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High Sensitive Detection of Carbon Dioxide by Pyrimido[1,2-a]benzimidazole derivative: Combining Experimental and Theoretical Studies

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In present paper, a "light-up" chemsensor with a highly specificity for carbon dioxide detection using Pyrimido[1,2-a]benzimidazole derivative (P1H) in liquid media has been developed. The results show that the P1H reacts with carbon dioxide activated by basic ion to form carboxylic acid compound (P1-COOH). These results provide a possible method for carboxylation reactions of P1H using carbon dioxide based on vinyl carbanion as well. The complete reaction mechanism cycle was described by DFT calculation as well.

1. Introduction

With the deterioration of global warming and its secondary induced disasters, researches on greenhouse gases chemistry have caught urgent attention.[1] The capture and utilization of these gases have been greatly promoted in both laboratorial and industrial application for the last decades.[2-3] Among those researches, the detection, capture and conversion of the abundant, easily available and renewable carbon dioxide as green C1 feedstock have been considered as a sustainable strategy, seeking to balance the industrial development and environmental protection.[4-5]

Because of the inherent kinetic stability, carbon dioxide hardly reacts directly with the organic reactants without being activated by potent catalyst systems.[6] It is well known that the catalyst systems like metal-containing complexes, nitrogen-base (e.g. frustrated amidine and guanidines) and task-specific ionic liquids can activate the carbon dioxide efficiently.[7] Among those catalysts, some special nitrogen-based basic precursors including N-heterocyclic carbenes (NHCs)[8], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[9] and 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD)[10-11] are able to active and react with carbon dioxide to form zwitterionic adducts under CO_2 atmosphere. Unfortunately, these base-CO_2 adducts have been proved to be extremely unstable and unobtainable in the presence of ambient moisture. Strict operation condition, such as the water-free and oxygen-free conditions, is necessary for these reactions [12]. For example, direct carboxylation of C-H bond with carbon dioxide is an important reaction in organic synthesis via using CO_2 as the electrophile and other organometallic reagents as nucleophile.[12] Typically, nucleophile such as organolithium, organozinc and organic manganese are universally taken as precursors, and this method is always limited by low catalytic performances, harsh reaction conditions, and restricted substrate scope.[13]

Photosynthesis in nature is a process utilized by plants and other organisms to convert light energy to chemical energy via reaction between carbon dioxide and water in mild condition [14]. The key step of photosynthesis is that RuBP enzyme reacts with carbon dioxide which leads to the atmospheric carbon dioxide fixation at its C2 center in the carboxylation reactions(figure 1).[15] The reaction proceeds through several elemental steps, including enolization and deprotonation, yielding the 2,3-enediolate, a carbanion that contains double phosphate ester and is the substrate of carbon dioxide addition(figure 1).[16] These researches indicate that the carbanion hold an efficient capture and acivation for carbon dioxide, and transfer carbon dioxide to carboxylic acid compound.
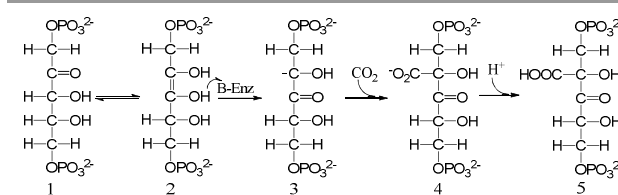

Figure 1. Suggested multistep mechanism for the carboxylation reaction catalyzed by rubiso.

It has been said that nature is the best teacher. As a consequence, discovering a biomimetic precursor, such as carbanion, which is able to directly and blandly detection, capture and convert unactivated CO_2 to generate ambient stable chemicals rather than zwitterionic adducts, was intensively desired in mild reaction condition.[16] Herein,

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taking inspiration from nature, we report an high effective method for sensitive detection of carbon dioxide using carbanion in mild condition. The results indicate that the P1H can react with carbon dioxide rapidly and sensitively in the presence of excess F^- ion to form the carboxylation product. The reaction mechanism was confirmed by its spectroscopic analysis. Furthermore, theoretical calculations provided detailed explanations to the phenomena.

