596 nm was observed upon exposure to an increasing volume of CO_2 gas (Fig. 4a). As shown in Fig. 4b, after being bubbled with about 15 mL of CO_2 gas, the mixture emitted bright orange light, and no additional change in the emission spectrum was observed. The same phenomenon can be observed by the addition of F^- followed by bubbling with CO_2 gas (Fig. 5). The selectivity of complex **1** to CH_3COO^- for CO_2 is extremely high as there are no apparent changes in phosphorescence intensity upon treatment with CO, N_2, O_2 or argon gas. The CO_2 detection limit of this complex was calculated to be ca. 6.45×10^{-6} M (Fig. S1).

The CO_2/N_2 mixtures with different percentage of CO_2 were bubbled into the detecting solution to check how the PL of **1** responded to variations in the fraction of CO_2 (f_{CO2}). As shown in Fig. S2, PL spectrum of **1** was intensified with increasing percentage of CO_2, which further indicates the high sensitivity of **1**. In addition, the plot shows a characteristic linear signal over the whole concentration range (Fig. S2). From this calibration curve, the amount of CO_2 in the gas mixture can be quantified.

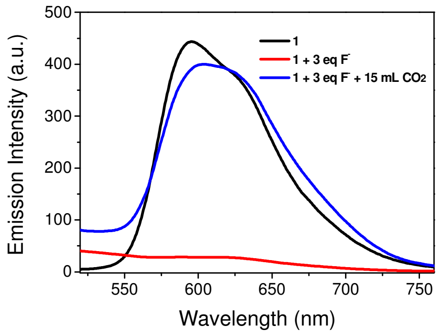


Fig. 5 Changes in the phosphorescence spectra of complex **1** in CH_3CN solution (10 µM) containing F^- (3 equiv.) with 15 mL CO_2 gas.

To check if complex **1** can be reversibly switched by treatment with CH_3COO^- followed by CO_2 bubbling, we conducted experiments with on–off cycling between **1** and **1**-$OOCCH_3$. It was observed that complex **1** was not degraded after five cycles of treatment with CH_3COO^- followed by CO_2 bubbling, indicating the good cyclability of our probe (Fig. 6).

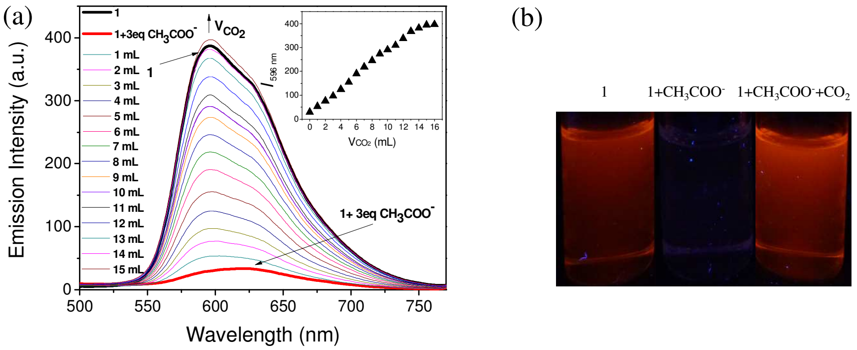


Fig. 4 **(a)** Changes in the phosphorescence spectra of **1** in CH_3CN solution (10 µM) containing CH_3COO^- (3 equiv.) with different volumes of CO_2 gas (0–15 mL). Inset: titration curve of **1** solution (10 µM) containing CH_3COO^- (3 equiv.) with CO_2 gas (0–15 mL). (b) Photos of the emission of **1**, **1**+CH_3COO^-, and **1**+CH_3COO^- with CO_2 bubbling in CH_3CN.

