Chem. Mater. **2003,** *15,* 372−374

Optical Sensing of Small Hydroxyl-Containing Molecules in New Crystalline Lamellar Arrays of Co(II) and *N*-(4-Pyridyl)benzamide

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Received July 18, 2002
Revised Manuscript Received November 14, 2002

In recent years, chemical sensing has attracted the interest of many research groups, especially in the areas of photochemical and photophysical sensing.[1] One of the important areas in contemporary sensor development is the design and synthesis of functionalized molecular models that trigger a measurable response upon exposure to a specific family of analytes.[2] Current detection systems consist of the chemoselective sensor coupled with a transducer device, which may use optical methods, a conducting polymer, or Langmuir−Blodgett multilayer, a quartz crystal microbalance (QCM), or a surface acoustic wave (SAW) device, to quantify the analytes.[3] While the analytical instrumentation for these kinds of transducers is relatively advanced, well-characterized chemically sensitive layers are still needed. A number of solution-based probes, sol−gel films, and molecular sieves systems with sensitivity to inorganic ions[4] and volatile organic compounds[5] (VOC) have recently been reported. However, in terms of practicality, solid-state sensors are often more desirable systems, as such devices would minimize sample contamination and, after regeneration of the sensing element, can be used again.[6] Recently, supramolecular architectures designed from noncovalent interactions have been employed for the fabrication of functional materials with a targeted utility in chemical sensory devices.[5g,h,7] Following on our recent report on the preparation of crystalline solids of 1-, 2-, and 3-D noncovalent networks formed via complexes of *N*-(4-pyridyl)benzamide (NPBA),[8] herein we report a new structure, namely, Co$(NPBA)_2(H_2O)_2(NO_3)_2$ (**1**), Figure 1, with a functional lamellar-like supramolecular arrangement that, upon activation by removal of solvent, forms a chromatic chemoselective sensor for small (≈5 Å) hydroxyl-containing molecules.

The Co-complex **1** was synthesized by slow evaporation of a mixture of the nitrate salt of Co(II) and NPBA in an ethanol:water mixture (80:20) at room temperature over 2 days (yield 83%). The formulation of **1** was confirmed by X-ray crystallography[9] and elemental analysis. When microcrystals of **1** are heated to 110 °C, a deep purple crystalline material is generated (**2**) with the molecular formula corresponding to desolvated **1**. The Co-complex **2** is obtained as a crystalline solid as evident from its X-ray powder diffraction pattern and was characterized with elemental analysis and UV−vis reflectance and Resonance Raman spectroscopies.

The single-crystal X-ray diffraction study on **1** reveals that the Co^{2+} centers exist in an octahedral configuration as *trans*-Co$(NPBA)_2(H_2O)_2(NO_3)_2$, Figure 1. The supramolecular structure of **1** exhibits a remarkable $\pi-\pi$ stacking ensemble along the *ac* plane generated from the stacking of phenyl and pyridyl moieties of adjacent molecular units with average inter-ring contacts of 3.63 Å and forms two-dimensional layers similar to those found in lamellar solids, Scheme 1.[7a] These lamellar-like layers are interconnected by hydrogen bonds generated between the solvent and the nitrite ions and the carboxamide moieties of NPBA units along the *b*-direction.

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(1) Gopel, W. *Microelectron. Eng.* **1996**, *32*, 75−110.

(2) (a) *Fluorescent Chemosensors for Ion and Molecular Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1997; Vol. 492. (b) Beer, P. D.; Schmitt, P. *Curr. Opin. Chem. Biol.* **1997**, *1*, 475−482. (c) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515−1566.

(3) (a) Rabolt, J. F.; Santo, R.; Schlotter, N. E.; Swalen, J. D. *ZBM J. Res. Dew* **1982**, *26*, 209−216. (b) Yang, L.; Saavedra, S. S.; Armstrong, N. R.; Hayes *J. Anal. Chem.* **1994**, *66*, 1254−1263. (c) Mirkin, C. A.; Valentine, J. R.; Ofer, D.; Hickman, J. J.; Wrighton, M. S. *ACS Symp. Ser.* **1992**, *487*, 218−236. (d) Hillman, A. R.; Loveday, D. C.; Swann, M. J.; Bruckenstein, S.; Wilde, C. P. *ACS Symp. Ser.* **1992**, *487*, 150−163. (e) Zellers, E. T.; Zhang, *G.-Z. AnuZ. Chem.* **1992**, *64*, 1277−1284. (f) Szmacinski, H.; Lakowicz, J. R. *ACS Symp. Ser.* **1993**, *538*, 196−226. (g) DeQuan, L.; Buscher, C. T.; Swanson, B. I. *Chem. Mater.* **1994**, *6*, 803−810.

