

Research Article

Synthesis, Characterization, and Crystal Structure of Pyridinium Tetrakis{1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedionato}lanthanate(III) Complex

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Received 5 June 2014; Accepted 20 July 2014; Published 30 September 2014

Academic Editor: Paul R. Raithby

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The reaction of 1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedione with lanthanum(III) trichloride in the presence of pyridine leads to halide ligand exchange, yielding a novel pyridinium tetrakis{1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedionato}lanthanate(III) complex with four polycyclic aromatic hydrocarbon moieties. This reaction easily proceeds under mild conditions (25°C, 24 h) producing the complex in a 90% isolated yield. The complex was characterized by infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and positive fast atom bombardment mass spectrometry, and its precise structure was determined by single crystal X-ray diffraction. Ultraviolet-visible spectroscopy, fluorescence spectroscopy, and X-ray analysis demonstrated that the four pyrene moieties were independently oriented.

1. Introduction

In recent years, lanthanide(III) complexes with β -diketonato ligands consisting of various aromatic components have attracted numerous researchers [1]. These compounds represent well-known electronic and luminescent materials with numerous applications in material chemistry [2–4]. In addition, polycyclic aromatic hydrocarbons (PAHs), such as pyrene and perirene, have been highlighted by numerous researchers because of their electronic and luminescent properties [5–9]. From our recent work, the structures of the octadentate lanthanide(III) complex derived by X-ray analysis were reported to be unexpectedly cone-like [10]. The present study focuses on the synthesis and investigation of the structural properties of the novel octacoordinate lanthanum(III) complex with four bidentate β -diketonato ligands having four PAH (pyrene) moieties and one pyridinium ion as a counter cation. We also confirmed the exact

structure of the octadentate lanthanide coordination complex having highly aggregated PAHs by X-ray analysis.

2. Materials and Methods

All the reagents and solvents were obtained from commercial sources and were used as received. Infrared spectra were recorded on a HITACHI FT-IR 410X instrument using the KBr method. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained on a Bruker 400 MHz Avance400S spectrometer at 293 K in chloroform-d³ using tetramethylsilane (Me_4Si) as an internal reference. Positive fast atom bombardment mass spectrometry (pos. FAB-MS) spectra were obtained on a Noppon Densi JEOL JMS-SX102A spectrometer using nitrobenzylalcohol (NBA) as the matrix and dichloromethane (DCM) as the solvent. This instrument was operated in the positive ion mode using

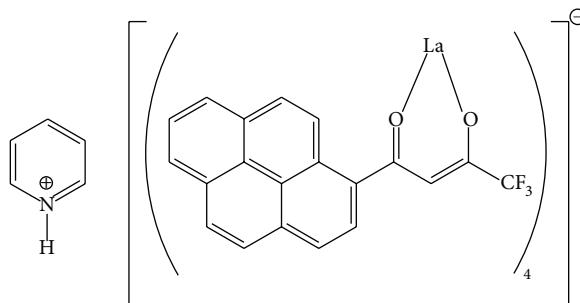


FIGURE 1: Structure of pyridinium tetrakis{1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedionato}lanthanate(III).

an *m/z* range of 100–2000. Elemental analysis was performed on a YANAKO MT-5 CHN analyzer. IR, ultraviolet-visible (UV-vis), and fluorescence spectral measurements were performed in dichloromethane at room temperature. A HITACHI F-2500 spectrophotometer was used for obtaining UV-vis spectra and a JASCO V-550 spectrophotometer was used for fluorescence spectra.

2.1. Preparation of Pyridinium Tetrakis{1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedionato}lanthanate(III) (Figure 1). An ethanolic solution (10 mL) of anhydrous LaCl₃ (245 mg, 1.0 mmol) was added to an ethanol-dichloromethane mixed solution (30 mL (1:1, v/v)) of 1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedione (1.36 g, 4.0 mmol). Pyridine (0.34 mL, 5.1 mmol) was then added to the solution and stirred for 24 h at room temperature. The resulting precipitate was collected and washed with ethanol and then dried under reduced pressure to yield a yellow powder (1.50 g, 90%).

¹H-NMR (400 MHz, CDCl₃) 6.40 (s, 4H, β-diketone C-H), 7.50–8.40 (m, 45H, pyrenyl + pyridinium C-H), 8.80 (s, 4H, pyridinium N-H). Elemental analysis: La 8.22% (8.33%, calcd), C 65.98% (66.23%, calcd), H 3.30% (3.26%, calcd), N 0.81% (0.84%, calcd). Pos.FAB-MS: *m/z*. 1669 [M + H]⁺, 1496 [M-pyridinium+H]⁺. IR spectrum in KBr: selected band at 1608 cm⁻¹ (C-O).

