

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Fabrication of Micro- and Nanoscale Crystals and Thin Films of a Phthalocyanine

Xiaoyu Wang^a; Lian Li^a; Hong Ye^b; Ke Yang^a; Yanping Wang^a; Daniel J. Sandman^a

^a Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA ^b The MathWorks, Inc., Natick, MA

To cite this Article Wang, Xiaoyu , Li, Lian , Ye, Hong , Yang, Ke , Wang, Yanping and Sandman, Daniel J.(2007) 'Fabrication of Micro- and Nanoscale Crystals and Thin Films of a Phthalocyanine', *Journal of Macromolecular Science, Part A*, 44: 12, 1323 – 1327

To link to this Article: DOI: 10.1080/10601320701610754

URL: <http://dx.doi.org/10.1080/10601320701610754>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Fabrication of Micro- and Nanoscale Crystals and Thin Films of a Phthalocyanine

XIAOYU WANG,¹ LIAN LI,¹ HONG YE,² KE YANG,¹ YANPING WANG,¹ and DANIEL J. SANDMAN¹

¹*Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA*

²*The MathWorks, Inc., Natick, MA*

Micro- and nanosized crystals of 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–phthalocyanine (Pc) were successfully fabricated through the reprecipitation approach followed by ultrasonication treatment from acetone solution. Phthalocyanine thin films were prepared by vacuum sublimation, spin-coating and drop-cast methods, respectively. Field emission scanning electron microscopy (FESEM), UV/VIS/NIR spectroscopy, polarizing optical microscopy and luminescence spectrometry were applied to study phthalocyanine crystal's surface morphology, electronic absorption, birefringence and light emission properties accordingly. The electronic absorption maximum of Pc nanocrystals shifts to longer wavelength compared to that in acetone solution. Birefringence phenomena exist for Pc crystals with different sizes. Fluorescence is observed for both the Pc in acetone solution and thin film.

Keywords: phthalocyanines; reprecipitation method; nanocrystals

1 Introduction

The first synthesis of phthalocyanine (Pc) was reported by Braun and Tcherniac in 1907 (1). The full study and elucidation of the molecular structure of Pc and metal Pcs began around 1930 (2–9), and the applications of Pc and metal Pcs have also been studied extensively (10–12) because of their many unique properties, such as high purity due to the ease of crystallization and sublimation, extraordinary thermal and chemical stability, attractive optical properties, high strength, etc. Their classical applications include serving as dyes and catalysts (13). More applications recently in material science include organic semiconductors, photoconductive Pcs, charge generating materials, nonlinear optical (NLO) materials, photodynamic reagents for skin cancer therapy and sensors (14–19). Phthalocyanines are usually cyclotetramers of phthalonitrile monomers. The molecular structures of relevant phthalocyanines are given in Figure 1.

For metal Pcs, there are about seventy different elemental ions that can be placed in the central cavity of Pc, and the

central metal cations strongly influence the metal Pc's physical properties (10). Normally, the Pc macrocycle exists as a dianion (Pc^{2-}) even though it can be oxidized or reduced to a different oxidation state. Many ions, such as Fe^{2+} , Cu^{2+} , etc., are held so tightly that they can not be removed without destroying Pc macrocycle, and most metal ions do not cause a significant distortion of the Pc macrocycle, even though a few of ions such as Pb^{2+} are too large to be accommodated entirely in the cavity and thus lie above the plane of the Pc ring. Some large lanthanide metal cations prefer to form a complex that consists of two Pc rings. These complexes have a sandwich-type structure which has very interesting physical properties, especially electrochromism (20).

In this research, micron- and nanoscale crystals of 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–phthalocyanine were fabricated, and its ultra thin films were also prepared by vacuum sublimation and spin-coating and drop cast methods, respectively. We used UV/VIS/NIR spectroscopy to evaluate the phthalocyanines' optical absorption, and applied field emission scanning electron microscope (FESEM) to observe and analyze their size and surface morphology directly. A polarizing microscope was used to evaluate 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–Pc birefringence phenomena for thin films fabricated by vacuum sublimation and spin-coating methods, respectively. A luminescence spectrometer was used to study the thin film's light emission properties.