(4) (a) Walkup, G. K.; Imperiali, B. *J. Am. Chem. Soc.* **1996**, *118*, 3053. (b) Ishikawa, J.; Sakamoto, H.; Nakao, S.; Wada, H. *J. Org. Chem.* **1999**, *64*, 1913. (c) McFarland, S. A.; Finney, N. S. *J. Am. Chem. Soc.* **2001**, *123*, 1260. (d) Chen, C. T.; Huang, W. P. *J. Am. Chem. Soc.* **2002**, *124*, 6246. (e) Niikura, K.; Metzger, A.; Anslyn, E. V. *J. Am. Chem. Soc.* **1998**, *120*, 8533. (f) Ojida, A.; Mito-oka, Y.; Inoue, M.; Hamachi, I. *J. Am. Chem. Soc.* **2002**, *124*, 6256. (g) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372. (h) Anzenbacher, P., Jr.; Tyson, D. S.; Jursikova, K.; Castellano, F. N. *J. Am. Chem. Soc.* **2002**, *124*, 6232.

(5) (a) Ikeda, H.; Nakamura, M.; Ise, N.; Oguma, N.; Nakamura, A.; Ikeda, T.; Toda, F.; Ueno, A. *J. Am. Chem. Soc.* **1996**, *118*, 10980. (b) Yan, Y.; Bein, T. *Chem. Mater.* **1992**, *4*, 975. (c) Meinershagen J. L.; Nein, T. *J. Am. Chem. Soc.* **1999**, *121*, 448. (d) Katz, E.; Buckmann, A. F.; Willner, I. *J. Am. Chem. Soc.* **2001**, *123*, 10752. (e) Svetlicic, V.; Schmidt, A. J.; Miller, L. L. *Chem. Mater.* **1998**, *10*, 3305. (f) Williams, A. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 4366. (g) Pugh, V. J.; Hu, Q. S.; Zuo, X.; Lewis, F. D.; Pu, L. *J. Org. Chem.* **2001**, *66*, 6136. (h) Rudzinski, C. M.; Young, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 1723. (i) Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763. (j) Extrom, C. L.; Pomije, M. K.; Mann, K. R. *Chem. Mater.* **1998**, *10*, 942. (k) Noonan, G. O.; Ledford, J. S. *Chem. Mater.* **1995**, *7*, 1117. (l) Mohr, G. J.; Demuth, C.; Spichiger-Keller, U. E. *Anal. Chem.* **1998**, *70*, 3868.

(6) (a) Dickinson, T. A.; White, J. M.; Kauer, J. S.; Walt, D. R. *Nature* **1996**, *382*, 697. (b) Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* **2000**, *100*, 2595−2626.

(7) (a) Mallouk, T. E.; Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 209. (b) Mortellaro, M. A.; Nocera, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 7414. (c) Hiraoka, S.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 10239. (d) Yu, S.-Y.; Kusukawa, T.; Biradha, K.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2665. (e) Ibukuro, F.; Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **1998**, *120*, 8561. (f) Biradha, K.; Aoyagi, M.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2397.

(8) Noveron, J. C.; Lah, M. S.; Del Sesto, R. E.; Arif, A. M.; Miller, J. S.; Stang, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 6613.

