Inorg. Chem. **2006**, *45*, 1667−1676

Inorganic Chemistry

Article

Synthesis, Structure, and Spectroscopic and Magnetic Properties of Mesomorphic Octakis(hexylthio)-Substituted Phthalocyanine Rare-Earth Metal Sandwich Complexes

Ayşe Gül Gürek,[†] Tamara Basova,*[,‡] Dominique Luneau,*[,§,||] Colette Lebrun,[||] Evgeny Kol'tsov,[‡] Aseel K. Hassan,*[,⊥] and Vefa Ahsen*[,†,#]

Department of Chemistry, Gebze Institute of Technology, P.O. Box 141, 41400 Gebze-Kocaeli, Turkey, Nikolaev Institute of Inorganic Chemistry, Lavrentiev Pr. 3, Novosibirsk 630090, Russia, TÜBITAK Marmara Research Center, Materials Research Institute, P.O. Box 21, 41470 Gebze-Kocaeli, Turkey, Laboratoire des Multimatériaux et Interfaces (UMR 5615), Université Claude Bernard Lyon I, Bât. J. Raulin Campus de la Doua, 69622 Villeurbanne Cedex, France, Service de Chimie Inorganique et Biologique, DRFMC, CEA-Grenoble, 17 rue des Martys 38054 Grenoble Cedex 9, France, and Materials and Electronics Research Institute (MERI), Sheffield Hallam University City Campus, Pond Street, Sheffield S1 1WB, U.K.

Received October 10, 2005

The syntheses of new bis[octakis(hexylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes $[(C_6S)_8\text{-}Pc]_2M$ (M = Gd^{III}, Dy^{III}, and Sm^{III}) (**2**–**4**, respectively) are described. These compounds are very soluble in most common organic solvents. They have been fully characterized using elemental analysis, infrared, UV–vis spectroscopy, and mass spectrometry. The crystal structures of compounds **2**–**4** have been determined by X-ray diffraction on a single crystal. They are isostructural and crystallize in the monoclinic space group (space group *C*2/*c*). Their lattice constants have been determined in the following order: (**2**) $a = 31.629(4)$ Å, $b = 32.861(4)$ Å, $c = 20.482(2)$ Å, $\beta = 126.922(2)°$, $V = 17019(3)$ Å^3; (**3**) $a = 31.595(2)$ Å, $b = 32.816(2)$ Å, $c = 20.481(1)$ Å, $\beta = 127.005(1)°$, $V = 16958(2)$ Å^3; (**4**) $a = 31.563(2)$ Å, $b = 32.796(2)$ Å, $c = 20.481(1)$ Å, $\beta = 127.032°$, $V = 16924(2)$ Å^3. The magnetic properties of compounds **2**–**4** were studied, and it was revealed that the lanthanide ions and the radical delocalized on the two phthalocyanine rings are weakly interacting. The mesogenic properties of these new materials were studied by differential scanning calorimetry and optical microscopy. These phthalocyanine derivatives form columnar-hexagonal (Col$_h$) mesophases. Thin films of bis[octakis(hexylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes (**2**–**4**) were prepared by a spin-coating technique. Thermally induced molecular reorganization within films of bis[octakis(hexylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes (**2**–**4**) was studied by the methods of ellipsometry, UV–vis absorption spectroscopy, and atomic force microscopy. Heat treatment produces molecular ordering, which is believed to be due to stacking interaction between neighboring phthalocyanine moieties.

Introduction

Phthalocyanines (Pcs) have been widely used as dyes and pigments because of their high thermal and chemical stability. They now draw interest as materials for optical recording media, nonlinear optical application, light absorption, electric conduction, photoconduction, energy conversion, electrode, chemical sensor, and catalyst.[1,2] The synthesis of Pcs with the ability to be deposited in thin films has received greater

---

* To whom correspondence should be addressed. E-mail: basova@che.nsk.su (T.B.), Dominique.luneau@univ-lyon1.fr (D.L.), a.hassan@ac.uk (A.K.H.), ahsen@gyte.edu.tr (V.A.).

[†] Gebze Institute of Technology.

[‡] Nikolaev Institute of Inorganic Chemistry.

[§] Université Claude Bernard Lyon I.

[||] CEA-Grenoble.

[⊥] Sheffield Hallam University City Campus.

[#] TÜBITAK Marmara Research Center, Materials Research Institute.

(1) Leznof, C. C., Lever, A. B. P., Eds. *Phthalocyanines, Properties and Applications*; VCH: Weinheim, Germany, 1989, 1993, 1993, and 1996; Vols. 1−4.

(2) (a) McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure, Function*; Cambridge University Press: Cambridge, U.K., 1998. (b) Simon, J.; Bassoul, P. *Design of Molecular Materials: Supramolecular Engineering*; Wiley-VCH: Weinheim, Germany, 2000.

10.1021/ic051754n CCC: $33.50

attention for practical reasons. Pc compounds with various substituted groups have been synthesized.[3] The most common substituents are alkyl, alkoxy, or alkoxymethyl chains.[4]

When substituents are placed on the Pc ring, not only does the solubility of the compound increase but supramolecular organization can be achieved too. Pc mesogenity was first demonstrated in alkoxymethyl-substituted copper phthalocyanine in 1982.[5] The aromatic ring can be considered as the core of a discotic mesogen, forming a supramolecular organization and exhibiting columnar mesophases. Liquid-crystalline Pcs offer the possibility of combining the optoelectronic properties of Pcs with the orientational control of conventional liquid-crystal systems. The columnar architecture of the mesophase suggests the possibility of using them as anisotropic conductors.[4c] Since the discovery of mesogenity, a variety of mesogenic Pcs have been prepared.[2,6] The application potential of Pc films heavily depends on the ability to prepare them in thin films by vacuum deposition, organic molecular beam epitaxy,[7,8] and Langmuir−Blodgett film formation.[9,10] Spin-coating technology has also been demonstrated as a useful method of preparing oriented Pc films.[2,11,12] The relationship between the physical properties of Pc films and the molecular orientation was widely investigated in recent years by employing different experimental techniques.[9,10,13,14]

Sandwich-type phthalocyaninato double deckers, in which the large conjugated π systems are held in close proximity by rare-earth ions, have attracted great attention because of their application in organic materials science.[15,16] These types of molecules have recently been found to be good candidates for potential applications in the fields of molecular electronics, molecular optronics, and molecular iono-electronics.[17,18] One of the main applications of bis(Pc)s is as resistive or voltammetric sensors. In these applications, the variations in the conductive or electrochemical properties of bis(phthalocyaninato)lanthanide complexes are measured upon of their films to gases or liquids.[19] The structures of the rare-earth bis(Pc) complexes have been studied. Several structures of the bis(phthalocyaninato)lanthanide complexes have been reported.[20] X-ray diffraction studies of bis(phthalocyaninato)lanthanide complexes show that they are sandwich-type compounds in which the lanthanide metal ion (M^{3+}) is 8-fold-coordinated to the isoindole nitrogens of the Pc rings. The difference in the Pc ring distortions has been suggested to arise from the localization of the unpaired spin on the more distorted ring, and initial descriptions of the UV−vis absorption spectra of the bis(phthalocyaninato)lanthanide complexes appeared to be consistent with a localized model.[17b,18b,21]

---

(3) Gürek, A. G.; Bekaroğlu, Ö. *J. Chem. Soc., Dalton Trans*. **1994**, 1419.

(4) (a) van der Pol, J. F.; Neelman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W. *Trav. Chim. Pays-Bas* **1988**, *107*, 615. (b) Souten, P. G.; Warman, J. W.; Haas, M. P.; van Nostrum, C. F.; Gelinck, G. H.; Nolte, R. J. M.; Copyn, M. J.; Zwikker, J. W.; Engel, M. K.; Hanack, M.; Chang, Y. H.; Ford, W. T. *J. Am. Chem. Soc*. **1994**, *116*, 6880. (c) Simon, J.; Bassoul, P. Phthalocyanine-Based Liquid Crystals: Towards Submicronic Devices. In *Phthalocyanines, Properties and Application*; Leznof, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, Germany, 1993; Vol. 2, p 223. (d) Guillon, D.; Skoulios, A.; Piechocki, C.; Simon, J.; Weber, P. *Mol. Cryst. Liq. Cryst*. **1983**, *100*, 275. (e) Piechocki, C.; Simon, J.; André, J. J.; Guillon, D.; Petit, P.; Skoulios, A.; Weber, P. *Chem. Phys. Lett*. **1985**, *122*, 124. (f) Engel, M. K.; Bassoul, P.; Bosio, L.; Lehmann, H.; Hancak, M.; Simon, J. *Liq. Cryst*. **1993**, *15*, 709. (g) Ohta, K.; Jacquemin, L.; Sirlin, C.; Bosio, L.; Simon, J. *New J. Chem*. **1988**, *12*, 751. (h) Clarkson, G. J.; McKeown, N. B.; Treacher, K. E. *J. Chem. Soc., Perkin Trans*. **1995**, *1*, 1817.

(5) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc*. **1982**, *104*, 5245.