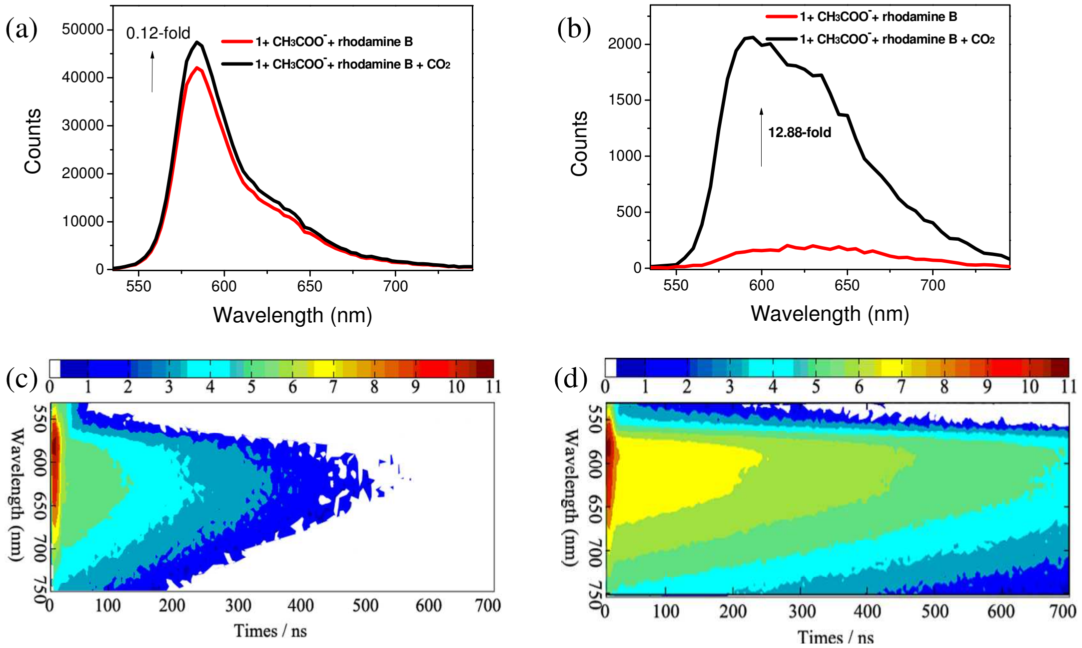


Fig. 7 PL spectra of the mixture of complex **1** solution containing CH_3COO^- and rhodamine B with bubbling of 15 mL CO_2 gas (a) in a steady state (red line, **1** containing CH_3COO^- and rhodamine B; black line, treatment of mixture by bubbling 15 mL CO_2) and (b) at delay time of 100 ns (red line, **1** containing CH_3COO^- and rhodamine B; black line, treatment of the mixture by bubbling 15 mL CO_2) excited at 365 nm. (c) Time-resolved emission spectra of the mixture of complex **1** solution containing CH_3COO^- and rhodamine B. (d) Time-resolved emission spectra of the mixture of complex **1** solution containing CH_3COO^- and rhodamine B with bubbling of 15 mL CO_2 gas. Scale bar in (c) and (d) refers to the emission intensity.

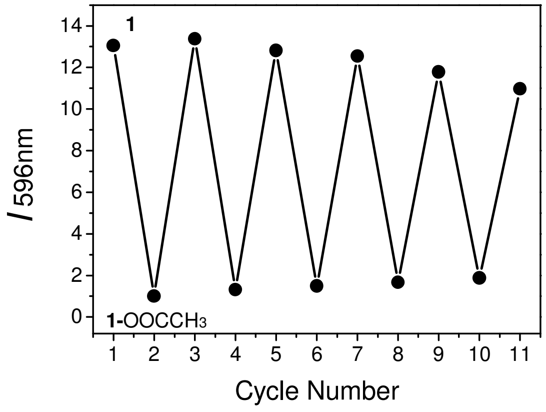


Fig. 6 Reversible phosphorescence intensity (I_{596nm}) change between **1**-$OOCCH_3$ (bottom points) and **1** (top points), which corresponds to the repeated treatment of **1** by the addition of CH_3COO^- followed by CO_2 bubbling.

Time-resolved phosphorescence assay

Time-resolved emission spectra (TRES) provide essential information about luminophore as a function of time. The emission spectra on time-intensity-wavelength contour plot can be set up by recording phosphorescence decay at various wavelength, which can gain insight into chemical surroundings of the luminophore and their decay profile. In particular, one of the most important features of **1** is the long phosphorescence lifetime (τ), which is beneficial for avoiding the interference of short-lived background fluorescence emission. Therefore, complex **1** is envisioned to be useful for the detection of CO_2 gas in the presence of short-lived fluorescence emission by employing the time-resolved PL technique. Here, rhodamine B (RB) with the τ value of 1.67 ns (Fig. S3) was selected as a typical source of short-lived background fluorescence because its broad emission band can overlap with that of **1**. The emission lifetime of **1** in CH_3CN solution was measured to be τ = 227 ns (Fig. S3), which is long enough to carry out the TRPT experiment. The steady-state PL spectrum for the mixture of complex **1** with CH_3COO^- and RB was dominated by the strong emission of RB. The emission maximum at 584 nm was assigned to RB (Fig. 7a, red line and Fig. S4), which made us hardly observe the emission band from **1** with CH_3COO^-. Then, 15 mL CO_2 gas was bubbled into the mixture to allow reaction with complex **1** containing CH_3COO^-. However, very slight change from the steady-state spectrum (Fig. 7a, black line) was observed, which revealed that the detection of probe suffered from severe interference due to the background fluorescence. In sharp contrast, apparent emission variation in the time-gated PL spectrum acquired after 100 ns delay of the mixture was observed with 12.9-fold increase in the phosphorescent emission intensity (Fig. 7b). The time-resolved emission spectra of the mixture are portrayed in Figs. 7c and 7d. As can be seen from Fig. 7c, the emission intensity of the mixture of complex **1** with CH_3COO^- and RB was very strong at 584 nm within 10 ns because of the strong emission of RB, while the signal quickly became weaker after about 20 ns because the phosphorescence of complex **1** was quenched by CH_3COO^-. By bubbling 15 mL CO_2 gas into the mixture, distinct emission intensity enhancement at 596 nm was observed in TRES even after 200 ns due to the recovery of long-lived phosphorescence of complex **1**. This clearly points out that TRES can help us easily distinguish the difference between short-lived fluorescence from RB and long-lived phosphorescence from complex **1** after the time delay between photoexcitation and acquisition of signals. This result highlights the promising application of long-lived phosphorescent probes in time-resolved assays.