(9) Crystal data for **1**: $C_{24}H_{24}N_6O_{10}Co$, Mr = 615.42, light pink prism of dimensions 0.38 × 0.25 × 0.23 mm, triclinic, space group $P\bar{1}$, $a = 7.5034(4)$ Å, $b = 9.1080(5)$ Å, $c = 10.0299(6)$ Å, $\alpha = 75.329(3)°$, $\beta = 72.812\ (2)°$, $\chi = 82.161(2)°$, $V = 632.08(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.617$ mg m^{-3}. The data were collected at 200(1) K on a Nonius KappaCCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 4132 reflections were measured, of which 2733 were unique. The structure refinement by full-matrix least-squares on F^2 and Fourier transform techniques and location of hydrogen atoms and their isotropic refinement were done using SHELXTL-97 (Bruker-AXS, Inc. Madison, WI). Final residuals were R1 = 0.0398 and wR2 = 0.0868. Further crystallographic data can be obtained from the Supporting Information.

10.1021/cm025643n CCC: $25.00

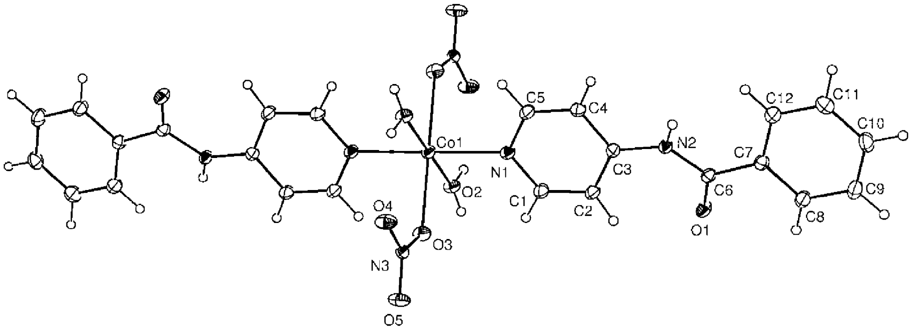
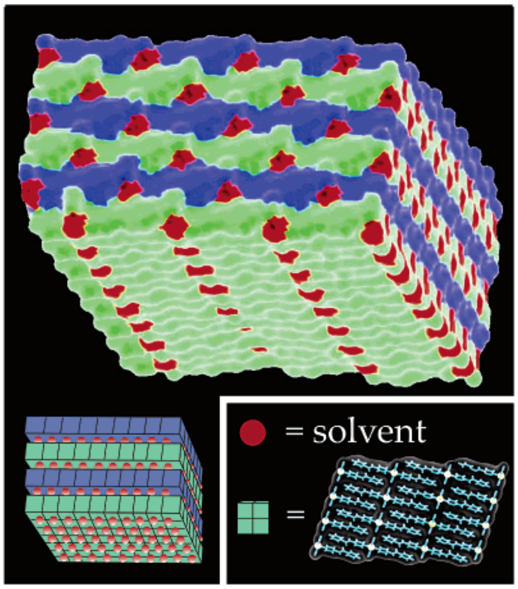


Figure 1. Structure of Co(NPBA)$_2$(H$_2$O)$_2$(NO$_3$)$_2$ (**1**).

Scheme 1. Supramolecular Structure of 1 Forms Lamellar-like Solids with Solvent between Layers



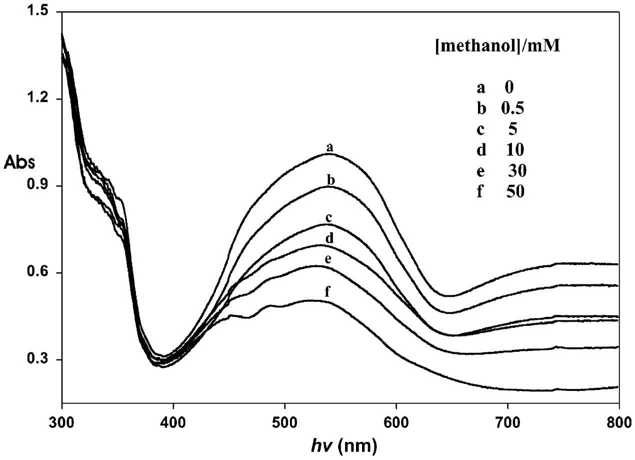


Figure 2. UV−vis reflectance spectra of a sensor layer of Co-complex **2** after exposure to various solutions of methanol in dichloromethane.