(6) (a) Masurel, D.; Sirlin, C.; Simon, J. *New J. Chem*. **1987**, *11*, 455. (b) Kroon, J. M.; Koehrost, R. B. M.; Van Dijk, M.; Sanders, G. M.; Sudhölter, E. J. R. *J. Mater Chem*. **1997**, *7*, 615. (c) Gürek, A. G.; Ahsen, V.; Heinemann, F.; Zugenmaier, P. *Mol. Cryst. Liq. Cryst*. **2000**, *338*, 75. (d) Dabak, S.; Ahsen, V.; Heinemann, F.; Zugenmaiere, P. *Mol. Cryst. Liq. Cryst*. **2000**, *348*, 111. (e) Gürek, A. G.; Durmuş, M.; Ahsen, V. *New J. Chem*. **2004**, *28*, 693.

(7) Evans, D. A.; Steiner, H. J.; Middleton, R.; Jones, T. S.; Chen, C. H.; Horn, K.; Park, S.; Kampen, T. U.; Tenne, D.; Zahn, D. R. T.; Patchett, A.; McGovern, I. T. *Appl. Surf. Sci*. **2001**, *175−176*, 374.

(8) Schmidt, A.; Chan, L. K.; Back, A.; Armstrong, N. R. Epitaxial Phthalolcyanine Ultrathin Films Grown by Organic Molecular Beam Epitaxy (OMBE). In *Phthalocyanines, Properties and Applications*; Leznof, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, Germany, 1996; Vol. 4, p 307.

(9) Rella, R.; Serra, A.; Siciliano, P.; Tepore, A.; Valli, L.; Zocco, A. *Supramol. Sci*. **1997**, *4*, 461.

(10) Nakahara, H.; Sun, K. Z.; Fukuda, K.; Azuma, N.; Nishi, H.; Uchida, H.; Katsube, T. *J. Mater. Chem*. **1995**, *5*, 395.

(11) Hassan, B. M.; Li, H.; McKeown, N. B. *J. Mater. Chem*. **2000**, *10*, 39.

(12) Ali-Adib, Z.; Clarkson, G. J.; McKeown, N. B.; Treacher, K. E.; Gleeson, H. F.; Stennett, A. S. *J. Mater. Chem*. **1998**, *8*, 2371.

(13) Ueda, Y.; Watanabe, M.; Yamaguchi, H. *Mol. Cryst. Liq. Cryst*. **1995**, *267*, 175.

(14) Chau, L.-K.; Chen, S.-Y.; Armstrong, N. R.; Collins, G. E. *Mol. Cryst. Liq. Cryst*. **1994**, *252*, 67.

(15) Kirin, I. S.; Moskalev, P. N.; Makashev, Yu. A. *Russ. J. Inorg. Chem*. **1965**, *10*, 1065.

(16) Kirin, I. S.; Moskalev, P. N.; Ivannikova, N. V. *Russ. J. Inorg. Chem*. **1967**, *12*, 497.

(17) (a) Andre, J.-J.; Holczer, K.; Petit, P.; Riou, M.-T.; Clarisse, C.; Even, R.; Fourmigue, M.; Simon, J. *Chem. Phys. Lett*. **1985**, *115*, 463. (b) Markovitsi, D.; Train-Thi, T.-H.; Even, R.; Simon, J. *Chem. Phys. Lett*. **1987**, *142*, 107. (c) Mardru, M.; Guillaud, G.; Al sadoun, M.; Maitrot, C.; Clarisse, C.; Le Contellec, M.; Andre, M. J.-J.; Simon, J. *Chem. Phys. Lett*. **1987**, *142*, 103. (d) Turek, P.; Petit, P.; Andre, J.-J.; Simon, J.; Even, R.; Boudjema, B.; Guillaud, G.; Maitrot, M. *J. Am. Chem. Soc*. **1987**, *109*, 5119. (e) Simon, J.; Tournilhac, F.; Andre, J.-J. *Appl. Phys*. **1987**, *62*, 3304. (f) Toupance, T.; Ahsen, V.; Simon, J. *J. Chem. Soc., Chem. Commun*. **1994**, 75. (g) Toupance, T.; Ahsen, V.; Simon, J. *J. Am. Chem. Soc*. **1994**, *116*, 5352.

(18) (a) Maitrot, M.; Guillaud, G.; Boudjema, B.; Andre, J.-J.; Strzelecka, H.; Simon, J.; Even, R. *Chem. Phys. Lett*. **1987**, *133*, 59. (b) Tran-Thi, T.-H.; Markovitsi, D.; Even, R.; Simon, J. *Chem. Phys. Lett*. **1987**, *139*, 207. (c) Belarbi, Z.; Maitrot, M.; Ohta, K.; Simon, J.; Andre, J.-J.; Petit, P. *Chem. Phys. Lett*. **1988**, *143*, 400. (d) Madru, R.; Guillard, G.; Al Sadoun, M.; Maitrot, M.; Andre, J.-J.; Simon, J.; Even, R. *Chem. Phys. Lett*. **1988**, *145*, 343.

(19) (a) Aroca, R.; Bolourchi, H.; Battsti, D.; Najafi, K. *Langmuir* **1993**, *9*, 3138. (b) Gorbunova, Y.; Rodriguez-Méndez, M. L.; Souto, J.; Tomilova, L.; de Saja, J. A. *Chem. Mater*. **1995**, *7*, 1443. (c) Arrieta, A.; Rodriguez-Méndez, M. L.; de Saja, J. A. *Sens. Actuators, B* **2003**, *95*, 357.

(20) (a) Kosuga, K.; Tsutsui, M.; Patterson, R. C.; Tatsumi, K.; Van Opdenbosch, N.; Pepe, G., Jr.; Meyer, E. F. *J. Am. Chem. Soc*. **1980**, *102*, 4835. (b) Engel, M. K. *Rep. Kawamura Inst. Chem. Res*. **1997**, *8*, 11. (c) De Cian, A.; Moussavi, M.; Fischer, J.; Weiss, R. *Inorg. Chem*. **1985**, *24*, 3162. (d) Moussavi, M.; De Cian, A.; Fischer, J.; Weiss, R. *Inorg. Chem*. **1988**, *27*, 1287. (e) Sullivan, B. W.; Dominey, R. N.; Helms, J. H.; Schwartz, M. L.; Ter Haar, W.; Hatfield, W. E. *Mol. Cryst. Liq. Cryst*. **1985**, *120*, 433. (f) Darovskikh, A. N.; Frank-Kamenetskaya, O. V.; Fundamenskii, V. S.; Golubev, A. M. *Sov. Phys. Crystallogr*. **1986**, *31*, 165. (g) Darovskikh, A. N.; Tytsenko, A. K.; Frank-Kamenetskaya, O. V.; Fundamenskii, V. S.; Moskalev, P. N. *Sov. Phys. Crystallogr*. **1984**, *29*, 273. (h) Darovskikh, A. N.; Frank-Kamenetskaya, O. V.; Fundamenskii, V. S.; Golynskaya, O. A. *Sov. Phys. Crystallogr*. **1985**, *3*, 631. (i) Paillaud, J. L.; Drillon, M.; De Cian, A.; Fischer, J.; Weiss, R. G.; Villeneuve, R. *Phys. Rev. Lett*. **1991**, *67*, 244. (j) Gürek, A. G.; Ahsen, V.; Luneau, D.; Pècaut, J. *Inorg. Chem*. **2001**, *40*, 4793.

Early examples of octakis(alkylthio)-substituted Pcs have been described in the literature.[3,6c,d,22−28] In this paper, we present the results of experimental work on an investigation of the liquid-crystalline properties and the crystal structure of bis[octakis(hexylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes $[(C_6S)_8Pc]_2M$ (M = Gd^{III}, Dy^{III}, and Sm^{III}) (**2**−**4**, respectively). Substituents on the periphery of macrocycle rings in bis(Pc)s are known to influence the physicochemical properties of these compounds. It has been already shown that paraffinic chain substituted bis(Pc)s exhibit liquid-crystalline properties.[28−30] The investigation of the thermally induced molecular reorganization within spin-coated films of bis[octakis(hexylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes (**2**−**4**) by the methods of ellipsometry, UV−vis absorption spectroscopy, and atomic force microscopy (AFM) is also reported.

Experimental Section

Materials. 1,2-Bis(hexylthio)-4,5-dicyanobenzene (**1**) was synthesized according to a reported procedure.[3] All other reagents and solvents were of reagent-grade quality, were obtained from commercial suppliers, and were dried as described by Perrin and Armarego[31] before use.

Measurements. Elemental analysis was performed on a Carlo Erba elemental analyzer. Infrared spectra in KBr pellets were recorded on a Bio-Rad FTS 175C Fourier transform infrared spectrophotometer. The mass spectra were recorded on a LCQ ion trap (Thermofinnigan, San Jose, CA), equipped with an electrospray (ES) source. ES full scan spectra, in the range of *m*/*z* 50−2000 amu or *m*/*z* 2000−3000 amu, were obtained by infusion through fused-silica tubing at 2−10 μL min^{-1}. The solutions were analyzed in the positive mode. The LCQ calibration (*m*/*z* 50−2000) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine, MRFA, and Ultra mark 1621). An ES-Tuning Mix solution (Agilent) was used to calibrate the spectrometer between 2000 and 3000 amu. The temperature of the heated capillary of the LCQ was set to the range of 180−200 °C, and the ion spray voltage was in the range of 1−7 kV with an injection time of 5−200 ms. Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with a O-SMA, Si-diode array in backscattering geometry. The 488-nm, 150-mW line of an Ar laser was used for the spectral excitation.