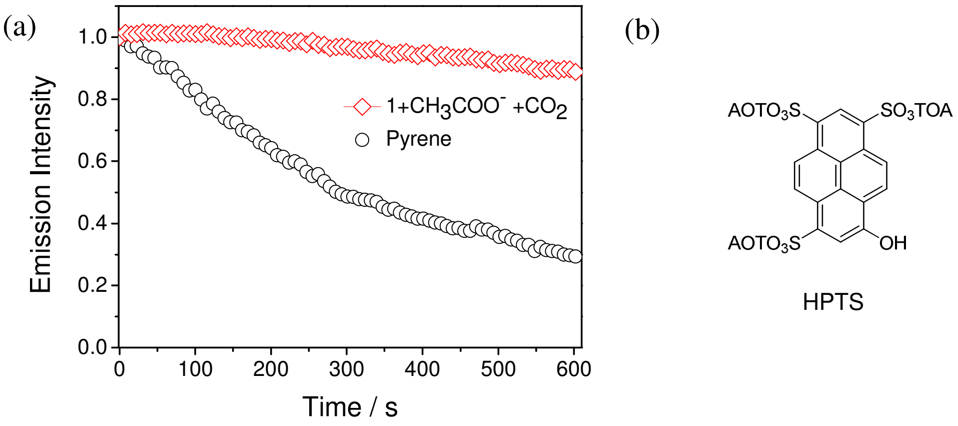


Fig. 8 (a) Emission intensity of a solution of complex **1** containing CH_3COO^- with bubbling of CO_2 gas and pyrene under continuous laser excitation (at 405 nm). (b) Chemical structures of HPTS and pyrene.

Photostability

Considering that continuous excitation often results in the photobleaching of fluorescent sensors and thus high photostability becomes a very important issue for fluorescent sensors. Particularly, in real-life applications, high photostability makes a sensor suitable for long-duration measurements and validating the accuracy of quantitation. Hence, the photobleaching experiments were carried out between the complex **1** and pyrene under the same excitation conditions (405 nm, laser as the excitation source) in CH_3CN solution. The pyrene has a very similar structure as 8-hydroxypyrene-1,3,6-trisulfonate (HPTS) (Fig. 8b), which is the state-of-the-art sensor for CO_2 gas.[4d] As shown in Fig. 8a, after continuous excitation at 405 nm for 600 seconds, which is long enough to perform the identification in practical applications, the emission intensity of complex **1** only decreased to 90% of its initial value. Such high photostablility of complex **1** suggests that it is suitable for long-duration measurements and accurate quantitation. In contrast, the emission intensity of pyrene decreased to 29% of the original value due to photobleaching. This result demonstrates that our phosphorescent sensor shows higher photostability and reduced photobleaching than that of an organic pyrene, which is very important for the "real-world" usage of a sensor.