2. Experimental

2.1 Chemicals and reagents

All commercially available reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. Absorption spectrometry was performed using Gold S54T spectrophotometer of Lengguang Company, and fluorescence spectrometry was performed using F-7000 FL Spectrophotometer of Hitachi. Melting points were determined in open capillaries. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AVANCE 500 spectrometer with use of the deuterated solvoent as the lock and TMS as an internal reference. Elemental analysis was performed on Elementar Vario vario EL III. Mass spectra were acquired using a triple quadrupole mass spectrometer (6430 QqQLC/MS system; Agilent Technologies, USA) equipped with an orthogonal ESI source.The crystals for X-ray diffraction analyses were grown in dichloromethane by adding n-hexane to slow diffuse. The X-ray diffraction experiment was carried out using Bruker SMART APEX-II Single-crystal diffractometer. Tetrabutylammonium salts (F^-, AcO^-, Cl^-, Br^- and I^-) were all >98% pure and the solutions used in titrations were prepared in fresh dry acetonitrile (CH_3CN).
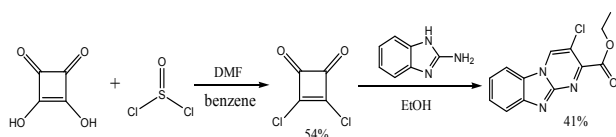
Scheme S1. The synthesis of compound **P1H**

2.2 Synthesis of 3,4-Dichlorocyclobutene-1,2-dione

A mixture of squaric acid (1.14 g, 10 mmol), thionyl dichloride (1.8 ml, 20 mmol) and DMF (200ul) in dry benzene (10 ml) was refluxed for 6 h at 60℃. The solvent was evaporated in vacuo and hexane (20 ml) was added, then the soluble products were separated from gummy precipitates. Concentrating and cooling to give yellow crystalline which was used in the next step without further purification (0.82 g, 5.4mmol), yield 54%.

2.3 Synthesis of P1H

A anhydrous ethanol (30ml) solution of 2-aminobenzimidazole (798mg, 6mmol) was added into fresh 3,4-Dichlorocyclobutene-1,2-dione (750mg, 5mmol) under vigorous stirring, and the mixture was stirred at room temperature for 20min. Then the solvent was removed in vacuo and the residue purified on a column (1% methanol in chloroform as eluent) to give P1H in 41% yield (563mg, 2.08mmol) M.P. 252-253℃. ^{1}H NMR (400 MHz, DMSO-d_6) ppm 10.08 (s, 1H), 8.39 (d, J = 8.22 Hz, 1H), 7.94 (d, J = 8.26 Hz, 1H), 7.70-7.46 (m, 2H), 4.49 (q, J = 7.11 Hz, 2H), 1.46-1.32 (m, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6), 163.35(1C), 152.60(1C), 147.44(1C), 145.28(1C), 137.23(1C), 127.60(1C), 127.38(1C), 123.23(1C), 120.24(1C), 113.93(1C), 110.99(1C), 63.15(1C), 14.45(1C). Anal. Calcd for P1H: C, 56.64; H, 3.66; N, 15.24. Found: C, 56.60; H, 3.70; N, 15.21.

2.4 Computational detailed

All the theoretical calculations were performed with Gaussian 09 suite programs.[17] Geometrical optimization, including transition structure searches were performed by the hybrid density functional B3LYP methods[18,19] and standard 6–311G(d,p) basis set. All reactants and intermediate had no imaginary frequency, and the transition states were ascertained by vibrational analysis with only one imaginary frequency mode. The zero-point energy was calculated by using the vibrational frequencies. In the case of transition states, the vibration was associated with a movement in the direction of the reaction coordinate. Intrinsic reaction coordinate calculations, at the same level of theory, were performed to ensure that the transition states led to the expected reactants and products. The solvent effects have been considered using a relatively simple self-consistent reaction field (SCRF) method, based on the polarizable continuum model (PCM).[20] The solvent used in this calculation is DMF. The values of the relative energies with zero-point energy correction (ΔE_0) were calculated and used on the basis of the total energies of the stationary points.

