Ordered Phases in *n*-Heptacosane (C₂₇H₅₆). Structure Determination of the MdcI Phase

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n-Heptacosane (C₂₇H₅₆) is known to have a rich polymorphism. With increasing temperature, the following phase transitions are observed: Oi → Odci → MdcI → RIII ...> RIV → L. The MdcI form is known to be isomorphous with the modification B in *n*-tritriacontane (C₃₃H₆₈). Two possible space groups were given in the literature for the B-form of C₃₃H₆₈: monoclinic (*Aa*) and orthorhombic (*A2₁am*). We have determined the structure of the *n*-heptacosane at 325 K combining lattice energy minimization calculations and Rietveld refinement using accurate X-ray diffraction data. We have shown that the MdcI form of heptacosane is monoclinic (*Aa*, *Z* = 4). Moreover, at each phase transition Oi → Odci → MdcI, a substantial decrease in intensity of the 0 0 *l* reflections and an increase in the interlayer spacing due to end-gauche defects are observed. In addition, each phase transition is characterized by subtle appearance and disappearance of reflections observed at large angles of diffraction. These characteristics are powerful tools for phase identification in binary or ternary phase diagrams of *n*-alkanes.

1. Introduction

n-Alkanes (hereafter denoted by C_{*n*}) have been the subject in recent years of numerous researches in which calorimetric and crystallographic measurements^{1–12} have shown that *n*-alkanes exhibit a rich and complex polymorphism. In the range from C₈ to C₂₈ and in the “low temperature” domain (the “high temperature”

domain is defined as that where the rotator phases and the liquid phase are observed), seven forms are identified: triclinic Tp (*P* $\bar{1}$, *Z* = 1)¹² in C₈ to C₂₄, triclinic Ti (*P* $\bar{1}$, *Z* = 2)² in C₉ and C₁₁, monoclinic M011 (*P*2₁/*a*, *Z* = 2)^{1,3,4} in C₂₆ and C₂₈, orthorhombic Op (*Pca*2₁, *Z* = 4)^{3,4,13} in C₂₈, orthorhombic Oi (*Pcam*, *Z* = 4)¹⁴ in odd alkanes, orthorhombic Odci (*Pnam*, *Z* = 4)^{4,5} in C₂₃ to C₂₇, and monoclinic MdcI (*Aa*, *Z* = 4)^{5,15} in C₂₅ and C₂₇. [T, O, and M stand for triclinic, orthorhombic, and monoclinic, respectively. For Tp and Ti, the letter “p” stands for “pair” (the French word for even) and “i” for “impair” (for odd). For Odci and MdcI, the “dci” stands for “défauts de conformation” (for conformational defects). For the monoclinic M011 phase, we use the common notation *Mhkl* introduced by Sullivan and Weeks,¹⁶ where (*hkl*) describes the plane formed by the methyl end groups (CH₃) in the referential of the orthorhombic subcell.]

Ungar¹⁵ has suggested that the MdcI phase of C₂₅ and C₂₇ is isomorphous with the phase B of tritriacontane (C₃₃H₆₈) studied by Piesczek et al.,¹⁷ who had identified it as monoclinic (*Aa*, β = 91.2°, *Z* = 4) from single-crystal data. Recently, Dorset^{18,19} suggested from

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(1) Roblès, L.; Mondieig, D.; Haget, Y.; Cuevas-Diarte, M. A. *J. Chim. Phys.* **1998**, *95*, 92–111.

(2) Espeau, P.; Roblès, L.; Mondieig, D.; Haget, Y.; Cuevas-Diarte, M. A.; Oonk, H. A. *J. Chim. Phys.* **1996**, *93*, 1217.

(3) Poirier, B. Ph.D. Thesis, University of Bordeaux I, France, 1996.

(4) Rajabalee, F. European Ph.D. Thesis, University of Bordeaux I, France, 1998.

(5) Nozaki, K.; Higashitani, N.; Yamamoto, T.; Hara, T. *J. Chem. Phys.* **1995**, *103* (13), 5762–5766.

(6) Reinhardt, E. C.; Fenrych, J.; Basson, I. *J. Phys.: Condensed Matter* **1994**, *6*, 7605–7616.