Detection mechanism of CO_2 gas

In order to confirm the detection mechanism of CO_2 gas by **1**, the interactions of **1** with CH_3COO^- and CO_2 gas were investigated by ^{1}H NMR technique. Fig. 9 shows the change of chemical shifts of **1** upon addition of 3 equiv. of CH_3COO^-. As we can see from the ^{1}H NMR spectra, the resonance signals of protons on the cyclometalated ligands showed little change. In contrast, the partial negative charge on nitrogen, which was generated by the interaction between CH_3COO^- and -NH unit, led to the proton signals on 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline ligand exhibiting an obvious upfield shift. After bubbling the CO_2 gas into a solution of complex **1** containing CH_3COO^-, the chemical shifts of protons on the ancillary ligand were recovered to some extent due to the destruction of hydrogen bond. But, this restoration was not complete, which might be caused by the influence of the presence of acetate, acidic condition and the increase of viscosity after bubbling of CO_2 gas into the solution. As a control study, 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline ligand was used to react with CH_3COO^- and CO_2 gas to further confirm the detection mechanism. Compared with complex **1**, the same variation trend in chemical shifts was observed in DMSO-*d*$_6$ after addition of CH_3COO^- in the ^{1}H NMR spectra. The exposure of L-OOCCH$_3$ to CO_2 gas induced almost complete recovery of the chemical shifts of all protons (Fig. S5). Fig. 10 shows the ^{13}C NMR spectrum of 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline that was first exposed to CH_3COO^- and then bubbled with CO_2 in DMSO-*d*$_6$. The chemical shifts of carbon atoms due to the formation of hydrogen bond can be well recovered by the exposure of 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline to CO_2 gas. In addition, a new characteristic signal at ~160 ppm was observed, which can be assigned to HCO_3^- anion based on the literature results.[16] These results are consistent with the observed photoluminescence changes and support the proposal above that hydrogen bond is formed upon CH_3COO^- treatment which is followed by destruction of the bond via the interaction with CO_2.

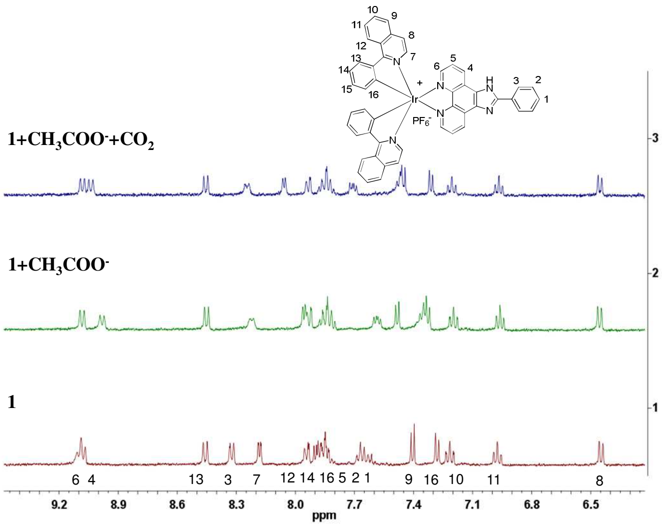


Fig. 9 Partial ^{1}H NMR spectra of **1, 1**+CH_3COO^- and **1**+CH_3COO^- treated with CO_2 in CD_3CN-*d*$_3$**.**

As a further control study, 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline ligand was used to prepare the corresponding *N*-dithiolate derivative by interaction with carbon disulfide, which is an isoelectronic analogue of CO_2. The *N*-dithiolate derivative was prepared by using 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline ligand which was treated with KOH for 4 h followed by reaction with CS_2 in DMSO solution (Fig. S6). The ^{13}C NMR spectroscopic technique shows that a new carbon signal at ~216 ppm appeared (Fig. S6), indicating that the stable *N*-dithiolate adduct was formed. Collectively, these results provide support for the conclusions that complex **1** reacted with CO_2 gas to form the intermediate complex **1b**, and then the original complex **1** was recovered after the decomposition of **1b**.

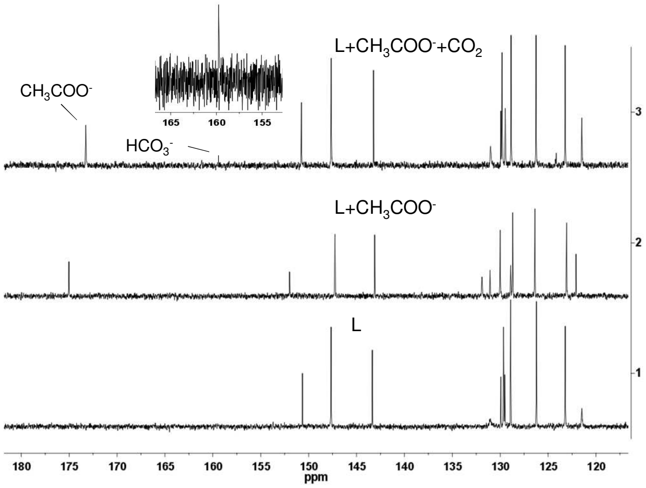


Fig. 10 Partial ^{13}C NMR spectra of L**,** L+CH_3COO^- and L+CH_3COO^- treated with CO_2 in DMSO-*d*$_6$.