Synthesis. Bis[4,5,4′,5′,4″,5″,4‴,5‴-octakis(hexylthio)phthalocyanine]gadolinium(III) (2). A round-bottomed flask fitted with a condenser was degassed and flame-dried under dry argon. The flask was charged under argon with the dinitrile derivative **1** (1.81 g, 5 mmol), anhydrous Gd(OAc)$_3$ (0.27 g, 0.80 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 405 μL, 2.70 mmol), and 16 mL of hexan-1-ol. The mixture was refluxed under argon for 48 h. Evaporation of the hexan-1-ol under reduced pressure left a greenish-brown waxy residue. It was dissolved and heated under reflux in methanol (30 mL) and then separated by decantation. This purification step was repeated three times. Purification was further achieved by (i) column chromatography over silica gel [CH_2Cl_2/*n*-hexane, 5:3 (v/v)] and (ii) two successive preparative thin-layer chromatographies [silica gel; eluent CH_2Cl_2/*n*-hexane, 1:1 (v/v); $R_f = 0.60$]. Crystallization from a CH_2Cl_2/EtOH (5:1, v/v) mixture led to 0.55 g (29%) of brownish-green crystals. Anal. Calcd for $C_{160}H_{224}GdN_{16}S_{16}$ (M_w = 3041): C, 63.17; H, 7.42; N, 7.37. Found: C, 62.75; H, 7.22; N, 7.12. IR (KBr): ν_{max} (cm^{-1}) 3020, 2980, 2820, 1580, 1500, 1450, 1400, 1380, 1310, 1280, 1070, 940, 750. MS (ES−MS): *m*/*z* (%) 3042 $[M + H]^+$ (100), 1521 $[M]^{2+}$ (5).

Bis[4,5,4′,5′,4″,5″,4‴,5‴-octakis(hexylthio)phthalocyanine]dysprosium(III) (3). Compound **3** was prepared by the same procedure as that described for **2** by starting with **1** (1.81 g, 5 mmol), anhydrous Dy(OAc)$_3$ (0.28 g, 0.80 mmol), DBU (408 μL, 2.70 mmol), and 16 mL of hexan-1-ol. The purification of **3** was further achieved by (i) column chromatography over silica gel [CH_2Cl_2/*n*-hexane, 5:3 (v/v)] and (ii) two successive preparative thin-layer chromatographies [silica gel; eluent CH_2Cl_2/*n*-hexane, 1:1 (v/v); $R_f = 0.65$]. Crystallization from a CH_2Cl_2/EtOH (5:1, v/v) mixture led to 0.68 g (36%) of brownish-green crystals. Anal. Calcd for $C_{160}H_{224}DyN_{16}S_{16}$ (M_w = 3045): C, 63.07; H, 7.41; N, 7.36. Found: C, 63.13; H, 7.65; N, 7.32. IR (KBr) ν_{max} (cm^{-1}): 3025, 2980, 2825, 1580, 1500, 1440, 1400, 1380, 1320, 1280, 1070, 940, 750. MS (ES−MS): *m*/*z* (%) 3046 $[M + H]^+$ (100), 1523 $[M]^{2+}$ (12).

Bis[4,5,4′,5′,4″,5″,4‴,5‴-octakis(hexylthio)phthalocyanine]samarium(III) (4). Compound **4** was prepared by the same procedure as that described for **2** by starting with **1** (1.81 g, 5 mmol), anhydrous Sm(OAc)$_3$ (0.262 g, 0.80 mmol), DBU (408 μL, 2.70 mmol), and 16 mL of hexan-1-ol. The purification of **4** was further achieved by (i) column chromatography over silica gel [CH_2Cl_2/*n*-hexane, 5:3 (v/v)] and (ii) two successive preparative thin-layer chromatographies [silica gel; eluent CH_2Cl_2/*n*-hexane, 1:1 (v/v); $R_f = 0.55$]. Crystallization from a CH_2Cl_2/EtOH (5:1, v/v) mixture led to 0.58 g (30%) of dark-green crystals. Anal. Calcd for $C_{160}H_{224}SmN_{16}S_{16}$ (M_w = 3034): C, 63.32; H, 7.44; N, 7.38. Found: C, 63.62; H, 7.87; N, 7.22. IR (KBr) ν_{max} (cm^{-1}): 3020, 2980, 2830, 1585, 1510, 1460, 1400, 1375, 1320, 1280, 1070, 940, 760. MS (ES− MS): *m*/*z* (%) 3035 $[M + H]^+$ (100), 1518 $[M]^{2+}$ (6).

Methods of Investigation of the Mesogenic Properties of Pcs. The phase-transition behavior of these compounds was observed by means of a polarizing microscope (Leitz Wetzler Orthoplan-pol.) equipped with a hot stage (Linkam TMS 93) and temperature controller (Linkam LNP). Transition temperatures were determined with a scan rate of 10 °C min^{-1} using a Mettler Toledo Star thermal analysis system/DSC 822. A differential scanning calorimetry (DSC) system was calibrated with indium from 3−4 mg samples under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo Star thermal analysis system/

---

(21) (a) Ishikawa, N.; Ohno, O.; Kaizu, Y. *J. Phys. Chem.* **1993**, *97*, 1004. (b) Van Cott, T. C.; Gasyna, Z.; Schatz, P. N.; Boyle, M. E. *J. Phys. Chem.* **1995**, *99*, 4820.

(22) Cho, I.; Lim, Y. *Mol. Cryst. Liq. Cryst.* **1988**, *154*, 9.

(23) Matsuda, H.; Okada, S.; Masaki, A.; Nakanishi, H.; Suda, Y.; Shigehara, K.; Yamada, A. *Proc. SPIE−Int. Soc. Opt. Eng.* **1990**, *1337*, 105.

(24) Suda, Y.; Shigehara, K.; Yamada, A.; Matsuda, H.; Okada, S.; Masaki, A.; Nakanishi, H. *Proc. SPIE−Int. Soc. Opt. Eng.* **1991**, *1560*, 75.

(25) (a) Lux, A.; Rozenberg, G. G.; Petritsch, K.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Synth. Met.* **1999**, *102*, 1527. (b) Gürol, I.; Ahsen, V.; Bekaroğlu, Ö. *J. Chem. Soc., Dalton Trans.* **1994**, 497.

(26) Eichorn, H.; Wöhrle, D.; Pressner, D. *Liq. Cryst.* **1997**, *22*, 643.

(27) Ban, K.; Nishizawa, K.; Ohta, K.; Shirari, H. *J. Mater. Chem.* **2000**, *10*, 1083.

(28) (a) Ban, K.; Nishizawa, K.; Ohta, K.; van de Craats, A. M.; Warman, J. M.; Yamamoto, I.; Shirari, H. *J. Mater. Chem.* **2001**, *11*, 321. (b) Komatsu, T.; Ohta, K.; Watanabe, T.; Ikemoto, H.; Fujimoto, T.; Yamamoto, I. *J. Mater. Chem.* **1994**, *4*, 537.

(29) Basova, T.; Kol'tsov, E.; Hassan, A. K.; Nabok, A.; Ray, A. K.; Gürek, A. G.; Ahsen, V. *J. Mater. Sci.: Mater. Electron.* **2004**, *15*, 623.

(30) Toupance, T.; Bassoul, P.; Mineau, L.; Simon, J. *J. Phys. Chem.* **1996**, *100* (28), 11704.

(31) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, U.K., 1980.

Table 1. Summary of Crystallographic Data for Compounds **2**−**4**

	2	**3**	**4**
formula	$C_{160}H_{224}N_{16}S_{16}Gd$	$C_{160}H_{224}N_{16}S_{16}Dy$	$C_{160}H_{224}N_{16}S_{16}Sm$
fw	3041.76	3047.01	3034.86
temperature (K)	298(2)	298(2)	298(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	31.595(2)	31.563(2)	31.629(4)
b (Å)	32.816(2)	32.796(2)	32.861(4)
c (Å)	20.481(1)	20.481(1)	20.482(2)
β (deg)	127.005(1)	127.032(1)	126.922(2)
V (Å^3)	16958(2)	16924(2)	17019(3)
Z	4	4	4
D_c (g cm^{-3})	1.191	1.196	1.184
μ_{abs} (mm^{-1})	0.639	0.690	0.592
R^a [$I > 2\sigma(I)$]	0.0434	0.0526	0.1052
Rw^a (all data)	0.1280	0.1464	0.2462

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $Rw(F^2) = \Sigma[w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

TGA/SDTA 851 at a heating rate of 10 °C min^{-1} in a nitrogen flow (50 mL min^{-1}).

Film Preparation and Characterization. A small volume of a solution of $[(C_6S)_8Pc]_2M$ molecules in chloroform (1 mg mL^{-1}) was dispensed via a glass pipet onto an ultrasonically cleaned substrate held onto a photoresist spinner (Microsystem model 4000). The speed of the substrate rotation was 2000 rpm. Spinning was continued for 30 s, during which time the solvent had evaporated to generate a film of the Pc derivative. Some films of $[(C_6S)_8Pc]_2M$ were heated to a temperature of 270 °C for a period of about 2 h and then slowly cooled to room temperature. The cooling rate was approximately 5 °C min^{-1}. The substrates used were varied according to experimental requirements for different characterization.

Absorption spectra of the solutions and films on quartz substrates were recorded with a UV−vis scanning spectrophotometer (Shimadzu UV−vis 3101 PC) in the range of 350−800 nm.