(7) Doucet, J.; Denicolo, I.; Craievich, A. F.; Germain, C. *J. Chem. Phys.* **1984**, *80*(4), 1647–1651.

(8) Craig, S. R.; Hastie, G. P.; Roberts, H. J.; Sherwood, J. N. *J. Mater. Chem.* **1994**, *4*(6), 977–981.

(9) M. Kobayashi, T. Kobayashi, Y. Ito, Y. Chatani and H. Tadokoro, *J. Chem. Phys.* **1980**, *72*, 2024.

(10) Sirota, E. B.; King, H. E., Jr.; Singer, D. M.; Shao, H. H. *J. Chem. Phys.* **1993**, *98*(7), 5809.

(11) Sirota, E. B.; King, H. E., Jr.; Shao, H. H.; Singer, D. M. *J. Phys. Chem.* **1995**, *99*, 798.

(12) Muller, A.; Lonsdale, L. *Acta Crystallogr.* **1948**, *1*, 129–131.

(13) Rajabalee, F.; Métivaud, V.; Mondieig, D.; Haget, Y.; Oonk, H. A. *J. Helv. Chim. Acta.* **1999**, *82*(11), 1916.

(14) Smith, A. E. *J. Chem. Phys.* **1953**, *21*, 2229–2231.

(15) Ungar, G. *J. Phys. Chem.* **1983**, *87*, 689–695.

(16) Sullivan, P. K.; Weeks, J. J. *J. Res. NBS A* **1970**, *74*, 203.

Figure 1. Experimental ($T = 325\text{K}$) and calculated diffraction patterns of C27 in the MdcI form using the profile fitting procedure of FULLPROF in the case of (a) Aa structure and (b) $A2_1am$ structure.

three-dimensional electron data from epitaxially oriented samples that the space group of this phase is most likely $A2_1am$. However, he added that the space group Aa could not be dismissed, as an equivalent model based on this latter structure also matches the 59 unique structure factor values.

As the temperature increases, the C27 undergoes the following transitions:

Oi $\rightarrow$ Odci $\rightarrow$ MdcI $\rightarrow$ RIII $\cdots$ $\rightarrow$ RIV $\rightarrow$ liquid at 312.9, 322.3, 325.9, 327.9, and 331.6 K, respectively. Except for RIII $\cdots$ $\rightarrow$ RIV, they are first-order transitions. The heat of transition of Oi $\rightarrow$ Odci, Odci $\rightarrow$ MdcI, MdcI $\rightarrow$ RIII and melting are 0.27, 2.47, 27.1, 62.8 kJ. mol $^{-1}$, respectively.

The purpose of this work is to determine which of the symmetries (orthorhombic or monoclinic) proposed for the MdcI phase of C27 is the right one. For this, accurate X-ray powder diffraction analyses were carried out. For symmetry identification and cell refinement, the FULLPROF²⁰ program, which involves the “profile-fitting”

procedure of Le Bail, was used. In addition, the structure of this phase has been determined by Rietveld refinement using a rigid body model.

2. Experimental Section

C27 was purchased from Fluka with a stated purity grade of 99.1% and was used without further purification. X-ray diffraction patterns were recorded with two different diffractometers using Cu K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$).

A Siemens D500 vertical powder diffractometer, which works in the reflection mode, was used. About 5 g of product was put in the sample holder and the data were collected with 0.04° 2θ steps and 5 s interval time.

A horizontally mounted INEL diffractometer equipped with a cylindrical position-sensitive detector (CPS120)²¹ and a liquid-nitrogen INEL CRY950 cryostat (80–460 K) was also used, with helium gas as heat exchanger in the sample holder. The detector in Debye–Scherrer geometry (transmission mode) enables a simultaneous recording of the profile over a 2θ range

(17) Piesczek, W.; Strobl, G. R.; Malzahn, K. *Acta Crystallogr.* **1974**, B30, 1278–1288.

(18) Dorset, D. L. *Z. Kristallogr.* **1999**, 214, 223–228.

(19) Dorset, D. L. *Z. Kristallogr.* **1999**, 214, 229–236.

(20) Rodriguez-Carvajal, J. FULLPROF, a program for Rietveld refinement and pattern matching analyses. *Abstracts of the satellite meeting on powder diffraction of the XVth congress of the International Union of Crystallography*, Toulouse, France, 1990.

