Synthesis and Spectral Properties of Lithium Naphthalocyanine: A Novel EPR Oximetry Probe

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A novel EPR oximetry probe, lithium naphthalocyanine (LiNc) dye has been sythesized successfully and has been characterized using UV–vis spectroscopy, X-ray diffraction and ESR techniques. X-ray diffraction pattern showed the crystalline nature of the synthesized powder and resembles that of typical naphthalocyanine. EPR measurements indicated a linear dynamic EPR line width ranging from 400 mG to 26 G with increasing oxygen concentration.

Phthalocyanines (Pc) and naphthalocyanines (Nc) have been widely utilized in industry and academia in a variety of applications such as dye stuffs, coatings in read and write CD-ROMs, and anti-cancer drugs. In general, a metal-substituted form of the phthalocyanine molecule has been applied. Among them, lithium phthalocyanine (LiPc) and naphthalocyanine (LiNc) are stable neutral radicals exhibiting an intrinsic semiconducting behavior with unusual magnetic properties.[1,2] The structure, morphology, electrical and magnetic properties of LiPc molecule has been studied intensively.[2–4] LiPc has interesting properties related to its structure and has been reported to crystallize in at least three different forms called x, α, and β. Both LiPc and LiNc are metallic-organic, paramagnetic crystallites that can be applied for in situ electron paramagnetic resonance (EPR) oximetric studies.[1–4] LiNc and Li_2Nc have not yet been studied well for their physical and magnetic properties. Previous report indicated some photophysical properties of Li_2Nc, but its preparative and structural characteristic features are unclear.[5] In the present work, we have prepared lithium naphthalocyanine using synthetic procedures and further characterized using UV–vis, X-ray diffraction and EPR techniques.

Lithium naphthalocyanine has been prepared by dissolving 2,3-dicyanonapthalene in *n*-pentanol under nitrogen. Appropriate amount of Li granules were added to this solution and refluxed at 150 °C for an hour. Finally, the crude product was separated by pouring into *t*-butyl methyl ether. The dark green product was further purified by extracting with *t*-butyl methyl ether. Chemical analysis showed satisfactory results and the amount of Li is intermediate between Li_2Nc and LiNc. The fraction of LiNc is calculated as 0.44% in the product. UV–vis spectra were measured using a CARY spectrophotometer from 400 nm to 1000 nm. X-ray diffraction measurements were performed using a Rigaku (RINT 1200) X-ray diffractometer operated at 40 KV and 30 mA with Cu Kα radiation (λ = 1.542). Analysis of the pattern was carried out using JADE software. ESR measurements were performed using a JEOL (JES-TE300) spectrometer. All the spectra were recorded under vacuum at low microwave power (13 μW), with low modulation amplitude (2 mG) and a low frequency (25 kHz). These parameters were used in order to avoid saturation.

Figure 1 shows the X-ray powder diffraction pattern of the product indicating several diffraction peaks corresponding to the highest degree of crystallinity. Some of the peaks are labeled with their 'd' spacing values. The maximum intensity peak at d = 1.53 nm represents the typical naphthalocyanine lattice spacing which is larger than the phthalocyanines.[6] There is another shoulder peak at d = 1.47 nm indicating a lower 'd' value which suggests the presence of another phase of the material. Similarly another peak at d = 0.66 follows d = 0.67. These results can also be caused by the presence of a possible aggregate of Li_2Nc and LiNc. The peak at 0.33 nm clearly indicates the molecular packing distance, i.e., the 'c' axis lattice parameter typical for naphthalocyanine molecule.[7] The peak value at 0.66 nm is twice the peak value of 0.33 nm. This may be due to the staggerd stacking of these molecules along the c-axis.

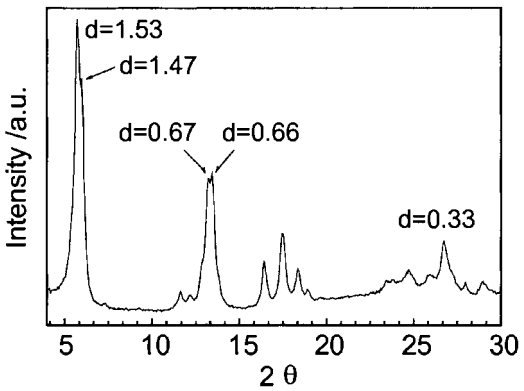

Figure 1. Powder X-ray diffraction pattern of lithium naphthalocyanine. The peak positions are marked with 'd' spacing in nanometer units.