Spectroscopic ellipsometric measurements on spun $[(C_6S)_8Pc]_2M$ films on silicon substrates were performed by using a Woolam TMVM 2000 rotating analyzer spectroscopic ellipsometer in the spectral range of 370−1000 nm. The angle of incidence was fixed at the angle of 60°. The dedicated software is used for data acquisition and analysis of the measured ellipsometric parameters $\Psi(\lambda)$ and $\Delta(\lambda)$.

Surface morphologies of spin-coated $[(C_6S)_8Pc]_2M$ films were investigated by using AFM. The tapping-mode AFM images were taken at room temperature using a Nanoscope IIIa instrument with tips of about 4 nm in radius.

X-ray Crystallography. Data for compounds **2**−**4** were collected at room temperature (298 K) with a Bruker SMART CCD diffractometer equipped with a graphite-monochromatized normal-focus molybdenum-target X-ray tube. The data were processed through the SAINT reduction and absorption correction software[32] to give 54 387 collected reflections, from which 20 361 were independent. The structures were solved and refined on F^2 using *SHELXTL*[33] software. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement steps, in calculated positions, and with isotropic thermal parameters. Crystallographic data and structure refinement parameters are summarized in Table 1, and selected bond lengths and angles are given in Table 2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $LnPc_2$[a]

	1 (Ln = Gd)	**2** (Ln = Dy)	**3** (Ln = Sm)
Ln−N1	2.435(3)	2.409(4)	2.468(3)
Ln−N2	2.431(3)	2.413(4)	2.466(4)
Ln−N3	2.428(3)	2.412(4)	2.460(4)
Ln−N4	2.423(3)	2.412(4)	2.439(4)
N1−Ln−N1#1	141.18(11)	141.25(18)	141.78(15)
N1−Ln−N2	69.64(9)	70.25(12)	68.61(11)
N1−Ln−N2#1	81.80(9)	81.11(12)	83.52(12)
N1−Ln−N3	108.37(9)	109.19(13)	106.67(13)
N1−Ln−N3#1	84.69(9)	83.84(12)	86.09(13)
N1−Ln−N4	70.36(8)	70.45(12)	69.33(11)
N1−Ln−N4#1	146.21(9)	146.03(12)	146.69(11)
N2−Ln−N2#1	84.90(12)	84.18(18)	86.32(19)
N2−Ln−N3	70.11(8)	70.36(12)	69.45(12)
N2−Ln−N3#1	146.56(9)	146.23(12)	146.96(11)
N2−Ln−N4	108.38(9)	109.04(13)	106.78(14)
N2−Ln−N4#1	141.58(10)	141.29(12)	141.90(11)
N3−Ln−N3#1	140.87(12)	141.02(18)	140.98(17)
N3−Ln−N4	69.80(9)	70.34(12)	69.17(12)
N3−Ln−N4#1	81.17(9)	80.73(13)	82.14(14)
N4−Ln−N4#1	83.75(12)	83.58(18)	84.99(18)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, y, $-z + 1/2$.

Magnetic Susceptibility Measurements. The magnetic properties were measured on a Quantum Design MPMS SQUID. The thermal dependence of the magnetic susceptibility was measured in the 6−300 K temperature range at a field strength of 0.5 T. The magnetization was measured at 2 K in the field range 0 T. The data were corrected for diamagnetism.

Results and Discussion

Synthesis and General Properties. The hexylthio-substituted Pc rare-earth metal double-decker complexes {$[(C_6S)_8Pc]_2Gd$ (**2**), $[(C_6S)_8Pc]_2Dy$ (**3**), and $[(C_6S)_8Pc]_2Sm$ (**4**)} were synthesized in one step (about 30% yield) using the chemical pathway[20j,34] starting from **1** according to the literature (Scheme 1).[23j] Purification was achieved by successive column and preparative thin-layer chromatographies and recrystallization from a CH_2Cl_2/EtOH mixture. Compounds **2**−**4** are soluble in most organic solvents ($CHCl_3$, *n*-hexane, CCl_4, diethyl ether, dimethylformamide, dimethyl sulfoxide, etc.) but insoluble in acetone, ethyl acetate, and alcohols.

Mass spectrometries of compounds **2**−**4** have been carried out showing parent ions at *m*/*z* 3042, 3046, and 3035, respectively, by using an ES technique. The first fragment ion corresponds to double-charged molecules (see the Experimental Section).

Crystal Structure. The crystal structures of compounds **2**−**4** were found to be isostructural to the lutetium compound previously described.[20j] A view of the molecular structure is shown in Figure 1 for compound **2**. The complex $[(C_6H_{13}S)_8Ln]$ is located on the 2-fold axis special position. The sandwiched lanthanum is 8-fold-coordinated by the isoindole nitrogen (N_{iso}) of the two Pc macrocycle rings, which are rotated by a staggering angle of 42.39° (**2**), 42.49° (**3**), and 42.45° (**4**). The geometry of the coordination polyhedron around the lanthanum ion is a slightly distorted

---

(32) *SAINT*, 4.050 ed.; Brucker Analytical X-ray Instruments, Inc.: Madison, WI, 1998.

(33) *SHELXTL*, 5.030 ed.; Brucker Analytical X-ray Instruments, Inc.: Madisson, WI, 1998.

(34) Belarbi, Z.; Sirlin, C.; Simon, J.; André, J.-J. *J. Phys. Chem.* **1989**, *93*, 8105.

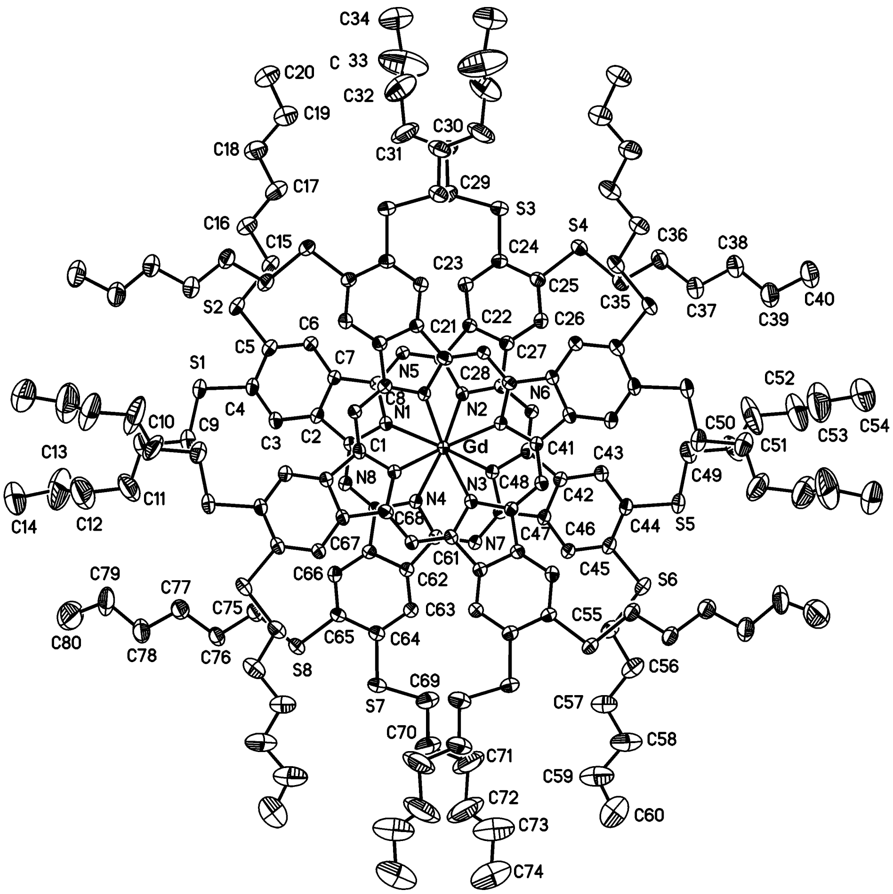
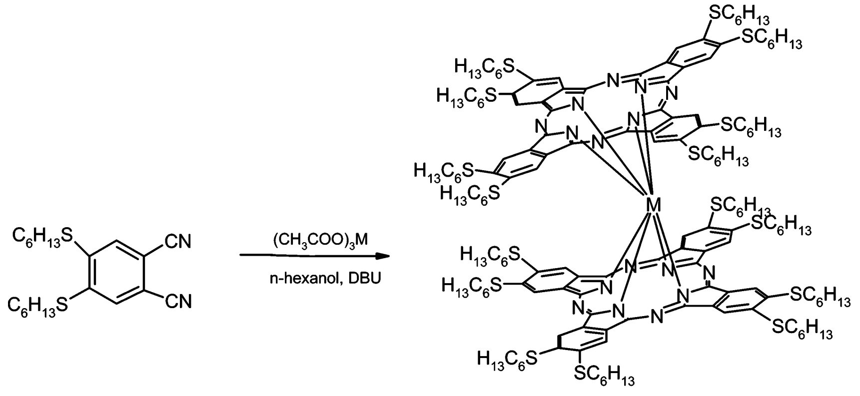


Figure 1. View of the molecular structure of the bis(phthalocyaninato)gadolinium(III) complex (**2**) with atom labeling and ellipsoids at 30% probability.