(21) Ballon, J.; Comparat, V.; Poux, J. *Nucl. Instrum. Methods* **1983**, 217, 213.

Figure 2. Experimental and calculated diffraction patterns of heptacosane ($C_{27}H_{56}$) using the profile fitting procedure of FULLPROF showing the appearance, disappearance, or changes in intensities of the reflections at each phase transition: (a) $Pcam$ (300 K); (b) $Pnam$ (320 K); (c) Aa (325 K).

between 4° and 120° . Monochromatic $Cu K\alpha_1$ was selected with an asymmetric focusing incident-beam curved quartz-monochromator. Around 2 mg of product was introduced in a sealed Lindemann capillary (diameter = 0.5 mm) that rotated perpendicularly to the X-ray beam during the experiment in order to improve averaging of the crystallites. The experiment took about 10 h.

As recommended,²² external calibration to convert the measured 4096 channels to 2θ degrees was applied using cubic $Na_2Ca_2Al_2F_4$ by means of cubic spline fittings. The peak

positions were determined after pseudo-Voigt fitting by the DIFFRACTINEL software.

Both data sets were used for cell refinement and phase identification. To analyze preferred orientations and changes of the intensities of the $00l$ reflections during the phase transition, the data obtained with the SIEMENS D500 diffractometer were more appropriate (because samples orient

(22) Evain, M.; Deniard, P.; Jouanneaux, A.; Brec, R. *J. Appl. Crystallogr.* **1993**, *26*, 563.

Table 1. Lattice Parameters of C₂₇H₅₆ in Oi (*Pcam*, *Z* = 4), Odci (*Pnam*, *Z* = 4), and Mdci (*Aa*, *Z* = 4) Forms

	space group	<i>T</i> (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)
Oi	<i>Pcam</i>	300	7.427(1)	4.952(1)	72.26(1)	90
Odci	<i>Pnam</i>	320	7.494(1)	4.969(1)	72.48(1)	90
Mdci	<i>Aa</i>	325	7.538(1)	4.973(1)	72.60(2)	91.32(3)

much more according to the symmetry of the holder). However profile-fitting refinements were carried out on the INEL data.

3. Results

(a) Phase Identification of the Mdci Form of C27. The profile-fitting performed at 325 K over the $10^\circ \leq 2\theta \leq 35^\circ$ angular range on the basis of the *A2₁am* structure indicates clearly that the calculated pattern does not match the experimental one. For example, while the experimental pattern shows unambiguously two peaks around $2\theta \approx 23^\circ$, only the 1 1 7 reflection is found in the calculated one (see Figure 1a). This is also the case for the 1 1 5 reflection at $2\theta \approx 22.2^\circ$.

With the *Aa* group, the agreement between experimental and calculated profiles is very good. We can see (Figure 1b) that the two couples of observed peaks at $2\theta \approx 22.2^\circ$ and 23° correspond to the splitting of the 1 1 5 reflection into 1 1 5 and $\bar{1}$ 1 5 and the splitting of the 1 1 7 reflection into 1 1 7 and $\bar{1}$ 1 7.

The *A2₁am* space group for the Mdci phase of C27 is therefore unambiguously excluded.

(b) Lattice Parameters and Indexing of the Reflections in the Oi, Odci, and Mdci Form of C27. The lattice parameters obtained for the Oi, Odci, and Mdci forms at *T* = 300, 320, and 325 K, respectively, are given in Table 1. The indexing of the three diffraction patterns is given in Figure 2. Due to the long *c* parameter (compared to the *a* and *b* ones) in *n*-alkanes, several indexings are possible for a single reflection. To overcome this difficulty for the Oi phase, we used the similarity of the scattering with the scattering from the Oi phase of C23. For the latter compound single-crystal diffraction data are available.¹⁴ For the Odci and Mdci phases, the technique of indexing is explained elsewhere.²³

In all three cases, the calculated pattern fits very well the observed one, confirming the reliability of the lattice parameters as well as the space groups, especially the monoclinic group for the Mdci phase.

The transition Oi → Odci is mainly characterized by (1) the disappearance of the reflections identified by the symbol ■ in Figure 2a and (2) the appearance of the 0 1 27 and 0 1 29 reflections at $2\theta \approx 38.1^\circ$ and 40.5° , respectively.