Address correspondence to: Xiaoyu Wang, Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA 01854-5046. E-mail: xiaoyuwang2000@hotmail.com

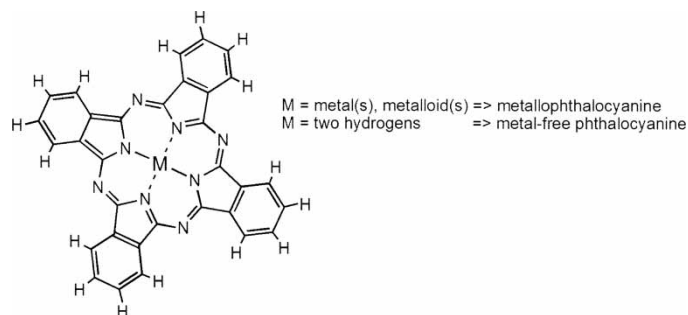


Fig. 1. General chemical structures of phthalocyanines.

2 Experimental

1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–phthalocyanine was purchased from Sigma-Aldrich and was recrystallized from acetone. Its molecular structure is given in Figure 2. The recrystallized 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–phthalocyanine acetone solution with concentration of 2×10^{-4} M was prepared. 100 μ l of this solution was injected into 10 ml deionized Milli-Q water under vigorous stirring. This is known as the reprecipitation method (21, 22). Then the solution was treated for 15 min using a VWR ultrasonic cleaner (1.9 L). The suspension formed without any visible particles or precipitates and its color is light green. FESEM samples were prepared by dropping the above solution on clean ITO-coated glass substrates and the samples were dried over 48 h before characterization by electron microscopy.

The recrystallized 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–Pc crystals were ground thoroughly with a mortar and pestle for 10 min before they were put into the tungsten crucible for vacuum sublimation. After the chamber pressure reached 10^{-7} torr, the crystal samples were gradually heated, then were evaporated and condensed on the glass substrates and ITO-coated glass slides for UV/VIS/NIR spectroscopy, polarizing microscopy, luminescence and FESEM study, respectively. Thin films of 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–Pc were also prepared from its acetone

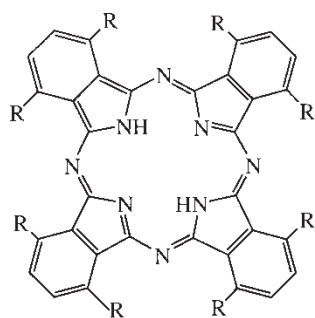


Fig. 2. Chemical structure of 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–phthalocyanine.

solution (2×10^{-4} M) through spin-coating (rpm = 1000) and drop-cast methods at room temperature.

A FESEM (JEOL Ltd, JSM-7410F) was operated under low accelerating voltage (0.6~0.8 KeV) which can minimize surface charging to obtain clear surface morphology and images of phthalocyanine micron- and nanocrystals and ultra thin films. A luminescence spectrometer (Perkin-Elmer Instruments, LS 55) was used to explore whether there is fluorescence for a phthalocyanine acetone solution and phthalocyanine thin film and the emission peaks selection is based on the thin films' electronic absorption maxima obtained by UV/VIS/NIR spectroscopy. A polarizing microscope (Fisher Scientific Company, 12-561-METL) was used to study the birefringence property of thin films and crystals of the Pc.

3 Results and Discussion

Micro- and nano-sized 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–phthalocyanine crystals were successfully prepared using ultrasound (42 k Hz) treatment. Figure 3 (a) and (b) show such phthalocyanine crystals image size and morphology obtained by FESEM with different magnifications. It was

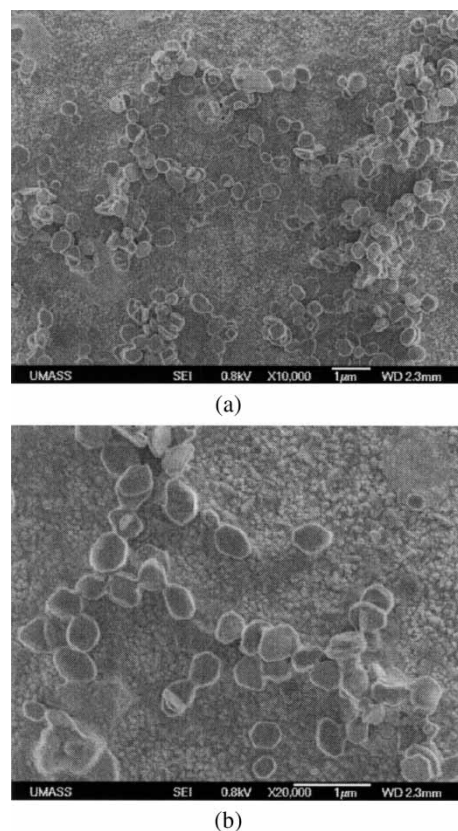


Fig. 3. FESEM images of micro- and nanoscale 1, 4, 8, 11, 15, 18, 22, 25–octabutoxy–29H, 31H–phthalocyanine crystals fabricated by ultrasonication method under different magnification (a) X 10000, (b) X 20000.