The absorption spectra for lithium napthalocyanine have been recorded in acetone, acetonitrile, THF, pyridine and DMSO as shown in Figure 2. The spectra obtained in acetone, acetonitrile and THF were similar, indicating the absorption bands maximum around 420 nm, 670 nm and 920 nm, whereas the spectrum obtained in DMSO showed a sharp absorption band at 740 nm compared to other bands indicating better solubility in this solvent. Our spectral features obtained in acetone, acetonitrile, and THF solvents are similar to the previously reported spectrum of radical aggregate $[Li_2Nc(LiNc)_n]$ in pyridine.[5]

LiPc and LiNc molecules are important candidates for EPR oximetry. Significant amount of EPR studies have been carried out using LiPc.[1–4,8,9] LiPc is notable for its narrow EPR line width of 20 mG obtained for the 'x' form of the crystals.[4] Figure 3 shows the EPR spectra of LiNc measured in vacuum and in the presence of oxygen. A line width (ΔH) of ~400 mG is obtained. This linewidth is broad compared to LiPc (20 mG) powder meas-

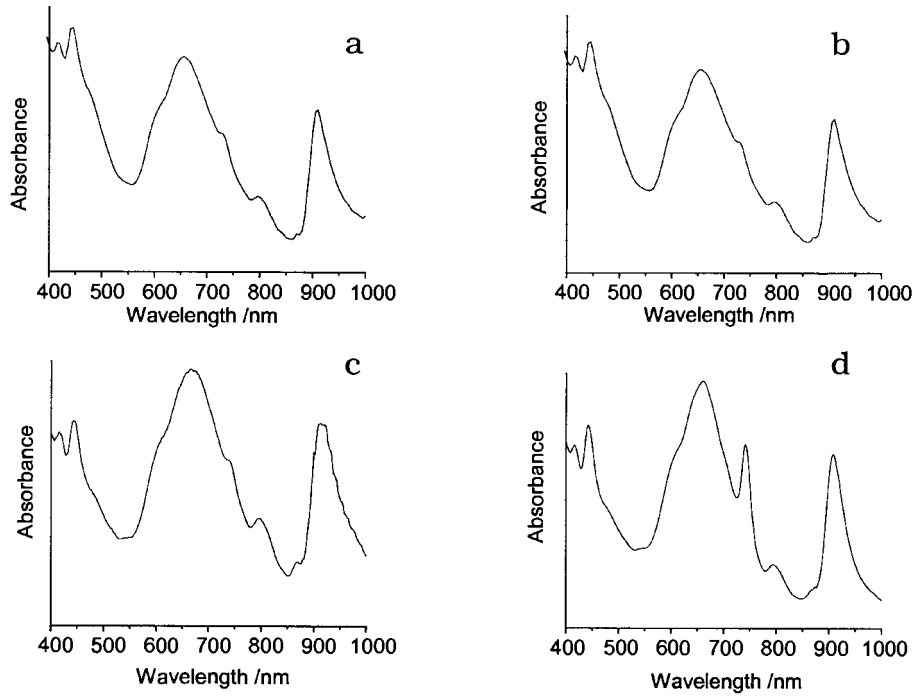

Figure 2. Visible spectra of lithium naphthalocyanine in a) acetonitrile, b) THF c) Pyridine, and d) DMSO. Spectrum obtained in DMSO showed a sharp absorption band at 740 nm indicating better solubility in this solvent.

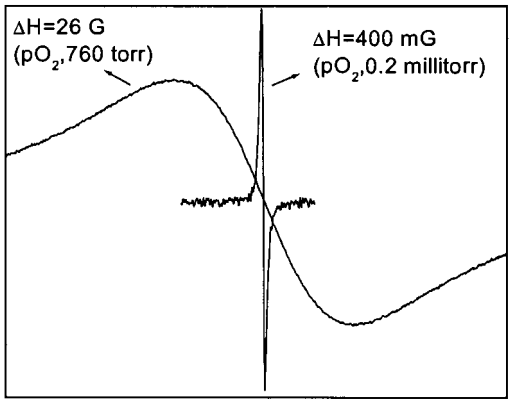

Figure 3. EPR spectrum of Lithium naphthalocyanine powder. A peak to peak line width of 400 mG (pO_2, 0.2 millitorr) is obtained. This line width broadens up to 26 G (pO_2, 760 torr) with increase in oxygen concentration.

ured at similar conditions. This line width of 400 mG (pO_2: 0.2 millitorr) was observed for LiNc increases linearly up to 26 G (pO_2: 760 torr) with increase in the oxygen concentration. Such a wide linear EPR line width variation for this molecule has been observed for the first time. We have also calculated the spin density (6.8×10^{20} spins/gram) for this compound using diphenylpicrylhydrazyl (DPPH) as a standard reference material. LiNc is expected to have a higher degree of delocalization in π bonding due to the extended naphthalocyanine rings that can enhance the dynamic range for oxygen sensitivity in comparison to LiPc. A perfect linearity has been obtained from 0% to 100% oxygen concentration with a slope value of 30 mG/torr. The details of the linear dynamic range for oxygen sensitivity measurements will be reported in a future publication.[9]

In summary, we have synthesized lithium naphthalocyanine and characterized using UV–vis spectroscopy, X-ray diffraction and EPR techniques. The wide EPR spectral line width variations (from 400 mG to 26 G) of the presently synthesized LiNc with increasing oxygen concentration indicate its potential application in EPR oximetry. In situ oxygen sensitivity studies of LiNc using EPR for oximetry are in progress.[9] We are also involved in the preparation and investigation of the physical properties of LiNc as particulate and as thin films on various alkali halide substrates in order to study its epitaxial nature.[10]

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