Porphyrin/$MgCl_2$/Silica Gel Composite as a Cobalt-free Humidity Indicator

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In order to develop cobalt-free humidity indicator, the composite consisted of porphyrin, $MgCl_2$, and silica gel was prepared. The composite exhibited a reversible color change from green to purple under dry and humid conditions, respectively.

Silica gel (SiO_2) is most commonly used as a desiccant. The ability of desiccant is usually checked by use of a $CoCl_2/SiO_2$ humidity indicator which is transformed to $Co(H_2O)_6/SiO_2$ under humid conditions, revealing a color change from blue to purple. Recently, considerable caution has been paid in using $CoCl_2/SiO_2$ humidity indicators because IARC has determined that the $CoCl_2$ is carcinogenic to humans.[1] In Europe, for example, the use of $CoCl_2/SiO_2$ humidity indicators in desiccants placed in the packages are controlled by by-law.[2] Therefore, we need to develop a safe humidity indicator without carcinogenic chemicals.

Recently, commercially available cobalt-free humidity indicators have been developed. However, these materials have showed only small color change between dry and humid conditions compared with $CoCl_2/SiO_2$. NeoBLUE[3] and Chameleon C,[4] for example, showed the increase of absorbance at 533 nm and the shift of the absorption maximum from 460 to 510 with a decrease of absorbance under humid conditions, respectively. Therefore, our attentions are paid to develop the humidity indicator having large color change.

Porphyrins can absorb visible light to exhibit a characteristic color depending on the central metal, the solvent, pH, and aggregation with other chromophores.[5] In particular, free-base tetraphenylporphyrin (H_2TPP) are sensitive to pH. Indeed, by addition of aqueous HCl solution to $CHCl_3$–MeOH solution of H_2TPP,[6] the maximum absorbance of H_2TPP largely shifted from 514 to 658 nm, as shown in Figure 1A(a, b). The absorption at 658 nm can be assigned to be the protonated porphyrin (H_4TPP^{2+}). If pH can be easily controlled with humidity in SiO_2, the porphyrin chromophores can operate as a humidity indicator of SiO_2.

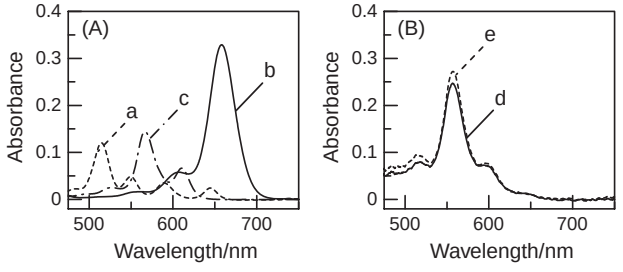
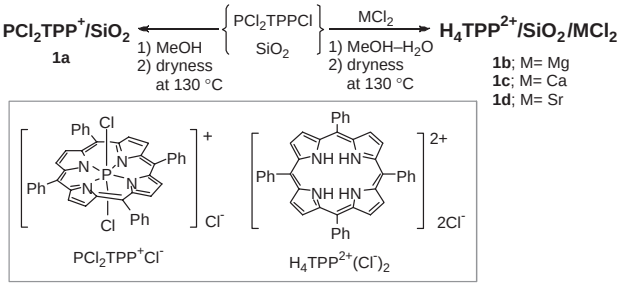


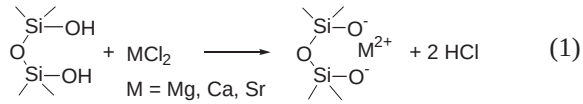
Figure 1. (A) Absorption spectra of H_2TPP in MeOH (a), H_4TPP^{2+} in $CHCl_3$–MeOH solution (b), and PCl_2TPPCl in MeOH (c). (B) Microscopic analysis of **1a** under dry (d) and humid conditions (e).



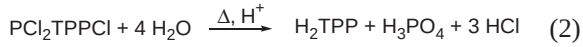
Scheme 1. Synthesis of the composites (**1a**–**1d**).

As has been reported earlier,[7,8] H_2TPP has very low solubility in MeOH but dichloro(tetraphenylporphyrinato)phosphorous chloride (PCl_2TPPCl) is more soluble due to the existence of a cationic complex. Moreover, the PCl_2TPPCl was found to be non-toxic: $LD_{50} > 2$ g/kg.[9] At first, therefore, we began by preparing the composite between SiO_2 and PCl_2TPPCl. Into a MeOH solution (15 mL) of the PCl_2TPP (1.25 mg), SiO_2 (25 g, particle size 1.7–4.0 mm, surface area 636 m^2/g) were added. Almost PCl_2TPPCl was adsorbed on SiO_2. The particles were filtrated, and heated at 130 °C overnight to yield the purple PCl_2TPP^+/SiO_2 composite (**1a**; content of PCl_2TPPCl = 50 ppm) (Scheme 1). Microscopic analysis[10] showed that an absorption band of **1a** appeared at 557 and 596 nm (Figure 1B(d)). These absorptions corresponded to a characteristic absorption band of PCl_2TPP, which appeared at 566 and 610 nm in MeOH (Figure 1A(c)).