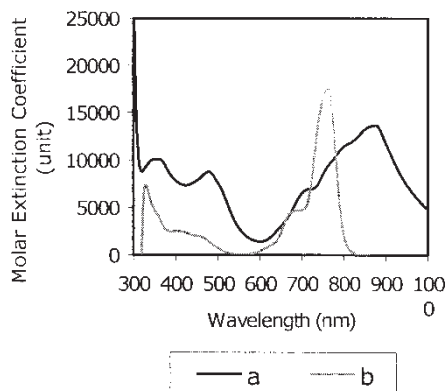


Fig. 4. Electronic absorption comparison.

found that the shape of most of these crystals is that of a hexagon and the size range is 200 nm to 500 nm.

UV/VIS/NIR spectroscopy was used to study and compare the electronic absorption spectra for micro- and nano-sized phthalocyanine crystals in aqueous solution and the phthalocyanine acetone solution. Figure 4 shows the electronic adsorption comparison for this phthalocyanine in different forms. It was noticed that maximum absorption wavelengths are 760 nm and 872 nm for phthalocyanine acetone solution and microcrystalline form, respectively. Thus, there is red a shift in the maximum of 0.21 eV for micro- and nanoscale phthalocyanine crystals. Fox et al. (23) also reported UV-VIS spectrum of 1, 4, 8, 11, 15, 18, 22, 25-octabutoxy-29H, 31H-Pc, in which the absorption maximum is 760 nm. This is consistent with our results. However, to the best of our knowledge, no one studied the electronic spectra for micro- and nano-sized Pc crystals.

Phthalocyanine ultra thin films prepared by vacuum sublimation were characterized by FESEM shown in Figure 5. The left upper area is conductive carbon paste used for decreasing charging on the sample surface, the other area is a thin film, which is very uniform and smooth under one thousand-fold magnification. A polarizing microscope was used to study the film's birefringence properties. Figure 6 (a) and (b) show phthalocyanine thin film images when the two

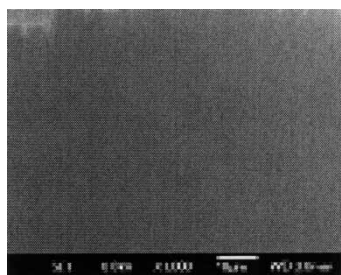


Fig. 5. SEM image of phthalocyanine ultra thin for (a) phthalocyanine micro- and nanoscale film prepared by vacuum sublimation (X 1000) crystals and (b) phthalocyanine acetone solution.

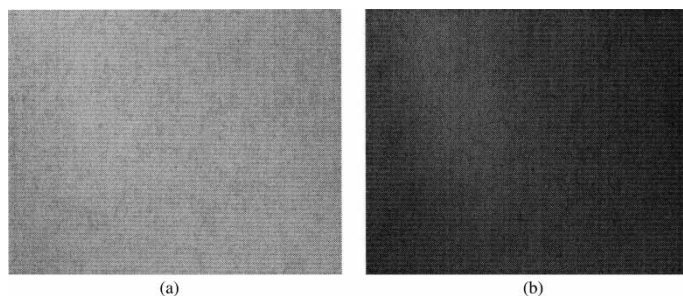


Fig. 6. Phthalocyanine ultra thin film optical images under (a) parallel polarizers and, (b) crossed polarizer (X 200).

polarizers are parallel and perpendicular, respectively. We observed that there is a color variation for the thin films when two polarizers arrangement direction is changed for 0° to 90° , which means that there is an orientation in the thin film structure.

UV/VIS/NIR spectroscopy was used to study the electronic absorption spectrum of phthalocyanine ultra thin films fabricated by vacuum sublimation and spin-coating methods, respectively, and their absorption maxima are

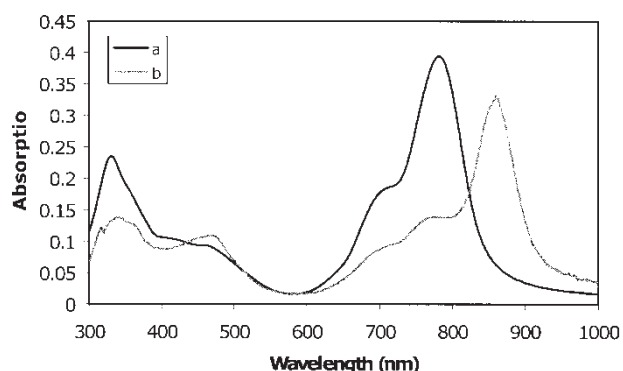


Fig. 7. Electronic absorption spectra for phthalocyanine (a) ultra thin films fabricated by vacuum sublimation and (b) spin-coating methods.