Scheme 1. Synthetic Route of Bis[octakis(hexylthio)phthalocyaninato] Rare-Earth Metal(III) Complexes



	M
2	Gd
3	Dy
4	Sm

antiprism. The four N_{iso}'s deviate by ±0.001 Å (**2** and **3**) and ±0.005 Å (**4**) from their mean plane so that they are practically coplanar. The lanthanum ion is located at 1.421 Å (Gd), 1.399 Å (Dy), 1.467 Å (Sm) from this mean plane. The $Ln-N_{iso}$ bond lengths are not equal and range from 2.423 to 2.435 Å (Gd), from 2.412 to 2.409 Å (Dy), and from 2.439 to 2.468 Å (Sm) (Table 2). The interplanar distances between the two Pc rings, defined as the distance between the mean planes of the four N_{iso}'s, are 2.842 Å (Gd), 2.798 Å (Dy), and 2.934 Å (Sm), which are in the range (2.67−2.70 Å) of the values normally reported for $LnPc_2$ or $[LnPc_2]^-$ complexes. The Pc rings are distorted from planarity, as was generally observed, and have a saucer shape.

In the crystal, the molecules of $[(C_6H_{13}S)_8Pc]_2Ln$ are stacked in columns along the *a*-axis direction with a brickstone-like arrangement. The separation distance between the molecules in the column is equal to the *a*-axis length [31.629 Å (Gd), 31.595 Å (Dy), and 31.563 Å (Sm); Figure 2). However, the shortest intermolecular distances are found along the *c*-axis direction, where the molecule arrangement may be described as slipped-stacked columns (Figure 2) in

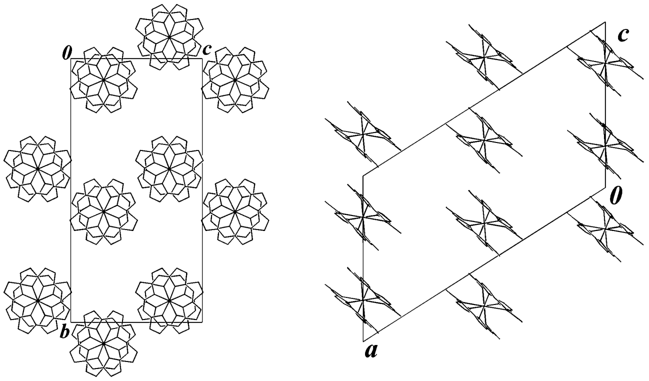


Figure 2. Crystal packing view along the *a* and *b* axes.

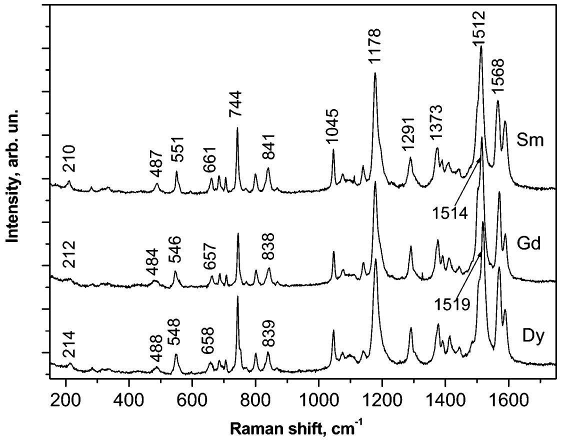


Figure 3. Raman spectra of $[(C_6S)_8Pc]_2M$ at room temperature.

which the lanthanum(III) ions make a zigzag chain with intermetallic Ln−Ln distances of 11.515 Å (Gd), 11.523 Å (Dy), and 11.503 Å (Sm) and Ln−Ln−Ln angles of 125.57° (Gd), 125.41° (Dy), and 125.82° (Sm). Along the columns (the *c*-axis direction), the shortest intermolecular distances, taking into account only the non-hydrogen atoms, are found between the C26 of the phenyl ring (C22−C23−C24−C25−C26) and the N6 nitrogen atom of a neighboring molecule. Shorter intermolecular distances are found between the peripheral chains ($C_6H_{13}S$), but they are not expected to play a role in the magnetic exchange interaction pathway because of the weakness of spin delocalization.

Spectral Characterization. The Raman spectra of $[(C_6S)_8Pc]_2M$ at room temperature are presented in Figure 3. The spectral interpretation was made on the basis of comparisons with the Raman spectra of other substituted and unsubstituted bis(Pc)s.[35−39] Because of similar electronic and molecular structures, all members of the series of lanthanide bis(Pc)s show similar Raman characteristics. Vibrational frequencies in the range of 1300−1600 cm^{-1} are attributed to isoindole ring stretching and the aza group stretching.[35−39] The Raman bands in the range from 550 to 700 cm^{-1} and at 838−841 cm^{-1} correspond to Pc breathing.[34−38] There are several peaks lying in the range of 1000−1300 cm^{-1}, which are assigned to aromatic C−H bending. The low-frequency modes in the range of 210−500 cm^{-1} are characterized by a high contribution of metal−nitrogen stretching vibrations. Aza and isoindole stretching vibrations show a dependence on the central lanthanide ion. The frequency of vibration is found to increase with a decrease of the lanthanide ionic radius. This fact agrees with that found for other bis(Pc)s and reveals an increase of the $\pi-\pi$ interaction between two aromatic rings of the bis(Pc) along with a decrease of the central metal ionic radius.[39]

The absorption spectra of $[(C_6S)_8Pc]_2M$ solutions in chloroform are presented in Figure 4 (solid lines). The spectra of solutions in chloroform are characterized by an intense electronic absorption in the visible region: Q bands at 704, 711, and 714 nm for Dy, Gd, and Sm, respectively, and a B band in the near-ultraviolet at 392 nm. The blue-shift trend of the Q band in absorption spectra of $[(C_6S)_8Pc]_2M$ solutions along with the decrease of the lanthanide ionic radius is also apparent.

Mesogenic Properties of the $[(C_6S)_8Pc)]_2M$ (M = Gd^{III}, Dy^{III}, and Sm^{III}) Complexes. The series of bis[octakis-(alkylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes $[(C_nS)_8Pc]_2M$ (M = Eu^{III}, Tb^{III}, and Lu^{III}; $n = 8$, 10, 12, 14, and 16) have been synthesized, and their mesomorphism has been investigated by Ohta and co-workers.[28a] In the present work, we have investigated the mesogenic properties of the sandwich bis(Pc)s substituted with hexylthio groups $[(C_6S)_8Pc]_2M$ (M = Gd^{III}, Dy^{III}, and Sm^{III}). The phase-transition temperatures were determined by DSC. The DSC measurements were performed on about 4-mg samples of the virgin materials with a scanning rate of 10 °C min^{-1} over the temperature range of 25−290 °C. In Table 3, the phase-transition temperatures and the corresponding enthalpy changes of the $[(C_6S)_8Pc]_2M$ (M = Gd^{III}, Dy^{III}, and Sm^{III}) complexes (**2**−**4**) have been summarized. The sharpness of the melting point gives an indication of the purity of the compound. The clearing point enthalpy is much smaller than the melting enthalpy, which is due to the fact that for the mesophase-to-isotropic transition the structural rearrangement of the molecules is far more relevant than that for the solid-to-mesophase transition.

The mesophases of the Pc derivatives $[(C_6S)_8Pc]_2M$ (M = Gd^{III}, Dy^{III}, and Sm^{III}) (**2**−**4**, respectively) are apparently stable up to the decomposition temperature. The thermal stabilities of **2**−**4** have been investigated by TGA: the decompositions start at around 300 °C and become more significant around 400 °C (Table 4).

$[(C_6S)_8Pc]_2M$ (M = Gd^{III}, Dy^{III}, and Sm^{III}) (**2**−**4**, respectively) complexes show only one mesophase, Col$_h$. Transition temperatures of the octakis(alkylthio)-substituted mono(Pc)s are generally lower in comparison with those of their oxygen analogues[40] but also decrease with increasing chain length.[25,27,41] At the same time, in comparison with the

---

(35) Jiang, J.; Cornelissen, U.; Arnold, D.; Sun, X.; Homborg, H. *Polyhedron* **2001**, *20*, 557.

(36) Jiang, J.; Rintoul, L.; Arnold, D. *Polyhedron* **2000**, *19*, 1381.

(37) Battisti, D.; Tomilova, L.; Aroca, R. *Chem. Mater.* **1992**, *4*, 1323.

(38) Aroca, R.; Clavijo, R.; Jennings, C.; Kovacs, G.; Duff, J.; Loutfy, R. *Spectrochim. Acta* **1989**, *45A*, 957.

(39) Pan, N.; Rintoul, L.; Arnold, D.; Jiang, J. *Polyhedron* **2002**, *21*, 1905.

(40) Ford, W. T.; Summer, L.; Zhu, W.; Change, Y. H.; Um, P.; Choi, K. H.; Heiney, P. A.; Maliszewskyj, N. C. *New J. Chem.* **1994**, *18*, 495.

(41) Van der Pool, J. F.; Neelmen, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W. *Liq. Cryst.* **1989**, *6*, 577.

