2-(4-Pyridyl)imino nitroxide-tetraphenylporphyrin zinc(II): A chemosensing ensemble for nicotine

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2-(4-Pyridyl)imino nitroxide and tetraphenylporphyrin zinc(II) formed a stable complex by noncovalent bonding in a nonpolar solution. Nicotine displaced 2-(4-pyridyl)imino nitroxide when it was added to a solution of 2-(4-pyridyl)imino nitroxide-tetraphenylporphyrin zinc(II). The fluorescence intensity of tetraphenylporphyrin zinc(II) was altered by sequentially addition of 2-(4-pyridyl)imino nitroxide and nicotine. This was used to develop a new method for detection of nicotine.

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In recent years, many chemosensing ensembles [1–5] have been reported for the detection of various analytes. In a typical chemosensing ensemble, an indicator first weakly binds to a host through non-covalent and hydrogen bonds. Then, the analyte of interest is added to the system and displaces the indicator from the host, which in turn induces a change in the spectrum of the system. Because the indicator and host are non-covalently bonded, chemosensing ensembles offer many advantages over traditional chemosensors, in which the receptor and reporter units are covalently linked. Using this chemosensing concept, new methods have been developed to detect analytes such as oxalate [6], amino acids [7–9], caffeine [10], cocaine [11], phosphate [12,13], chloride [14], carboxylated and phosphorylated sugars [15], glucose oxidase [16], and chiral carboxylic acids [17].

Nicotine is present in tobacco leaves and cigarette smoke, and has been used in pharmaceutical and synthetic applications and as an insecticide. Detection of nicotine is of particular importance in the tobacco industry and in toxicology [18–20]. Common nicotine detection methods include gas chromatography [21], liquid chromatography [22], and

capillary electrophoresis [23]. Herein, we report a new method for detection of nicotine based on 2-(4-pyridyl)imino nitroxide-tetraphenylporphyrin zinc(II).

The design rationale for the chemosensing ensemble is illustrated in Scheme 1. Porphyrin zinc(II) is highly fluorescent [24], and can easily form complexes with pyridine derivatives. For example, Yamauchi and co-worker [25,26] described formation of a tetraphenylporphyrin zinc(II) complex with 2-(4-pyridyl)nitronyl nitroxide. However, they only studied the spin properties of the excited state of this complex. In an earlier report [27], we detailed the fluorescence quenching caused by nitronyl nitroxide and imino nitroxide. Binding of either nitronyl or imino nitroxide to porphyrin zinc(II) is expected to quench its fluorescence. The absorption spectrum of 2-(4-pyridyl)nitronyl nitroxide shows peaks between 320–400 nm, and overlaps with the fluorescence spectrum of tetraphenylporphyrin zinc(II) (TPPZn). Accordingly, energy transfer will also contribute to quenching of the fluorescence of tetraphenylporphyrin zinc(II). For this reason, 2-(4-pyridyl)imino nitroxide (4-PIN), rather than 2-(4-pyridyl)nitronyl nitroxide, was chosen for the ensemble with TPPZn. Addition of a pyridine derivative to a mixed solution of 4-PIN and TPPZn will

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Scheme 1 Fluorescence detection of nicotine.

displace 4-PIN from TPPZn, and the fluorescence of the ensemble will increase. The 4-PIN and TPPZn ensemble, in which 4-PIN is the host and TPPZn is the indicator, can be used for detection of nicotine.

The inset in Figure 1 shows the absorption spectra of TPPZn in the presence of different amounts of 4-PIN in CH_2Cl_2 ¹⁾. As the amount of 4-PIN increased, the two Q-bands of TPPZn gradually red-shifted from 547 to 560 nm and from 586 to 600 nm. The association constant for 4-PIN and TPPZn in CH_2Cl_2 was calculated at 4714 L/mol using the Benesi-Hildebrand equation and data from the UV-Vis spectroscopic titration [28]. The absorption spectra of TPPZn in the presence of different amounts of 4-PIN were also measured in solvents of different polarities. In non-polar solvents, such as toluene, the Q-bands red-shifted, which indicates that the stable complex of 4-PIN and TPPZn can be formed in toluene. By contrast, in polar solvents such as CH_3CN , THF and DMF, the absorption spectrum of TPPZn did not change on addition of 4-PIN. This

result implies that TPPZn and 4-PIN cannot form a stable complex in polar solvents. Therefore, the subsequent fluorescence spectral studies were conducted in CH_2Cl_2 .