The transition Odci → Mdci is mainly characterized by (1) the disappearance of the reflections identified by the symbol ◇ in Figure 2b and (2) the splitting of the following reflections (shown by the arrows in Figure 2c): 1 1 29, 2 0 28, 2 1 27, 2 1 29, 1 2 28, 3 1 27, and 3 1 29. We note that only the splitting of *hkl* reflections with a large *l* are observed, since they are more separated in the high 2θ range.

Figure 3. Intensities of the 0 0 20 reflection in the solid ordered and rotator forms of heptacosane (C₂₇H₅₆) as a function of temperature.

Table 2. Profile Refinement Parameters of the Mdci Phase of C₂₇H₅₆

overall scale factor	0.0240(1)
lattice parameters	<i>a</i> = 7.538(1) Å <i>b</i> = 4.973(1) Å <i>c</i> = 72.60(2) Å β = 91.32(3)°
space group	<i>Aa</i>
center of the unit <i>X</i> ₀ , <i>Y</i> ₀ , <i>Z</i> ₀	0.0130, 0.2513(1), 0.2512
Euler angles (ϕ , θ , ψ)	177.62(1)°, −161.29(2)°, 76.51(1)°
pseudo-Voigt function	$\eta = \eta_0 + x \times 2\theta$ $\eta_0 = 0.26(6)$, $x = 0.006(3)$ −0.06(2), 0.05(1), 0.005(2)
peak shape parameters <i>U</i> , <i>V</i> , <i>W</i> (Å)	−0.020(4)
asymmetry parameters	0.36(2)
preferred orientation along <i>c</i>	<i>T</i> ₁₁ = 0.0795(7) Å ² <i>T</i> ₂₂ = 0.050(6) Å ² <i>T</i> ₃₃ = 0.016(8) Å ² <i>L</i> ₃₃ = 0.32(3) deg ²
TLS factors	

The splitting of these reflections gives additional evidence for the monoclinic symmetry (*Aa*) of the Mdci phase.

(c) Incidence of the Gauche Defects on the Intensities of the 0 0 /Reflections. Taking advantage of the preferred orientation observed along the (0 0 *l*) plane when the Bragg–Brentano geometry is used, we have recorded the diffraction patterns of C27 at different temperatures from *T* = 291 to 331 K. A sudden decrease in intensity of the 0 0 *l* reflections is observed at each transition, even if the effect is less pronounced for the Oi → Odci transition. As an example, the variation in intensity of the 0 0 20 reflection with temperature is shown in Figure 3. This fall off in intensity can be due to an increase in end-gauche defects (gt) as the intensities of the 0 0 *l* reflections reflect the orderliness of the methyl layer.^{24–26} The 0 0 20 reflection is no longer observed in the rotator forms.

The evolutions of the lattice parameters *a*, *b*, *c* and the volume of the cell with temperature in the three solid ordered phases Oi, Odci, and Mdci are shown in Figure 4a–d. In each phase, the four quantities increase

(24) Piper, S. H. *Biochem. J.* **1931**, 25, 2072–2094.

(25) Strobl, G.; Ewen, B.; Fischer, E. W.; Piesczek, W. *J. Chem. Phys.* **1975**, 61, 5257–5264.

(26) Dorset, D. L. *Acta Crystallogr.* **1995**, B51, 1021–1028.

(23) Rajabalee, F.; Métivaud, V.; Mondieig, D.; Cuevas-Diarte, M. A.; Haget, Y. *J. Mater. Res.* **1999**, 14(6), 2644.

Figure 4. Evolution of cell parameters and volume with temperature in the solid ordered phases of $C_{27}H_{56}$.

smoothly due to thermal expansion. For the a and b parameters (Figure 4a,b), a sudden increase of these parameters is observed during the Odci $\rightarrow$ Mdci phase transition; the effect is more pronounced in the a -direction than in the b -direction, but it is very weak compared to that in the c -direction, where an increase of about 0.05 and 0.25 Å is noted for the Oi $\rightarrow$ Odci and Odci $\rightarrow$ Mdci transitions, respectively. As far as the lattice volume is concerned, a sudden increase is ob-

served for the Odci $\rightarrow$ Mdci transition, confirming that it is indeed a first-order transition. Despite the fact that no break off appears in the variation of the lattice volume for the Oi $\rightarrow$ Odci transition, the narrowness in temperature of the DSC signal and the hysteresis phenomenon observed on cooling¹ show that this transition is a first-order one ($\Delta H_{tr} = 2.47 \text{ kJ mol}^{-1}$).