3. Results and discussion

At the beginning, a yellow solid P1H with luminescence was synthesized inadvertently by adding an EtOH solution of 2-aminobenzimidazole into fresh squaric acid dichloride under vigorous stirring (Scheme 1). The X-ray crystal structure of P1H is depicted in Figure 2. The whole fused heteroaromatic system is nearly planar except ethoxycarbonyl. The dihedral angle between the pyrimidine ring and ethoxycarbonyl arm is 76.63°. Unexpectedly, the chemical shifts（δ）of the H atom(C8-H) of pyrimidine ring is 10.08 ppm and 9.72ppm in DMSO-d6 and CD$_3$CN-d3, which mean that C8-H possesses relative acidity and easily forms a vinyl carbanion intermediate in the presence of base (Figure S1). This special feature emboldened us to build the hypothesis that carbon dioxide conversion can be implemented bases on P1H. This process is similar to imidazolium-based precursors of NHCs.
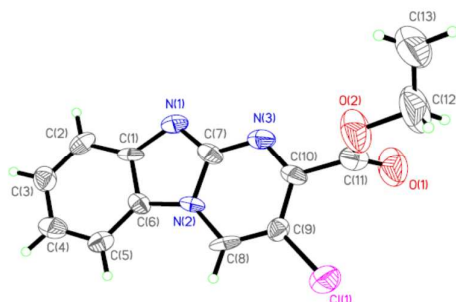
Figure 2. ORTEP diagram of compound P1H.

In order to test this hypothesis, we first investigated the possibilities of the deprotonation of C8-H with different basic anion using Uv-vis spectrum in CH_3CN. As shown in Figure 3, the absorption intensity of receptor P1H undergoes a significant increasing (from 0.455 to 0.937) and an obvious red shift (from 345 to 390nm) when adding excess basic F^- ion (as the tetrabutylammonium salt, TBAF). And the pale-yellow solution turns into an olivine color. Further examination revealed that P1H exhibited a highly selectivity for the fluoride anion over other anions (Figure S2).
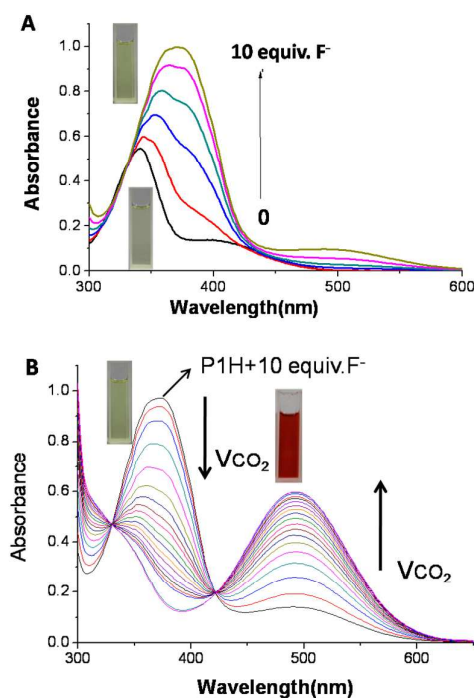

Figure 3. UV–vis spectra taken over the course of titration of receptor P1H (50μM) with [Bu₄N]F in CH_3CN and then bubbling with different volumes of CO_2.

Whereafter, CO_2 gas was injected into the CH_3CN solution above, a slight downdrift was observed at 390nm and the peak appeared at 510nm. It increased with the injection of carbon dioxide and quickly got saturated. The color of the solution was observed to be changed from olivine to red. This means that P1H allows for the sensing of carbon dioxide with high sensitivity. In fact, except for Yoon's group [21], there are few reports for the optical sensor for carbon dioxide.

For luminescence, the original emission band at 550nm (orange-yellow) of P1H was rapidly quenched in CH_3CN with the addition of F^- ion (10 equiv). Consistent with the UV-vis titration results, the emissive intensity of mixtures was dramatically enhanced and broadened with the injection of carbon dioxide gas (Figure 4). The mixtures presented a distinctly orange emission at 520nm. In the same way, addition of poorly basic anion AcO^-, Cl^-, Br^- and I^-, as expected, hardly induced any considerable variations in emission spectroscopies of P1H in CH_3CN solution (Figure S3).