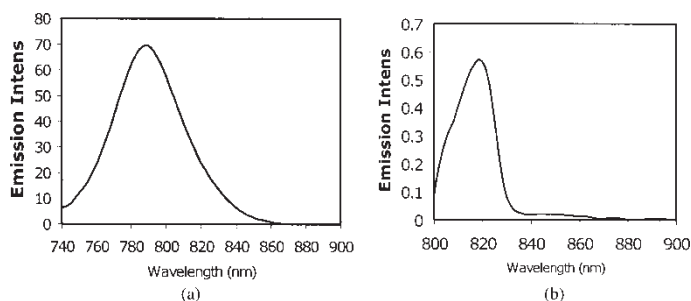


Fig. 8. Emission spectra of phthalocyanine, (a) in acetone solution (2×10^{-6} M), $\lambda_{\text{Excitation}} = 730$ nm, (b) phthalocyanine thin film fabricated by vacuum sublimation (Pressure = 10^{-7} Torr), $\lambda_{\text{Excitation}} = 760$ nm.

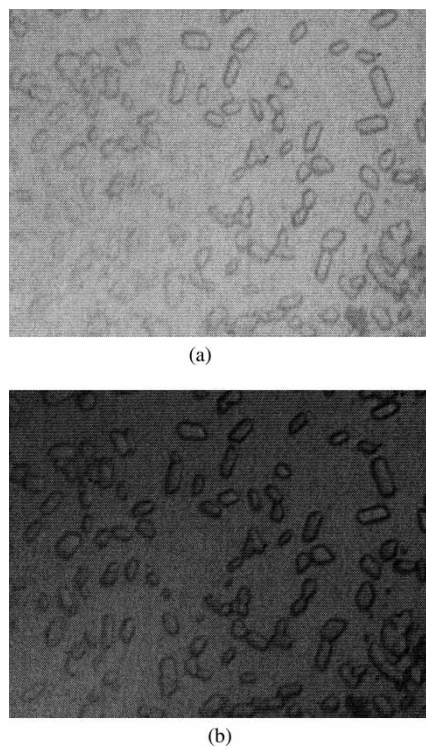


Fig. 9. Optical images of phthalocyanine crystals prepared by spin-coating under (a) parallel polarizers and (b) crossed polarizers (X 200).

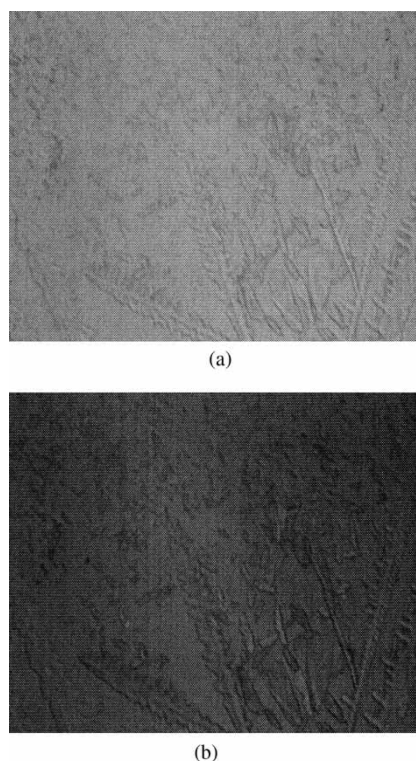


Fig. 10. Optical images of phthalocyanine crystals prepared by drop casting under (a) parallel polarizers and (b) crossed polarizers (X 200).

782 nm and 861 nm, respectively. The spectra are shown in Figure 7. There is an approximate shift of 0.15 eV for these two kinds of thin films. This is due to the difference of Pc crystals' size and orientation for the two thin films.

Based on the obtained UV/VIS/NIR spectra (Figure 4 and Figure 7), a luminescence spectrometer was used to detect fluorescence for the Pc acetone solution and Pc thin film fabricated by vacuum sublimation method, respectively. 730 nm and 760 nm were set as excitation wavelengths for Pc acetone solution and Pc thin film, respectively. Fluorescence was observed for both Pc acetone solution and Pc thin film. The emission maximum wavelengths are 788 nm and 819 nm, respectively. The results were shown in Figure 8.

A polarizing microscope was also used to characterize phthalocyanine thin films fabricated by spin-coating and drop cast approaches, respectively. Figures 9 and 10 show their images under parallel and perpendicular alignment of the two polarizers. It was found there are obvious birefringence phenomena for the spin-coating and drop cast thin films which consist of tiny crystals and tree-like crystals, respectively.