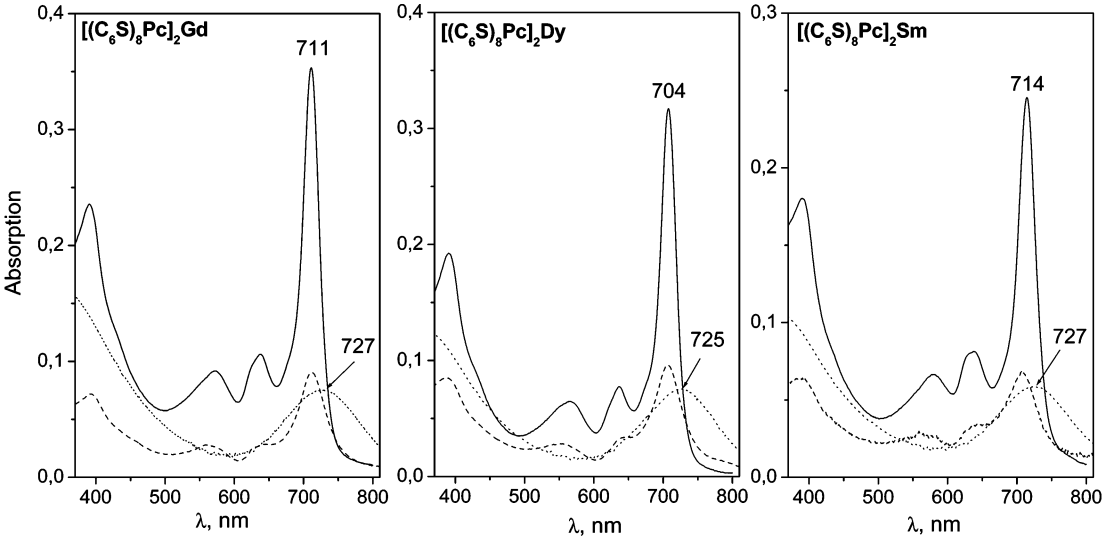


Figure 4. Absorption spectra of $[(C_6S)_8Pc]_2M$ solutions in chloroform (solid lines) and films on quarts before (dashed lines) and after (dotted lines) heating.

Table 3. Phase-Transition Temperature and Enthalpy Change Data of **2**−**4** Derivatives[a]

complex	phase $\xrightleftharpoons{T/°\mathrm{C}[\Delta H/\mathrm{kJ\ mol^{-1}}]}$ phase
$[(C_6S)_8Pc]_2Gd$ (**2**)	$\mathrm{K} \underset{81\ [29.86]}{\overset{52\ [22.75]}{\rightleftharpoons}} \mathrm{Col_h} \underset{265\ [10.98]}{\overset{258\ [7.18]}{\rightleftharpoons}} \mathrm{IL}$
$[(C_6S)_8Pc]_2Dy$ (**3**)	$\mathrm{K} \underset{82\ [25.12]}{\overset{55\ [15.53]}{\rightleftharpoons}} \mathrm{Col_h} \underset{263\ [10.54]}{\overset{250\ [8.19]}{\rightleftharpoons}} \mathrm{IL}$
$[(C_6S)_8Pc]_2Sm$ (**4**)	$\mathrm{K} \underset{81\ [28.38]}{\overset{60\ [16.92]}{\rightleftharpoons}} \mathrm{Col_h} \underset{248\ [8.74]}{\overset{240\ [6.64]}{\rightleftharpoons}} \mathrm{IL}$

[a] Phase nomenclature: K = crystal; Col_h = discotic hexagonal-columnar phase; IL = isotropic liquid.

Table 4. Thermal Properties of **2**−**4** Derivatives

complex	initial dec temp, °C	main dec temp, °C
2	300	378
3	310	391
4	304	396

analogue oxygen derivatives,[42−44] $[(C_6O)_8Pc]_2Gd$, $[(C_6O)_8Pc]_2Dy$, and $[(C_6O)_8Pc]_2Sm$, the alkylthio substitution results in decreasing melting points in octakis(alkylthio)-substituted bis(Pc)s.[28a,29] It can generally be said that alkylthio substitution according to alkyloxy substitution in mono- and bis(Pc) derivatives results in decreasing melting points.

Also, the phase-transition temperatures of complexes **2**−**4** have been determined by polarization microscopy as measured with DSC. The birefringent textures observed by polarizing optical microscopy were best observed upon cooling from the melt. The textures observed by microscopy for the studied complexes (**2**−**4**) are very similar to those described in refs 28a and 29. We deduced that the nature of the mesophases of $[(C_6S)_8Pc]_2Gd$, $[(C_6S)_8Pc]_2Dy$, and $[(C_6S)_8Pc]_2Sm$ are identical. Figure 5 shows the photomicrograph of the mesophase of the Sm^{III} complex at 140 °C. For this typical fan-shaped texture often observed for Col_h, these mesophases could be thus confirmed as the Col_h phases.[25−27,42−44]

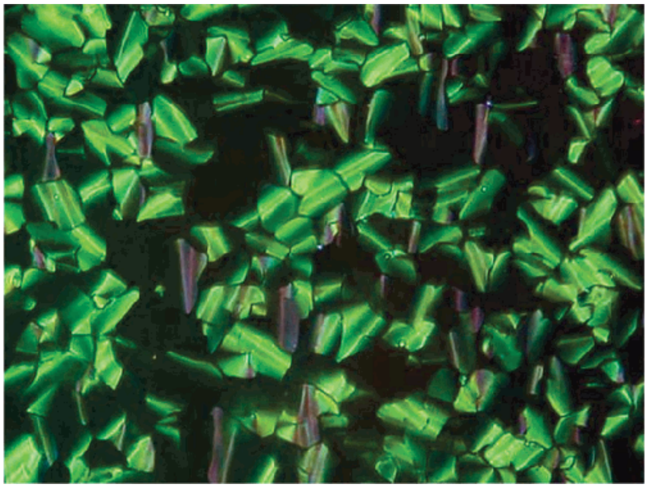


Figure 5. Optical texture of $[(C_6S)_8Pc]_2Sm$ (**4**) at 140 °C.

Film Properties. Absorption spectra of $[(C_6S)_8Pc]_2M$ films before and after heating are given in Figure 4. The spectra for $[(C_6S)_8Pc]_2M$ solutions in chloroform are also included for comparison. The absorption spectra of the films before heating (Figure 4, dashed lines) are similar to those of the chloroform solutions. The spectra of the $[(C_6S)_8Pc]_2M$ films after heating are significantly different from those before thermal treatment. As observed in Figure 4 (dotted lines), Q bands in the $[(C_6S)_8Pc]_2M$ films are broadened and the maxima are red shifted to 727, 725, and 727 nm for M = Gd, Dy, and Sm, correspondingly. According to the molecular exciton theory,[45] a red-shifted exciton is usually observed when there is a staggered slipped stacking involving inclined alignment of transition dipoles. The characteristic Q band

---

(42) van de Craats, A. M.; Warman, J. M.; Hasebe, H.; Naito, R.; Ohta, K. *J. Phys. Chem. B* **1997**, *101*, 9224.

(43) Sleven, J.; Görller-Wallard, C.; Binnemans, K. *Mater. Sci. Eng. C* **2001**, *18*, 229.

(44) Maeda, F.; Hatsuska, K.; Ohta, K.; Kimura, M. *J. Mater. Chem.* **2003**, *13*, 243.

(45) Kasha, M.; Rawls, H. R.; El-Bayoumi, A. *Pure Appl. Chem.* **1965**, *11*, 371.

Table 5. Thicknesses (*d*), Refractive Indexes (*n*), and Extinction Coefficients (*k*) of **2**−**4** Films before and after Heating

	n at 633 nm		*k* at 633 nm		*d*, nm	
	before heating	after heating	before heating	after heating	before heating	after heating
2	1.40	1.46	0.10	0.14	35.8	34.5
3	1.45	1.54	0.20	0.25	44.4	42.8
4	1.40	1.48	0.06	0.13	30.8	29.6

was considered as a probe in evaluating the self-assembling properties in solutions and films.[45] Indeed, the position of the Q-band absorption for $[(C_6S)_8Pc]_2M$ films provides good evidence for the change in molecular ordering. The films heated to the temperature of 270 °C and then slowly cooled from isotropic liquid to room temperature are characterized by a more ordered structure than the initial ones. The molecule arrangement in the films may be described by slipped-stacked columns as in the crystal structure presented in Figure 2.

The change in the film structure after heating also leads to changes of the thickness (*d*) and optical parameters (*n* and *k*) of the films. Table 5 compares the values of the film thicknesses and optical constants at 633 nm for all investigated bis(Pc) films before and after heating.