Conclusions

In summary, we have developed a novel phosphorescent probe based on an iridium(III) complex with 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline for CO_2 detection. After bubbling CO_2 into the detecting solution, the quenched phosphorescence by the addition of CH_3COO^- can be recovered. Photobleaching experiment demonstrates that this phosphorescent CO_2 probe shows higher photostability than some of the reported organic probes. More importantly, the time-resolved PL experiment demonstrates that **1** can be used to detect CO_2 in the presence of strong background fluorescence, which improves the sensitivity and signal-to-noise ratio of the sensor in complicated media. Our on-going work is focused on the development of novel luminescent sensors to detect CO_2 gas in living cells.

Experimental

General

Commercially available chemical reagents were used without further purification. The solvents were carefully dried and distilled from appropriate drying agents prior to use. NMR spectra were taken on a Bruker Ultrashield 400 MHz FT-NMR spectrometer. Mass spectra were obtained on a Bruker Autoflex matrix-assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS). UV-vis absorption spectra were recorded using an HP-8453 spectrophotometer. Photoluminescence spectra were measured on an Edinburgh LFS920 fluorescence spectrophotometer. Time-resolved emission spectra (TRES) and emission lifetimes were obtained through a time-correlated single photon counting (TCSPC) technique using an Edinburgh FL 920 instrument with a laser source (365 nm) as the excitation source. Time-gated acquisition of photoluminescence spectra were carried out by employing the TRES technique.

Synthesis of complex 1

The ligand 1-phenylisoquinoline was synthesized according to our previous report.[14b] The cyclometalated iridium(III) chloro-bridged dimer $[Ir(piq)_2Cl]_2$ was prepared according to the literature method.[17] A solution of $[Ir(piq)_2Cl]_2$ (0.079 mmol) and 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline (0.158 mmol) in CH_2Cl_2/MeOH (15 mL, 2:1 v/v) was heated to reflux. After 4 h, the red solution was cooled to room temperature, and then a 10-fold excess of potassium hexafluorophosphate was added. The suspension was stirred for 1 h and then was filtered to remove the insoluble inorganic salts. The solution was evaporated to dryness under reduced pressure. The crude product was applied to a silica gel column and eluted with CH_2Cl_2/acetone (10:1, v/v) to afford a red solid in 69% yield. ^{1}H NMR (400 MHz, CD_3CN), δ (ppm): 9.12 (t, 4H, J = 17.2 Hz, phenanthroline), 8.47 (d, 2H, J = 8.0 Hz. isoquinoline), 8.33 (d, 2H, J = 7.2 Hz, phenyl), 8.19 (d, 2H, J = 4.0 Hz, isoquinoline), 7.95 (d, 2H, J = 7.2 Hz, isoquinoline), 7.83–7.91 (m, 6H, isoquinoline), 7.69 (t, 3H, J = 12.0 Hz, phenyl), 7.41 (d, 2H, J = 4.0 Hz, isoquinoline), 7.29 (d, 2H, J = 4.0 Hz, isoquinoline), 7.24 (t, 2H, J = 14.0 Hz, isoquinoline), 6.99 (t, 2H, J = 16.0 Hz, isoquinoline), 6.46 (d, 2H, J = 8.0 Hz, isoquinoline). ^{13}C NMR (100 MHz, CD_3CN), δ (ppm): 168.6, 153.7, 153.0, 149.1, 145.8, 144.6, 141.0, 137.1, 132.2, 132.1, 131.9, 130.8, 130.5, 129.4, 129.2, 128.9, 127.5, 126.8, 126.6, 126.2, 122.3, 121.8 (aromatic). MALDI-TOF MS (*m/z*): 899.32 $(M - PF_6)^+$. Anal. calcd for $C_{49}H_{33}N_6PF_6Ir$: C, 56.43; H, 3.19; N, 8.06. Found: C, 56.65; H, 3.44; N, 7.90%.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of PL and NMR spectra]. See DOI: 10.1039/b000000x/

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Table of Content

A charged iridophosphor for time-resolved luminescent CO_2 gas identification

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A CO_2 gas probe based on a long-lived phosphorescent iridium(III) complex with 2-phenylimidazo-[4,5-*f*][1,10]phenanthroline ligand has been developed. Its quenched phosphorescence by the addition of CH_3COO^- can be recovered by bubbling CO_2 into the detecting solution. This probe exhibits high photostability. Time-resolved photoluminescence experiment has been performed for CO_2 detection, which can effectively remove the background fluorescence and improve the signal-to-noise ratio in complicated media.