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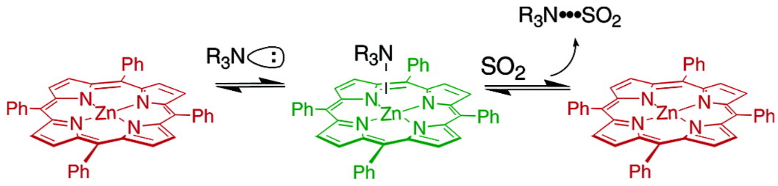

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Revisiting Noncovalent SO_2−Amine Chemistry: An Indicator−Displacement Assay for Colorimetric Detection of SO_2

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Sulfur dioxide, or SO_2, is an environmentally important gas.[1] It is formed upon burning sulfur-containing fuels, such as coal and oil. SO_2 then dissolves in water vapor to form acid and interacts with other gases and particles in the air to generate sulfates and other harmful products. SO_2 contributes to respiratory illnesses, the formation of acid rain, and atmospheric particles that can be transported over long distances and deposited far from the point of origin. SO_2 is colorless, and the development of optical sensors for this gas is ongoing. Most of these sensors are either based on pH indicators or involve chemical reaction of SO_2 and derived from it (bi)sulfite, with various dyes.[2] We present here a *supramolecular approach* for potential detection of SO_2. It includes a noncovalent indicator−displacement assay and is based on the old but rather forgotten donor−acceptor chemistry between SO_2 and amines. In the proposed sensing scheme, amines initially form colored coordination complexes with a metalloporphyrin (Figures 1 and 2A). Once introduced, SO_2 competes with the porphyrin for the amine, which eventually leads to the release of the porphyrin and changes in the solution color/absorption. The approach is simple and reliable. Varieties of amines and metalloporphyrins are available, and no covalent linkages between them are required. Accordingly, opportunities to tune and modify the system are very broad. Our results may also regenerate interest in the noncovalent chemistry of SO_2 and other important gases.[3]

A series of amines were tested (Table 1). In a typical experiment, an amine was added to a solution of Zn−tetraphenylporphyrin **1** in $CHCl_3$, and the absorbance changes were recorded (Figure 2). As expected, the solution changed from red to dark green; a bathochromic shift of $\Delta\lambda \sim 10$ nm was observed for the Soret band, indicating the formation of the corresponding **1**•amine complex. When SO_2 gas was briefly bubbled through the solution, the red color was basically restored; the Soret band returned to its position for the free porphyrin (Figure 2). The **1**•amine complex dissociated, and the SO_2•amine adduct was formed. Porphyrin **1** thus served as an indirect colorimetric indicator for SO_2. Under the same conditions, CO, CO_2, N_2O, and H_2O did not displace porphyrin **1**; no visible spectral changes were detected (see Supporting Information). More aggressive NO_2/N_2O_4 caused significant hypochromic changes in the absorbance, compared to SO_2, which is due to the chemical reaction with **1**.[4] These gases are typically present together with SO_2 in industrial exhausts.

That SO_2 and secondary or tertiary amines form stable, 1:1 charge-transfer complexes has been known for decades.[5−8] The structure of such complexes has been a subject of crystallographic[6] and computational[7] papers. Several complexes have been studied in solution.[8] For this project, we first revisited spectroscopic features of SO_2•amine complexes in apolar solution. Stepwise addition of piperidine or pyrrolidine to a solution of SO_2 in $CHCl_3$ at room temperature resulted in disappearance of the free SO_2 absorption[8] at $\lambda_{max} \sim 288$ nm (Figure 3).

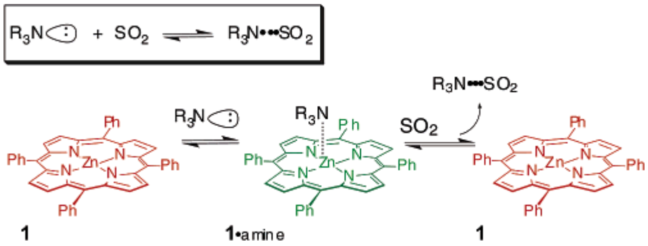

Figure 1. An indicator−displacement assay for the detection of SO_2. Porphyrin **1** is initially coordinated to amines and then displaced by SO_2.