(d) Structure Refinement of C27 Mdci Form. The structural refinement of the Mdci form was undertaken

Figure 5. Collected (open circles), calculated profiles (line), $2\theta_{hkl}$ position (vertical dashes), and plot difference between collected and calculated profiles: (a) in the 8° – 71° 2θ range, (b) magnification of the 7° – 25° 2θ range, and (c) magnification of the 25° – 71° 2θ range.

at 325 K considering the Aa space group. A rigid body approach (the chains were considered as totally trans) and the TLS formalism²⁷ were applied.

The full atomic coordinates were used as starting point for a Rietveld refinement with FULLPROF in the 7° – 69° 2θ range.

The background was linearly interpolated between manually selected experimental points. The parameters refined in the procedure were the overall scale factor, the lattice parameters, the overall temperature factor, the y parameter of the center of the asymmetric unit and its orientation, the peak shape parameters (U , V , W), the preferred orientation, the pseudo-Voigt function (η , x), the asymmetry parameters, and the translational mean square displacements and librational components. The results of the refinement are summarized in Table 2. This Rietveld refinement resulted in an R_p of 7.31%, an R_B value of 5.97%, and an R_{wp} value of 11.5%. The collected and calculated profiles are shown in Figure 5 together with the difference plot between them. As can be seen in Figure 6, which shows the structure projections perpendicularly to a , b , and c (parts a, b, and c of Figure 6, respectively), the molecule axis is slightly bend toward c . Concerning temperature factors, the highest factor is L_{33} ($L_{11} = L_{22} = 0$), indicating that the movement of the highest amplitude corresponds to libration along the c axis; the translational factors T_{11} and T_{22} are higher than T_{33} . These movements are precursory signs of the rotator form.

To confirm these results, intermolecular energy calculations were performed using the crystal packing program PCK83²⁸ with the model called “exp-6-1”. The values of the coefficients of the exponential repulsion, dispersion attraction, and Coulombic interaction between net charges for H–H and C–C were taken from

ref 29 and for H–C from ref 30. The net charges were taken from ref 27.

Considering the atomic coordinates in the structure obtained by Rietveld refinement and without further (position, orientation of the molecule, and lattice parameters) refinement, the calculation leads to a lattice energy of $-236 \text{ kJ}\cdot\text{mol}^{-1}$.

This negative value obtained without further refinement strengthens the results obtained by Rietveld refinement. It can be added that this result is quite satisfactory, as the sublimation enthalpy of C27 given by ref 31 is not very far from this value, $196 \pm 30 \text{ kJ mol}^{-1}$.

4. Discussion

This work has shown that the space group of the Mdc1 phase of C27 is monoclinic Aa . Orthorhombic symmetry could be excluded. C27 thus is isomorphous to C33.¹⁵ The structure determination of the Mdc1 phase of C27 by X-ray powder diffraction and Rietveld refinement corroborated this result.

Oi is orthorhombic ($Pcam$, $Z = 4$), as stated in the literature.^{1,14} The structure of Odci in C23 and C25 was identified by Nozaki et al.⁵ and later confirmed by us on these alkanes when we studied the binary system C23 + C25.²³ This work has shown that the Odci form of C27 is also orthorhombic $Pnam$ with four molecules per unit cell.

The sudden increase of the c parameter at each transition Oi $\rightarrow$ Odci and Odci $\rightarrow$ Mdc1 in C27 (see Figure 4c), which accounts for the end-gauche (gt) defects,^{32,33} is due to longitudinal shifts (this process has

(27) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1953**, *24*, 63.

(28) Williams, D. E. PCK83 (program no. 481). A Crystal Molecular Packing Analysing Program. *QCPE Bull.* **4**(3), 82–83.

(29) Williams, D. E.; Cox, S. R. *Acta Crystallogr.* **1984**, *B40*, 404–417.