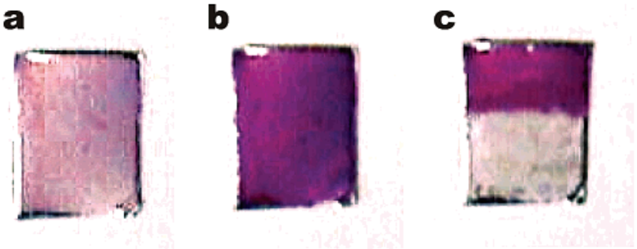


Figure 3. (a) Layered Co-complex **1** on aluminum plates. (b) Co-complex **2**. (c) After partial exposure to 0.5 M methanol solution in dichloromethane for 5 min.

The presence of Lewis (Co^{2+}) and Brönsted acid (NO$_3^-$) sites in **2** confer the crystalline solid with optical properties that allows it to exhibit a chromatic response toward hydroxyl-containing molecules. Co-complex **2** exhibits a strong absorbance band at 530 nm that can be followed with UV−vis reflectance spectroscopy. Exposure of freshly prepared crystalline samples of **2** to dichloromethane solutions of small alcohols such as methanol has a dramatic effect on the optical bands of **2** and allows for the quantitative sensing of various kinds of alcohols with a detection limit in the sub-millimolar range; see Figure 2. Co-complex **2** exhibited the highest sensitivity to methanol in the 0.1−100 mM range with a standard deviation ($n = 5$) determined to be from 1 to 5% within the measured range. The time needed for 95% of the total signal change is 3 h. When methanol is present in high concentrations (>0.5 M), a fast response time is obtained and detection is obtained within 5 min, Figure 3. The Co-complex **2** was investigated for its selectivity to different alcohols and the results are shown in Figure 4. After methanol, the next highest sensitivity was observed with ethanol and followed with *n*-propanol, phenol, and cyclopropanol under the same analytical conditions. This affinity trend was attributed to the size of the analytes and their ability to diffuse into the structure of **2**. Although Co-complex **2** is sensitive to water, the experiments above were performed under anhydrous conditions. Competitive binding studies between different kinds of alcohols and water are undistinguishable in the 1−100 mM range; however, excess water in acetone (>3 M) was observed to reconstitute Co-complex **1** in the cases when the bulkier alcohols were used.

To gain some insight into the mechanism of alcohol detection of Co-complex **2**, we followed the reaction of **2** and methanol with X-ray power diffraction (XRPD) and resonance Raman spectroscopy. When Co-complex **2** was exposed to a 100 mM solution of methanol in dichloromethane and followed with XRPD over a period of 30 min, a clear crystal phase change toward reconstitution of Co(NPBA)$_2$(CH$_3$OH)$_2$(NO$_3$)$_2$ is observed and suggests that methanol molecules diffused into the crystalline solid **2**; the results are shown in Figure 5. The XRPD of the reconstituted methanol adduct Co(NPBA)$_2$(CH$_3$OH)$_2$(NO$_3$)$_2$ matches the diffraction pattern, with only a slight loss of crystallinity, from single crystals with such composition. This behavior suggests that the

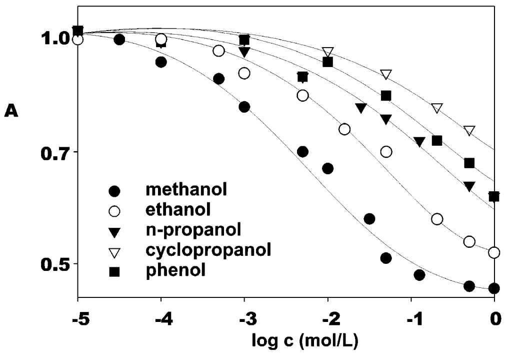


Figure 4. Response function measured at 530 nm of Co-complex **2** to various alcohols in dichloromethane. The solid lines were calculated according to ref 5l.