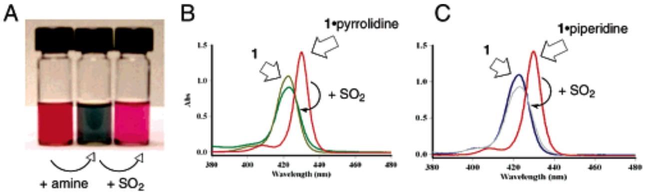

Figure 2. (A) Visual detection of SO_2 with porphyrin **1** ($CHCl_3$ solution, left vial) upon addition of pyrrolidine and then SO_2. (B and C) Absorbance spectra of porphyrin **1** and complexes **1**•pyrrolidine (B) and **1**•piperidine (C) in $CHCl_3$ at 23 ± 1 °C ([**1**] $\sim 2 \times 10^{-6}$ M, [amine] $\sim 10^{-3}$ M). Bubbling SO_2 results in instant hypsochromic shift of the Soret band, which returns to the initial $\lambda_{max} = 421$ nm for free porphyrin **1**.

Table 1. Association Constants for Complexes between Porphyrin **1** and Amines[a] and for Amines and SO_2[b] and [SO_2]/Amine Ratios, at which ~50% of Porphyrin **1** is Displaced[c,d]

amine	K_{assoc}(**1**•amine) M^{-1}	K_{assoc}(SO_2•amine) M^{-1}	[SO_2]/amine
pyrrolidine	1.8×10^4	2.0×10^4	2
piperidine	1.3×10^4	3.0×10^4	1
morpholine	1.1×10^4	1.0×10^3	30
diethylamine	7.0×10^2	2.2×10^4	1
quinuclidine	7.0×10^4	1.2×10^5	2

[a] Direct titration. [b] Displacement assay. [c] In $CHCl_3$ at 23 ± 1 °C. [d] All experiments were performed at least in duplicate showing good reproducibility.

Absorbance titration data supported the 1:1 stoichiometry between amine and SO_2, and the association constant values were in the range of 10^4 M^{-1}. The complexation process was also followed by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$. In particular, upon addition of SO_2, the ^1H NMR signals of the amine α-CH protons notably shifted downfield with $\Delta\delta \sim 0.2−0.3$ ppm. The SO_2•amine complexes were also obtained on a preparative scale by adding the corresponding amine to liquid SO_2 at −30 °C; they were characterized by UV−vis and NMR spectroscopy.

Amines strongly interact with metalloporphyrins. Used in these studies, Zn−porphyrin **1** forms stable **1**•amine complexes in $CHCl_3$.[9] The amine nitrogen is coordinated to the metal center. Stepwise addition of an amine to a solution of porphyrin **1** resulted in a bathochromic shift of $\Delta\lambda \sim 10$ nm of the Soret band. For

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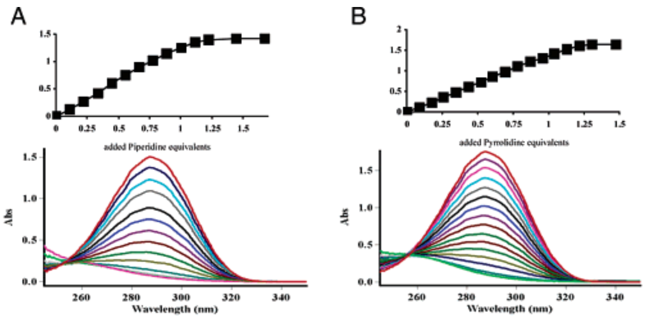

Figure 3. Titrations of SO_2 ($\lambda_{max} \sim 288$ nm) with piperidine (A) and pyrrolidine (B) in $CHCl_3$ at 23 ± 1 °C ($[SO_2] = 4 \times 10^{-3}$ M, $[\text{amine}] = 4 \times 10^{-4} - 7 \times 10^{-3}$ M).