(30) Williams, D. E.; Starr, T. L. *Comput. Chem.* **1977**, *1*, 173–177.

(31) Patente, V.; Pompili, T.; Scardala, P.; Ferro, D. *J. Chem Thermodyn.* **1991**, *23*, 379–396.

(32) Snyder, R. G.; Maroncelli, M.; Qi, S. P.; Strauss, H. L. *Science* **1981**, *214*, 188–190.

Figure 6. $C_{27}H_{56}$ structure projections of the Mdc1 phase: (a) plane perpendicular to a , (b) plane perpendicular to b , (c) plane perpendicular to c .

been described elsewhere^{18,34–39}). (Infrared measurements^{32,33} have shown that a sudden increase in the

concentration of end-gauche defects is recorded at each phase transition $Oi \rightarrow Odci$, $Odci \rightarrow Mdc1$ and $Mdc1 \rightarrow RIII$.) As a consequence, the layer surface is roughened and a decrease in intensities of the $00l$ reflections is observed (see Figure 3).

The indexing of the diffraction patterns of the ordered phases Oi , $Odci$, and $Mdc1$ of C_{27} confirms the relationship put forward already in a previous paper²³ for the odd alkanes C_{23} and C_{25} . For example, the peak at $2\theta \approx 39^\circ$ characteristic of the Oi phase is indexed as 0128 in C_{27} , 0126 in C_{25} , and 0124 in C_{23} . In other words, for a given odd alkane C_n , this peak is indexed as $01(n+1)$.

The peak at $2\theta \approx 41^\circ$ characteristic of the $Odci$ form is indexed as 1128 in C_{27} , 1126 in C_{25} , and 1124 in C_{23} ; for an odd alkane C_n , it is therefore indexed as $11(n+1)$.

In the same way, the peak at $2\theta \approx 55^\circ$ is indexed in the Oi and $Odci$ phases as $31(n+2)$. This peak is split into $31(n+2)$ and $\bar{3}1(n+2)$ in the $Mdc1$ phase of C_{25} and C_{27} . C_{23} does not show the $Mdc1$ phase. These characteristics are also observed for the other hkl reflections. A global study on the odd alkanes C_{13} to C_{27} and their mixed samples concerning the indexing will be the subject of our next paper.

With the exception of the $00l$ reflections, whose angular position (2θ) depend on the chain length, the other observed reflections are practically situated at the same angular position, their indexing depending on the alkane, as shown previously.

This aspect is very interesting, as our recent work on binary mixtures of n -alkanes^{4,23,40–42} has shown that these forms are also observed in binary systems of shorter alkanes. The identification of the phases can be done by simply comparing the diffraction pattern of a mixed sample with those corresponding to the Oi , $Odci$ and $Mdc1$ phases of the pure odd alkanes.

Supporting Information Available: Fractional atomic coordinates of $C_{27}H_{56}$ for the $Mdc1$ phase at 325 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM021118C

(33) Maroncelli, M.; Qi, S. P.; Strauss, H. L.; Snyder, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 6237–6247.

(34) Keller, A. *Philos. Mag.* **1961**, *6*, 329–343.

(35) Lüth, H.; Nyburg, S. C.; Robinson, P. M.; Scott, H. G. *Mol. Cryst. Liq. Cryst.* **1974**, *27*, 337–357.

(36) Takamizawa, K. *Polym. J.* **1982**, *14*(6), 441–456.

(37) Gerson, A. R.; Nyburg, S. C. *Acta Crystallogr.* **1994**, *B50*, 252–256.

(38) Hastie, G. P.; Roberts, K. J. *J. Mater. Sci.* **1994**, *29*, 1915–1919.

(39) Dorset, D. L. *Macromolecules* **1987**, *20*, 2782–2788.

(40) Métivaud, V.; Rajabalee, F.; Cuevas-Diarte, M. A.; Calvet, T.; Mondieig, D.; Haget, Y. *Anal. Chim. Acta* **1998**, *394*, 396–401.

(41) Métivaud, V. European Ph.D. Thesis, University of Bordeaux I, France, 1999.

(42) Métivaud, V.; Rajabalee, F.; Mondieig, D.; Haget, Y.; Cuevas-Diarte, M. A. *Chem. Mater.* **1999**, *11*, 117–122.