Under dry conditions



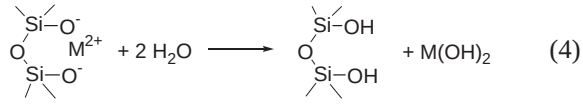
(1)



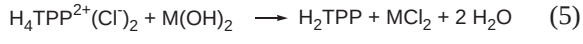
(2)

(3)

Under humid conditions



(4)



(5)

When **1a** stood under the humid conditions for 1 h, however, **1a** maintained entirely its original absorption, showing no color change (Figure 1B(e)).

Recently, it has been reported that acidic conditions were made by the reaction of SiO_2 with $CaCl_2$ (eq 1).[11] Therefore,

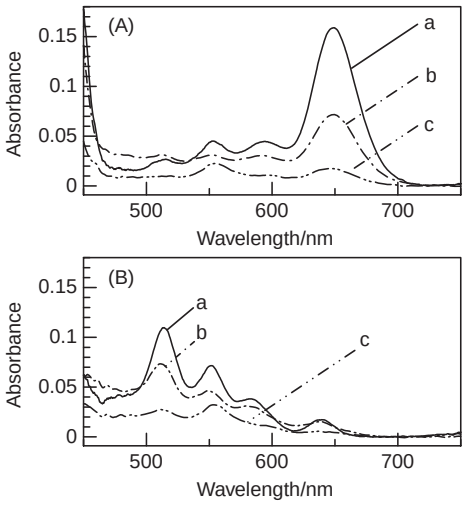


Figure 2. Microscopic analysis of $H_4TPP^{2+}/MCl_2/SiO_2$ **1b–1d** under dry (A) and humid (B) conditions; **1b** (a), **1c** (b), and **1d** (c): $[MCl_2] = 7.2$ mM.

we intended to prepare the porphyrin/MCl_2/SiO_2 composites **1b–1d** using alkaline earth metal chlorides ($MCl_2 = MgCl_2$, $CaCl_2$, and $SrCl_2$). The composites were prepared by mixing of SiO_2 (25 g) with MeOH solution (15 mL) of PCl_2TPPCl (1.25 mg) and aqueous solution (1 mL) of MCl_2 (7.2 mM), and followed by filtration and dryness at 130 °C overnight to yield **1b–1d** (Scheme 1). Under dry atmosphere, **1b–1d** had a strong absorption band at 649 nm due to the formation of H_4TPP^{2+} (Figure 2A). Therefore, the elimination of the central metal from PCl_2TPP^+ complexes (eq 2) and the protonation took place nearly quantitatively during the preparation (eq 3). It is well known that PCl_2TPP^+ undergoes demetallation under acidic conditions.[5] Among the three $H_4TPP^{2+}/MCl_2/SiO_2$, the greatest absorbance at 649 nm was observed in $H_4TPP^{2+}/MgCl_2/SiO_2$ (**1b**) (Figure 2A).[12] However, $SrCl_2$ was ineffective for the formation of $H_4TPP^{2+}/MCl_2/SiO_2$ composite at all. As the results of the preparation of **1b** using various concentrations of $MgCl_2$ (0–7.2 mM), the optimum concentration of $MgCl_2$ was determined to be 5.3 mM.

After **1b–1d** stood under humid conditions for 1 h, the absorbance at 649 nm (A_{649}) decreased while new absorption appeared at 514 nm with large absorbance along with weak absorptions at 552, 582, and 640 nm, resulting in a color change from green to purple (Figure 2B). The resulting absorptions can be unambiguously assigned to be the absorptions of H_2TPP (514, 550, 589, and 645 nm. See Figure 1A(a)). It is suggested that MCl_2/SiO_2 reacted with H_2O to give $M(OH)_2$, reverting pH from acidic to neutral, as has been reported (eq 4).[8] Thus the deprotonation from green H_4TPP^{2+} took place to give purple H_2TPP under humid conditions (eq 5).

We investigated whether the color changes were dependent on humidity. According to JIS method,[13] **1b** was exposed for 48 h to the air whose relative humidity (RH) was adjusted to 0, 20, 50, and 90% by an aqueous solution of sulfuric acid. The color change was evaluated by the fraction of A_{514} (F) in absorption spectra of **1b** after standing under given RH: $F = A_{514}/(A_{514} + A_{649})$. As shown in Figure 3, the F value was remarkably changed up to 20% of RH. Moreover, the humid purple **1b** was dried again at 130 °C and returned to a green color, showing the reversibility of the coloration ability.

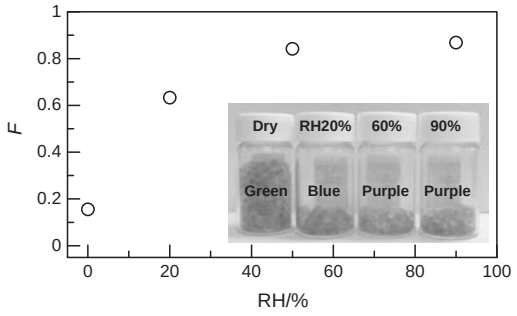


Figure 3. Dependence of absorption fraction (F) in absorption spectra of **1b** on relative humidity (RH): $F = A_{514}/(A_{514} + A_{649})$.

In conclusion, the porphyrin/$MgCl_2$/SiO_2 composite **1b** was developed as a new type of cobalt-free humidity indicator.[14] It showed the spectral change of 135 nm between dry and humid conditions. It was sensitive to the moisture on even low RH and will be safely used since H_2TPP is strongly adsorbed on SiO_2 and **1b** does not include the carcinogenic chemicals.

References and Notes

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