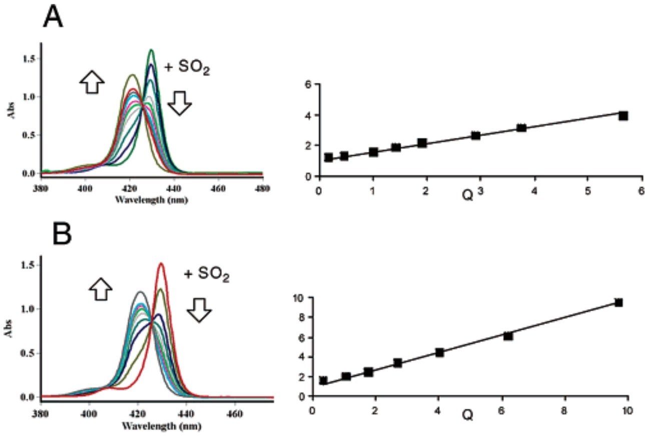

Figure 4. Absorbance spectra of complex **1**•quinuclidine (A) and **1**•pyrrolidine (B) upon addition of SO_2 in $CHCl_3$ at 23 ± 1 °C. Determination of the SO_2•amine association constants was performed by a competitive binding algorithm; see refs 10 and 11.

concentrated solutions, clear color changes were observed from purple−red to dark green. From the UV−vis experiments, the K_{assoc} values ranging from 7.0×10^2 (diethylamine) to 7.0×10^4 M^{-1} (quinuclidine) were obtained, which are in agreement with the literature (Table 1).[9]

In the indicator−displacement assay,[10] $\sim 10^2 - 10^3$-fold excess of amines versus **1** was used to ensure the quantitative formation of **1**•amine complexes at UV−vis concentrations (2×10^{-6} M). Solution of SO_2 in $CHCl_3$ was added stepwise to the solutions of **1** and the corresponding amine in $CHCl_3$, and the Soret absorbance was monitored. Hypsochromic shifts of the Soret band were observed, indicating the liberation of **1** and thus the formation of SO_2•amine adducts (Figure 4). The isosbestic points imply that clean transformation from the **1**•amine complexes to free porphyrin **1** takes place.

Using the algorithm developed by Anslyn and co-workers,[10,11] the K_{assoc} constants for SO_2•amine complexes were determined from the indicator−displacement titrations (Table 1). These are comparable to those obtained by direct titration experiments between SO_2 and the amines. For example, the K_{assoc} values for pyrrolidine and piperidine, obtained by direct titration, are 1.3×10^4 and 3.3×10^4 M^{-1}, respectively.

To estimate the sensitivity, the $[SO_2]$/amine ratios were determined in the displacement experiments, at which the concentrations of **1**•amine complexes and free **1** are roughly equal (Table 1). When binding constants between amines and porphyrin **1** are smaller than or comparable to those between amines and SO_2, the $[SO_2]$/amine ratios are small. For example, the K_{assoc} values for **1**•diethylamine and SO_2•diethylamine are 7.0×10^2 and 2.2×10^4 M^{-1}, respectively, and the $[SO_2]$/diethylamine ratio is 1. Morpholine is less basic than other tested amines ($pK_a = 8.3$ compared to $pK_a \geq 11$ for others) and, as a consequence, binds to SO_2 weaker than to the porphyrin. Accordingly, 30 equiv of SO_2 is required to displace 50% of porphyrin **1**. Considering that $10^2 - 10^3$-fold excess of amines versus **1** is necessary in the displacement assays, these calculations set the SO_2 detection limit at a low millimolar range and also can be used in the design of more sensitive systems.[12]

In conclusion, it is now possible to detect SO_2 utilizing its noncovalent chemistry with amines. The indicator−displacement approach once again proved to be useful. While there are obvious UV changes simply upon addition of SO_2 to an amine, incorporating the porphyrin in the assay brings the response into the visible region of the spectrum. The proposed system discriminates between SO_2 and such exhaust gases as CO_X, NO_X, and moisture. For this preliminary report, commercially available amines and a porphyrin were used; however, synthetic modification of both is possible to achieve more colorful responses. It would also be possible to modify the system for SO_2 detection in aqueous solutions and at the gas−solid interface.[13] We are working toward these goals and further testing the system selectivity with respect to other gases and volatiles.

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Supporting Information Available: Experimental procedures and spectra. This material is available free of charge via Internet at http://pubs.acs.org.

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