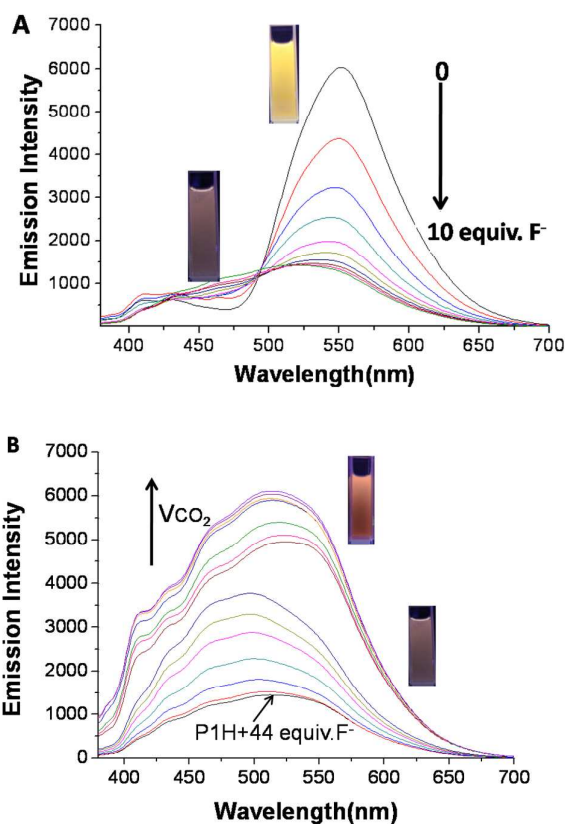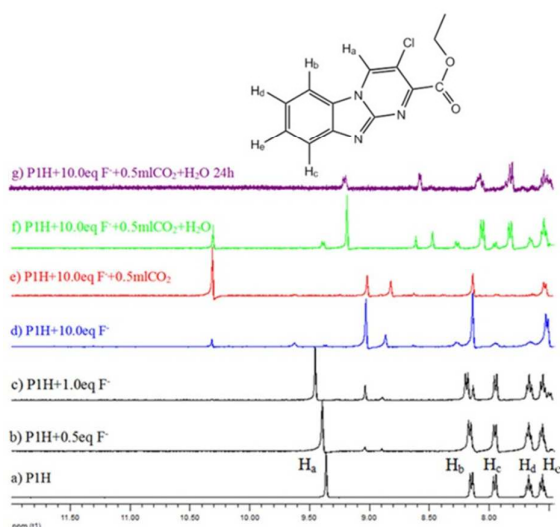**Figure 4**. Emission spectra taken upon addition of [Bu₄N]F to P1H (50.0 μM) in CH_3CN and then bubbling with different volumes of CO_2 with excitation at 360 nm.

Figure 5. ^{1}H NMR taken over the course of titration of receptor P1H (4.5mM) with [Bu$_4$N]F followed by CO$_2$ and subsequently H$_2$O in CD$_3$CN-d$_3$.

Based on these spectroscopic data, we confirmed that the P1H possess a strongly interaction with CO$_2$ gas in the presence of excess F$^-$ ion. Then, for a thorough insight into the underlying mechanism of the "capturing" process, ^{1}H NMR studies were carried out. Figure 5 displays the family of spectra recorded over the course of the ^{1}H NMR titration of P1H (4.5mM) with [Bu$_4$N]F followed by CO$_2$ and subsequently H$_2$O in CD$_3$CN-d$_3$. Both Ha and Hb signals are shifted downfield upon a small amount of F$^-$ ion addition (<1.0 equiv), these deshielding of the corresponding resonances (both Ha and Hb) can be ascribed to the strong polarization induced by the H-bonded fluoride anion as [P1-H···F]$^-$ formation. With addition of 10 times F$^-$ ion, the sharp Ha signal disappeared completely (the blue line, Figure 5d), which means excess F$^-$ ion will promote deprotonation of the H-band complexes, according to the equilibrium [P1H···F]$^-$ + F$^-$ ⇌ [P1]$^-$ + HF2$^-$. Results of ^{1}H NMR titrations were closely consistent with those others obtained from UV-vis titration experiments.

To our surprise, a sharp H signal appeared at 10.31 ppm after bubbling with only 0.5ml CO$_2$ gas into the CD$_3$CN-d$_3$ solution of deprotonated P1H (the red line, Figure 5e). This new signal suggests that the carboxy group may be formed in this process. As such, a reasonable speculation is that the stable CO$_2$ has been captured and converted into carboxylic acid (P1-COOH). Further support for the above assignment was obtained from infrared spectral analyses of P1H in the presence of excess fluoride ions and then exposure to CO$_2$ (Figure S4). Figure S4 displays a peak at approximately 1710 cm^{-1} (the blue) which can be attributed to the specific carbonyl C=O stretch of R-COOH. Additionally, mass spectrum analysis also was used to prove the forming of P1-COOH as final product (Figure S5). From figure S5, the molecular ion peak (m/z) in mass spectrum (318.5) can be assigned to P1-COOH compound. Based on above analyses, P1-COOH was formed via carboxylation of P1H with CO$_2$ in the presence of excess fluoride ions.