4 Conclusions

Micron and nano-sized phthalocyanine (Pc) crystals were successfully prepared by reprecipitation followed by ultrasonication and the shapes of these crystals are that of a hexagon. The electronic absorption maximum of micro- and nanocrystals of Pc shifts to longer wavelength (872 nm) compared to that of its ultra thin film (782 nm–861 nm) and Pc acetone solution (760 nm). There are birefringence phenomena for Pc crystals with different sizes. Fluorescence is observed for Pc acetone solution and Pc thin film.

5 Acknowledgements

This work was supported in part by Petroleum Research Fund Grant 40263-AC7 and NSF Grant S21007820000006. In the summer of 2006, Xiaoyu Wang was supported in part by a University of Massachusetts Lowell Faculty-Student Collaborative Research Grant.

6 References

1. Braun, A. and Tscheiniac, J. (1907) *Berichte der Deutschen Chemischen Gesellschaft*, **40**, 2709–14.
2. Byrne, G.T., Linstead, R.P. and Lowe, A.R. (1934) *Journal of the Chemical Society*, 1017–22.
3. Linstead, R.P. and Lowe, A.R. (1934) *Journal of the Chemical Society*, 1022–7.
4. Dent, C.E., Linstead, R.P. and Lowe, A.R. (1934) *Journal of the Chemical Society*, 1033–9.

5. Elvidge, J.A. and Linstead, R.P. (1955) *Journal of the Chemical Society*, 3536–41.
6. Dent, C.E. and Linstead, R.P. (1934) *Journal of the Chemical Society*, 1027–31.
7. Lenzoff, C.C. Syntheses of Metal-Free Substituted Phthalocyanines. In *Phthalocyanines Properties and Applications*; Leznoff, C.C. and Lever, A.B.P. (eds.); VCH Publishers: 1–54, 1989.
8. Robertson, J.M. (1936) *Journal of the Chemical Society*, 1195–1209.
9. Robertson, J.M. and Woodward, Ida. (1937) *Journal of the Chemical Society*, 219–30.
10. Lever, A.B.P. *The Phthalocyanines. Advances in Inorganic and Radiochemistry*. Emeleus, H.J. and Sharpe, A.G. (eds.); Academic Press, Vol. 7, 27–105, 1965.
11. Saji, T. Thin film phthalocyanine chemistry and technology. In *Phthalocyanines Properties and Applications*; Leznoff, C.C. and Lever, A.B.P. (eds.); VCH Publishers, Vol. 2, 163–195, 1989.
12. Kasuga, K. and Tsutsui, M. (1980) *Coordination Chemistry Reviews*, **32(1)**, 67–95.
13. McKeown, N.B. *Phthalocyanine Materials*; Cambridge University Press: 1998.
14. Xiao, K., Liu, Y., Yu, G. and Zhu, D. (2003) *Applied Physics A: Materials Science and Processing*, **77(3–4)**, 367–370.
15. Peumans, P. and Forrest, S.R. (2001) *Applied Physics Letters*, **79(1)**, 126–128.
16. Peumans, P., Uchida, S. and Forrest, S.R. (2003) *Nature*, **425(6954)**, 158–62.
17. Anthopoulos, T.D. and Shafai, T.S. (2003) *Applied Physics Letters*, **82(10)**, 1628–1630.
18. Newton, M.I., Starke, T.K.H., Willis, M.R. and McHale, G. (2000) *Sensors and Actuators, B: Chemical*, **B67(3)**, 307–311.
19. Spadavecchia, J., Ciccarella, G., Rella, R., Capone, S. and Siciliano, P. (2003) *Sensors and Actuators, B: Chemical*, **B96(3)**, 489–497.
20. Nicholson, M.M. Electrochromism and Display Devices. In *Phthalocyanines Properties and Applications*; Leznoff, C.C. and Lever, A.B.P. (eds.); VCH Publishers, Vol. 3, 75–117, 1989.
21. Kasai, H., Nalwa, H.S., Oikawa, H., Okada, S., Mastuda, H., Minami, N., Kakuta, A., Ono, K., Mukoh, A. and Nakanish, H. (1992) *Japanese Journal of Applied Physics, Part 2: Letters*, **31(8A)**, 1132–1134.
22. Wang, X., Yang, K., Ye, H., Wang, Y., Lee, J.S. and Sandman, D.J. (2006) *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **43(12)**, 1937–1943.
23. Fox, J.P. and Goldberg, D.P. (2003) *Inorganic Chemistry*, **42(25)**, 8181–8191.