The surface morphologies of $[(C_6S)_8Pc]_2M$ films were determined by AFM. AFM images of Pc films in Figures 6−8 show that the materials of $[(C_6S)_8Pc]_2M$ are distributed inhomogeneously in the as-deposited films. Numerous voids having diameters of around 10−20 nm are present in the films before thermal treatment (Figures 6a−8a). Subsequent heating of the films strongly modifies the films' surface morphologies. The surface of the $[(C_6S)_8Pc]_2Dy$ film looks smoother and more homogeneous after heating at 270 °C

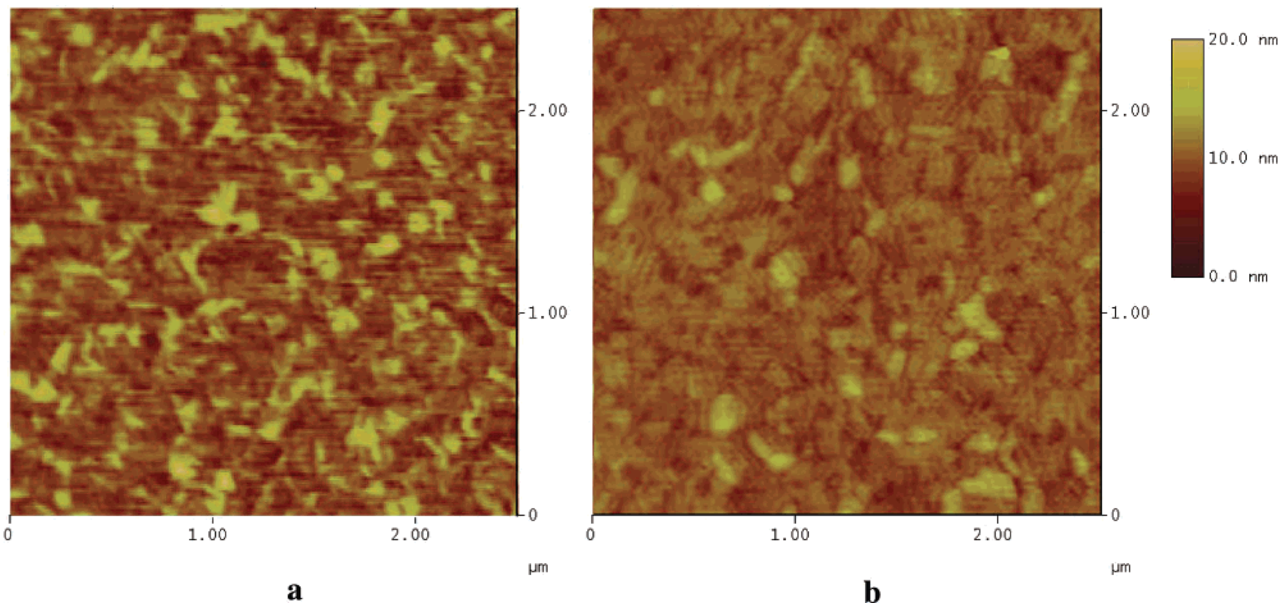


Figure 6. AFM image of $[(C_6S)_8Pc]_2Gd$ films before (a) and after (b) heating.

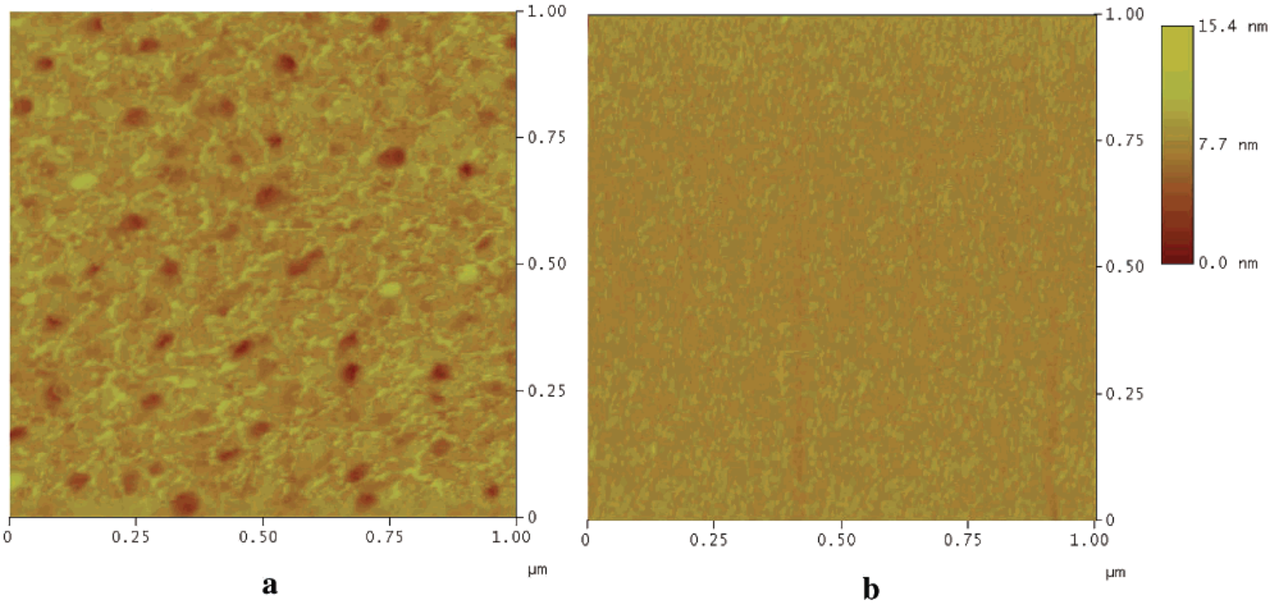


Figure 7. AFM image of $[(C_6S)_8Pc]_2Dy$ films before (a) and after (b) heating.

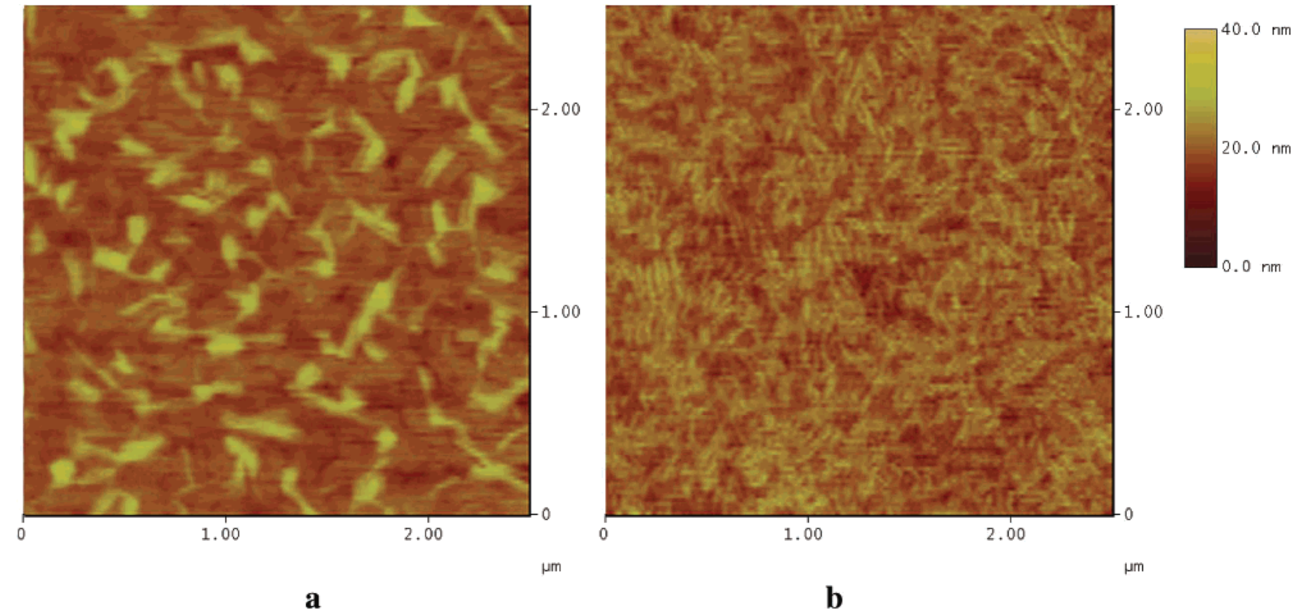


Figure 8. AFM image of $[(C_6S)_8Pc]_2Sm$ films before (a) and after (b) heating.

(Figure 7). AFM images of the $[(C_6S)_8Pc]_2Gd$ and $[(C_6S)_8Pc]_2Sm$ layers after heating (Figures 6b and 8b) show more ordering of microcrystallites in the films in comparison with those of as-deposited ones.

The present observations are similar to those obtained from the investigation on the films of liquid-crystalline mono-(Pc)s.[46−49] It has already been shown that the thermal treatment of films of Pc exhibiting mesogenic properties at temperatures higher than the temperature of the phase transition to the liquid-crystalline phase for several hours leads to the formation of films with ordered structure.[46−49]

Rapid deposition obtained by spin coating has a tendency to produce largely amorphous films containing microcrystalline domains. However, postdeposition annealing can induce substantial order if the Pc derivative has self-assembling properties such as mesogenity.

Magnetism. Several redox states are known for the double-decker Pc_2Ln molecules.[50]

$$Pc_2Ln^+ \xrightleftharpoons{e^-} Pc_2Ln \xrightleftharpoons{e^-} Pc_2Ln^- \xrightleftharpoons{e^-} Pc_2Ln^{2-} \xrightleftharpoons{e^-} Pc_2Ln^{3-}$$

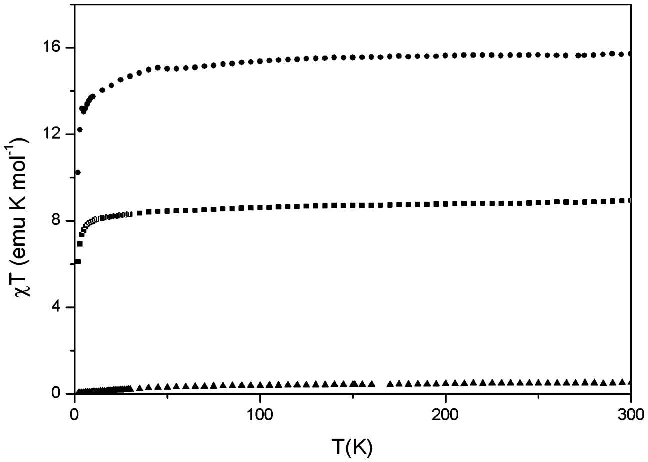


Figure 9. Temperature dependence of the product of the molar magnetic susceptibility (χ) with temperature (χT) for compounds **2** (black squares), **3** (black circles), and **4** (black triangles).