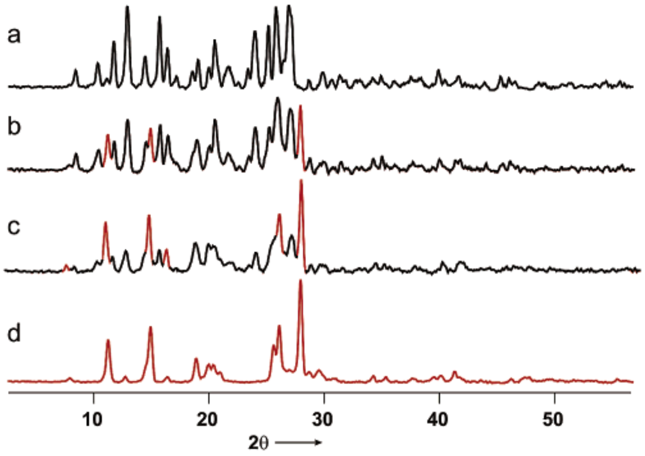
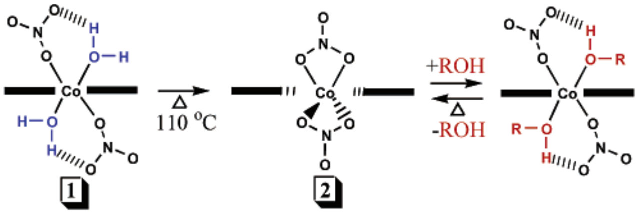


Figure 5. X-ray powder diffraction of (a) Co−Complex **2**, (b), (c) as it is exposed to methanol, and (d) reconstituted Co-(NPBA)$_2$(CH$_3$OH)$_2$(NO$_3$)$_2$ from **2**.

supramolecular milieu of **1** is preserved to some extent after desolvation and that an orchestrated mechanism of alcohol diffusion into **2** is at work during the sensing function.[10] These results are consistent with the recent finding that the absence of pores or tunnels does not preclude the diffusion of small molecules in crystals with bilayer arrangements.[11]

Resonance Raman spectroscopy analysis ($\lambda = 514$ nm) of a solid sample of **2** showed a change in the intensity pattern as well as a small shift ($\Delta 9$ cm^{-1}) to higher frequencies (1036 cm^{-1}) of the nitrate stretching frequencies as compared to **1**, both of which suggest that the remaining nitrate molecules adopt a bidentate mode of chelation to the metal center and suggest a tetrahedral configuration for the Co^{2+} centers, Scheme 2.[12] These results are consistent with the set of absorbance

Scheme 2



bands at 530 and 750 nm for **2**, which have been observed in other Co(II) systems with pseudo-tetrahedral configuration and are suggested to arise from the d−d transitions from a T$_h$ 3d^7 electronic configuration system.[13] It is thus likely, although speculative at this point, that the NPBA molecules in **2** retain the $\pi-\pi$ stacking arrangement while the Co^{2+} centers adopt a tetracoordinated system with the nitrate ions.

In conclusion, the present study has introduced a novel lamellar-like supramolecular arrangement that exhibits optical sensing properties toward alcohols when desolvated. Taken together, our results suggest that the crystalline solid **2** consists of periodic arrangements of substitutionally active Co(II) sites that are structurally assisted with NPBA and exhibit suitable optical properties that quantitatively respond to small alcohol molecules capable of diffusing into its crystalline phase. Attempts to study the applications of Co-complex **2** with more sensitive transducers devices such as a quartz crystal microbalance is underway. We are also exploring the ability of **2** to separate bulk quantities of alcohols from mixtures, as well as the introduction of rationally designed modifications in **2** for enantioselective separations and catalysis.

Acknowledgment. We thank Dr. Joel M. Harris for his assistance with the resonance Raman and solid-state UV−vis spectroscopies. Financial support by the National Institute of Health (Grant 5R01GM57052), the National Science Foundation (Grants CHE-9818472), and the NIH Postdoctoral Fellowship F32 (Grants GM66504-01) for J.C.N. are gratefully acknowledged.

Supporting Information Available: Tables of crystal data for **1**, additional experimental details, and resonance Raman data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Evans, O. R.; Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2001**, *123*, 10395.

(11) Atwood, J. L.; Barbour, L. J.; Jerga, A.; Schottel, B. L. *Science* **2002**, *298*, 1000.

(12) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley: New York, 1978. (b) Addison, C. C.; Logan, N.; Wallwork, S. C.; Barner, C. D. *Q. Rev.* **1971**, *25*, 289.

(13) (a) Solomon, E. I.; Rawlings, J.; McMillin, D. R.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 8046. (b) Mastropaolo, D.; Thich, J. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1977**, *99*, 424.