Steady state fluorescence experiments revealed quenching of TPPZn fluorescence by 4-PIN in CH_2Cl_2 . As shown in Figure 1, 4-PIN efficiently quenched the fluorescence of TPPZn in CH_2Cl_2 on excitation at 556 nm. The fluorescence intensity at 592 nm decreased 14-fold on addition of 65 equivalents of 4-PIN. Because of the coordination of Zn to N of the pyridine moiety of imino nitroxide, 4-PIN could quench the fluorescence in two ways. First, because of the presence of imino nitroxide, and second by photoinduced electron transfer (PET) from the imidazole moiety to the porphyrin. 4-PIN efficiently quenched the fluorescence of a 2×10^{-5} mol/L TPPZn solution in CH_2Cl_2 on excitation at 556 nm.

When nicotine was added to the mixed solution of TPPZn and 4-PIN, the nicotine N coordinated to Zn, and

Figure 1 Fluorescence quenching of 2.0×10^{-5} mol/L TPPZn by 4-PIN (0 to 1.3×10^{-3} mol/L) in CH_2Cl_2 with excitation at 556 nm. Inset: absorption spectra of 2.0×10^{-5} mol/L TPPZn in CH_2Cl_2 with 4-PIN (0 to 1.2×10^{-3} mol/L).

Figure 2 Fluorescence enhancement of the mixed solution of TPPZn (2.0×10^{-5} mol/L) and 4-PIN (7.2×10^{-4} mol/L) by nicotine (from 0 to 7.2×10^{-4} mol/L) in CH_2Cl_2 . Inset: the fluorescence response of the mixed solution of TPPZn (2.0×10^{-5} mol/L) and 4-PIN (7.2×10^{-4} mol/L) to the low concentration of nicotine from 0 to 2.0×10^{-5} mol/L.

1) UV-Vis spectra were carried out on a Hitachi U-3010 spectrophotometer using a quartz cell of 10 mm path. Fluorescence spectra were determined on a Hitachi F-4500 Fluorescence spectrometer using a fluorescence cell (10 mm). Determination conditions: temperature $20 \pm 1^\circ\text{C}$; Ex Slit-5 nm; EM Slit-5 nm; Voltage-950 V.

displaced 4-PIN. This increased the fluorescence intensity. Figure 2 shows the recovery of the fluorescence of a mixed solution of TPPZn (2×10^{-5} mol/L) and 4-PIN (7.2×10^{-4} mol/L) in the presence of different amounts of nicotine (2×10^{-5} to 7.2×10^{-4} mol/L) in CH_2Cl_2 . The Q-bands red-shifted from 592 to 608 nm and from 639 to 657 nm. When pyridine was added separately to the mixed solution of TPPZn and 4-PIN, the fluorescence intensity of the system increased but by less than with nicotine (Figure S1).

In conclusion, using the quenching effect of 4-PIN, we developed an ensemble, 2-(4-pyridyl)imino nitroxide tetraphenylporphyrin zinc(II), which could be used for simple “off-on” fluorescence detection of nicotine. These results could be used to develop new applications for nitroxides. Synthesis of new water-soluble porphyrin-metal-nitroxide systems for selective and sensitive detection of nicotine and its analogs will be investigated in future studies.

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Supporting Information

Figure S1 (a) Fluorescence enhancement of the mixed solution of TPPZn (2.0×10^{-5} mol/L) and 4-PIN (7.2×10^{-4} mol/L) by nicotine in the presence of triethylamine (0.036 mol/L); (b) the difference of fluorescence intensity of the mixed solution of TPPZn (2.0×10^{-5} mol/L) and 4-PIN (7.2×10^{-4} mol/L) by nicotine ($\lambda_{\text{ex}} = 608$ nm) in the presence of triethylamine (0.036 mol/L) or not triethylamine in CH_2Cl_2 .

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