Compounds **2**−**4** under study correspond to the neutral forms Pc_2Ln, in which one unpaired electron is delocalized on the two Pcs. Therefore, we may expect to have some magnetic interactions between the lanthanide and the Pc radical and also between the Pc, as we have previously shown for the Pc_2Lu derivatives.[20j] The thermal behavior of the product of the molar magnetic susceptibility with temperature (χT) is shown in Figure 9 for all three compounds (**2**−**4**). At room temperature, $\chi T = 8.9$ emu K mol^{-1} for **2** ($[(C_6S)_8Pc]_2Gd$), $\chi T = 14.62$ emu K mol^{-1} for **3** ($[(C_6S)_8Pc]_2Dy$), and $\chi T = 0.51$ emu K mol^{-1} for **4** ($[(C_6S)_8Pc]_2Sm$). These values are very close to the sum contributions expected for the free lanthanide plus one unpaired electron on the two Pc rings. Upon cooling, the χT variation is almost constant and decreases only at very low temperatures. In the case of the dysprosium derivative, the behavior is similar in many aspects to those recently reported for an anionic double-decker compound in which the magnetism is only due to the dysprosium.[51] In the case of the gadolinium derivative, the best fit of the experimental data was obtained by using the equation of the magnetic susceptibility, taking into account the weak Gd−radical(Pc) ferromagnetic interaction ($J_{Gd-rad} = +0.2$ cm^{-1}) and an intermolecular interaction of $\theta = -1.3$ cm^{-1}, with a value of $g = 2.05$. A ferromagnetic Gd−radical interaction is in agreement with previous magnetic studies of Gd−radical compounds for which the Gd−

---

(46) Cook, M. J. *J. Mater. Chem.* **1996**, *6*, 677.

(47) Treacher, K. E.; Clarkson, G. J.; Ali-Adib, Z.; McKeown, N. B. *J. Chem. Soc., Chem. Commun.* **1996**, 73.

(48) Basova, T.; Taşaltin, C.; Gürek, A. G.; Ebeoğlu, M. A.; Öztürk, Z. Z.; Ahsen, V. *Sens. Actuators, B* **2003**, *96*, 70.

(49) Basova, T.; Gürek, A. G.; Ahsen, V. *Mater. Sci. Eng. C* **2002**, *22/1*, 99.

(50) Kadish, K. M.; Nakanishi, T.; Gürek, A. G.; Ahsen, V.; Yılmaz, I. *J. Phys. Chem. B* **2001**, *105*, 9817.

(51) Ishikawa, N.; Sugita, M.; Okubo, T.; Tanaka, N.; Lino, T.; Kaizu, Y. *Inorg. Chem.* **2003**, *42*, 2440.

radical interactions are generally found to be ferromagnetic[52] except in the particular case where it has been found to be antiferromagnetic.[53] A tentative fit to the data of other models did not give better agreements. In the case of the samarium derivative, the χT value is due only to the radical part in agreement with the weak value normally observed for χT in samarium compounds. These results indicate that in compounds **2**−**4** the Ln−radical(Pc) magnetic interactions as well as the radical−radical interactions are weak. This latter result is surprising with regards to the magnetic behavior of the $LuPc_2$ compound for which we have shown that the radical was delocalized on both Pcs and that the radical interacted in a one-dimensional system with a magnetic interaction ($J_{rad-rad} = 12$ cm^{-1}).[20j] In compounds **2**−**4**, the interaction between the radicals seems to be quenched by the magnetic lanthanide. Further measurement of the magnetization using the micro-SQUID technique[54] on the gadolinium (**2**) and dysprosium (**3**) derivatives did not show any single-molecule magnetic properties, in contrast with recently reported results on anionic double-decker compounds.[55]

Conclusion

In this work, the syntheses of new bis[octakis(hexylthio)-phthalocyaninato] rare-earth metal(III) double-decker complexes $\{[(C_6S)_8Pc]_2M$, M = Gd^{III}, Dy^{III}, and Sm$^{III}\}$ were described, and the compounds were characterized by standard methods. First, single crystals of the alkylthio-substituted Pc rare-earth metal double-decker complexes (**2**−**4**) have been obtained only in this work with the hexylthio chains. Also, these complexes have the same mesogenic properties as other alkylthio-substituted double-decker Pc complexes. So, the hexylthio substitution in bis(Pc) complexes is more appropriate than that in longer alkylthio chains [(C_nS), $n = 8$, 10, 12, 14, 16, and 18] to obtain a single crystal and is suitable for the investigation of the X-ray diffraction experiments on a single crystal of the rare-earth metal(III) double-decker complexes. The crystal structures of compounds **2**−**4** have been determined by X-ray diffraction on a single crystal. They are isostructural and crystallize in the monoclinic space group (space group $C2/c$). Their lattice constants have been determined in the following order: (**2**) $a = 31.629(4)$ Å, $b = 32.861(4)$ Å, $c = 20.482(2)$ Å, $\beta = 126.922(2)°$, $V = 17019(3)$ Å^3; (**3**) $a = 31.595(2)$ Å, $b = 32.816(2)$ Å, $c = 20.481(1)$ Å, $\beta = 127.005(1)°$, $V = 16958(2)$ Å^3; (**4**) $a = 31.563(2)$ Å, $b = 32.796(2)$ Å, $c = 20.481(1)$ Å, $\beta = 127.032°$, $V = 16924(2)$ Å^3. The phase-transition temperatures of complexes **2**−**4** have been determined by polarization microscopy as measured with DSC. For this typical fan-shaped texture often observed for Col$_h$, these mesophases could be thus confirmed as the Col$_h$ phases.[25−27,42−44] It can generally be said that alkylthio substitution according to alkoxy substitution in mono- and bis(Pc) derivatives results in decreasing melting points. Also, compared with the previously reported series of bis[octakis(alkylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes $[(C_nS)_8Pc]_2M$ (M = Eu^{III}, Tb^{III}, and Lu^{III}; $n = 8$, 10, 12, 14, 16, and 18), the phase-transition temperatures of complexes **2**−**4** substituted with the hexylthio chains increase according to the length of the alkyl chain, as expected.[28a] The Q bands at around 700 nm in chloroform of these new compounds do not show any big differences in UV−vis absorption spectroscopy with respect to other bis(Pc)s substituted with longer alkylthia chains than the hexylthio chains, previously reported.[28a]

Thermally induced molecular reorganization within films of bis[octakis(hexylthio)phthalocyaninato] rare-earth metal(III) double-decker complexes (**2**−**4**) was studied by the methods of ellipsometry, UV−vis absorption spectroscopy, and AFM. The alteration of the film structure after heating leads to changes of the thickness and optical characteristics of the films. The broadened and red-shifted Q bands in the visible absorption spectra of the films after heating provide good evidence for molecular ordering and indicate a staggered slipped-stacking arrangement of molecules in the film. AFM microscopy is also consistent with independent optical methods.

These results indicate that in compounds **2**−**4** the Ln−radical(Pc) magnetic interactions as well as the radical−radical interactions are weak. In compounds **2**−**4**, the interaction between the radicals seems to be quenched by the magnetic lanthanide. Further measurement of the magnetization using the micro-SQUID technique[53] on the gadolinium (**2**) and dysprosium (**3**) derivatives did not show any single-molecule magnetic properties in contrast with recently reported results on anionic double-decker compounds. Future investigations will focus on the chemical sensor properties of these mesogenic compounds.

Acknowledgment. This work was financed by a NATO Collaborative Linkage Grant (Ref. No. CBP-NR-CLG 981510) and the Russian Science Support Foundation. D.L. thanks Dr. W. Wernsdorfer at Laboratoire Louis Néel at CNRS in Grenoble, France, for fruitful discussions and micro-SQUID measurements. Grants for travelling between France and Turkey were funded through the CNRS−TÜBITAK collaboration program. Grants for travelling between Russia and Turkey were funded through the NATO PC advanced fellowship program.

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051754N

---

(52) (a) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1992**, *31*, 741. (b) Sutter, L. J.-P.; Kahn, M. L.; Golhen, S.; Ouahab, L.; Kahn, O. *Chem.*—*Eur. J.* **1998**, *4*, 571. (c) Kahn, M. L.; Sutter, J.-P.; Golhen, S.; Guionneau, P.; Ouahab, L.; Kahn, O.; Chasseau, D. *J. Am. Chem. Soc.* **2000**, *122*, 3413. (d) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 913. (e) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1990**, *29*, 4223.

(53) (a) Lescop, C.; Luneau, D.; Belorizky, E.; Fries, P.; Guillot, M.; Rey, P. *Inorg. Chem.* **1999**, *38*, 5472. (b) Caneschi, A.; Dei, A.; Gatteschi, D.; Sorace, L.; Vostrikova, K. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 246. (c) Lescop, C.; Belorizky, E.; Luneau, D.; Rey, P. *Inorg. Chem.* **2002**, *41*, 3375. (d) Lescop, C.; Bussiere, G.; Beaulac, R.; Bélisle, H.; Belorizky, E.; Rey, P.; Reber, C.; Luneau, D. *J. Phys. Chem. Soc.* **2004**, *65*, 773.

(54) Wernsdorfer, W. *Adv. Chem. Phys.* **2001**, *118*, 99.

(55) Ishikawa, N.; Sugita, M.; Wernsdorfer, W. *J. Am. Chem. Soc.* **2005**, *127*, 3650.