Curiously, one drop deionized H$_2$O was added in above ^{1}H NMR titration solution for testing the moisture-sensitive of the P1-COOH. The Figure 5f indicated that the P1-COOH was not very stable in the presence of ambient moisture, and slowly decomposed to afford the initial P1H after 24 hours (Figure 5g and confirmed by TLC). This process is similar to decarboxylation of orotidine 5′-monophosphate to give uridine 5′-monophosphate by decarboxylase in organisms [22]. In practice, because of unstability, we failed to obtain pure P1-COOH adducts by means of fresh column chromatography.
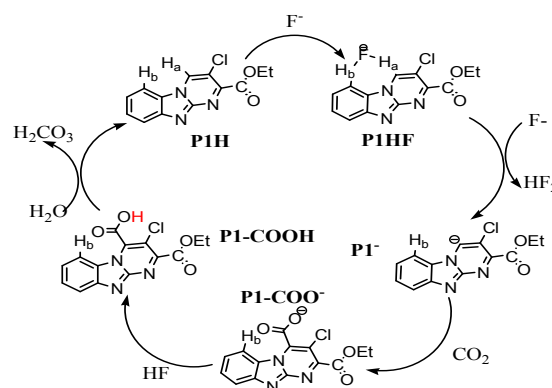
Scheme 2. proposed mechanism of the carboxylation via CO$_2$ gas for the P1H in the presence of [Bu$_4$N]F.

To the best of our knowledge, a tentative mechanism for P1H capturing CO$_2$ with the addition of excess F$^-$ ions in CH$_3$CN was detailedly illustrated in Scheme 1. Firstly, the adjacent Ha and Hb of P1H are able to coordinate with the additional F$^-$ ion by virtue of two strong hydrogen bonds; with addition of excess F$^-$ ions, the activated C-Ha bond will be fractured to afford an vinyl carbanion intermediate [P1]$^-$ and acid molecular HF. Finally, the nucleophilic [P1]$^-$ will immediately attack CO$_2$ at the carbonyl to produce the carboxylate P1-COO$^-$, which is easily acidized in the case of HF. In order to give an explanation for this reaction mechanism, density functional theory (DFT) calculation was carried out.
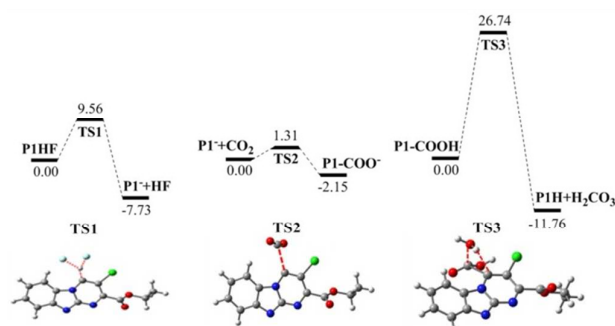
Figure 6. The reaction energy profile of carboxylation via CO$_2$ gas for the P1H in the presence of [Bu$_4$N]F (unit for energy: kcal mol^{-1}).

The first step is the deprotonation from P1HF by F$^-$ ion to form [P1]$^-$ anion. The energy barrier for this process is 9.56 kcal mol^{-1}. The next step is the addition of [P1]$^-$ ion to carbon dioxide to

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afford the carboxylate P1-COO⁻. The step holds an energy barrier of 1.31 kcal mol⁻¹ and exothermic heating of 2.15 kcal mol⁻¹. The P1-COO⁻ can easily accept proton from HF with a barrierless process to form P1-COOH. In fact, the P1-COOH is not stable in air at room temperature and able to react with water by decarboxylic reaction and give P1H. The energy barrier and reaction heat of this reaction is 26.74 and -11.76 kcal mol⁻¹. The high energy barrier shows that this reaction only can carry out very slowly.

4. Conclusions

In summary, we have developed a biomimetic "light-up" chemsensor with a highly specificity for carbon dioxide detection using Pyrimido[1,2-a]benzimidazole derivative (P1H) in liquid media. On the basis of spectroscopic and theoretical analyses, Pyrimido [1,2-a]benzimidazole tends to capture carbon dioxide to afford carboxylic acid in the presence of excess F⁻ ion in CH_3CN. By combining experimental and computational findings, the method also provides a possible method for carboxylation reactions of P1H using carbon dioxide based on vinyl carbanion. It will pave a practical way to accomplish high sensitive detection of carbon dioxide.

Acknowledgements

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