2.2. UV-Vis and Fluorescence Spectra of Pyridinium Tetrakis{1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedionato}lanthanate(III). The four pyrene moieties on the complex exhibited a large absorption coefficient and a long absorption wavelength ($\lambda_{\text{max}} = 390 \text{ nm}$, $\log \epsilon = 4.4$) in dichloromethane solution.

The fluorescence spectra of the complex provided a fluorescence excitation wavelength of $\lambda_{\text{em}} = 455 \text{ nm}$ ($\lambda_{\text{ex}} = 390 \text{ nm}$) both in the dichloromethane solution and in the solid. Fluorescence change was not observed by variable concentration fluorescence spectral measurement between $10^{-3} \text{ mol}/\text{dm}^3$ and $10^{-6} \text{ mol}/\text{dm}^3$ in the solution using a 1 mm quartz cell.

2.3. X-Ray Crystal Structure Determination of Pyridinium Tetrakis{1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedionato}lanthanate(III). Good crystals of the complex were obtained

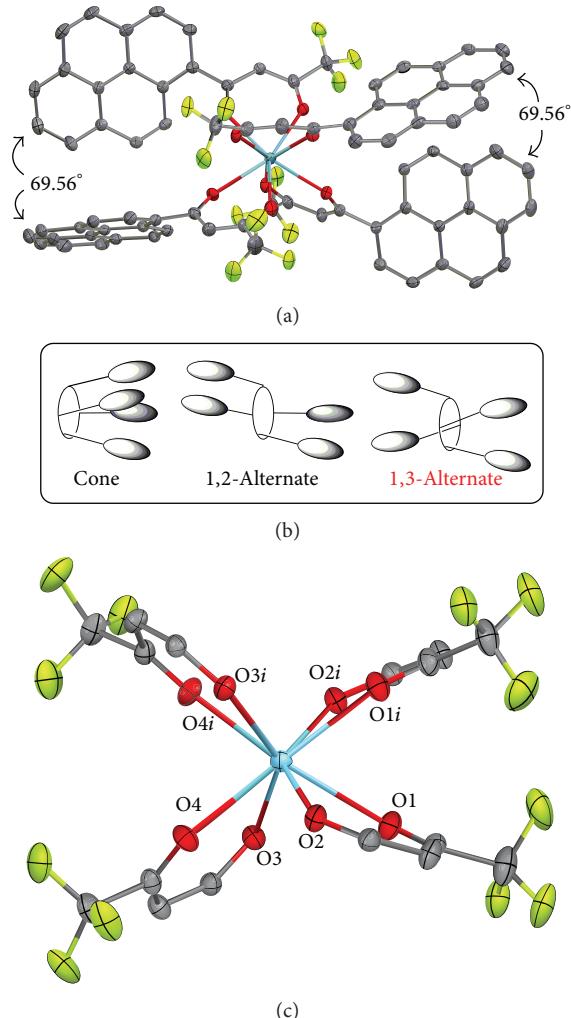


FIGURE 2: Molecular view (above) and the coordination structure around the lanthanum(III) ion (below) of the complex. Thermal ellipsoids are drawn on a 50% probability level. Blue, red, and pale green ellipsoid(s) indicate La, O, and F atom(s), respectively. Hydrogen atoms, a pyridinium cation, and a solvent toluene molecule are omitted for clarity. Symmetry code (i) is $-x + 2, y, -z + (1/2)$.

from a solution of toluene/ethanol (v/v = 1:1) at room temperature using the slow diffusion technique. The crystal data was recorded on a Bruker APEX II KY CCD diffractometer using Mo-K α -radiation ($\lambda = 0.71073 \text{ \AA}$). APEX2 software was used for the preliminary determination of the unit cell [11]. Integrated intensities and unit cell refinement were determined using the SAINT program [12]. The average residual for symmetry equivalent reflections was $R_{\text{int}} = 2.09\%$ with $R_{\sigma} = 1.56\%$. XPREP [13] determined the space group to be $C2/c$ (number 15) with $Z = 4$ for the formula moiety, $C_{92}H_{54}F_{12}LaNO_8$, including one toluene solvent molecule (C_7H_8). All absorption corrections were performed with SADABS program [14]. The structure was solved using the SHELXS Version 2013 direct method [15], and the subsequent structure refinements were performed with SHELXL Version 2013 program [16]. The final cycle of

TABLE 1: Crystallographic data of the complex.

Empirical formula	C ₉₂ H ₅₄ F ₁₂ LaNO ₈
Formula weight	1668.27
Temperature	90 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c (No. 15)
Unit cell dimensions	$a = 30.456(2)$ Å $b = 12.3617(8)$ Å $c = 23.2666(15)$ Å $\beta = 122.7730(10)^\circ$
Volume	7365.3(8) Å ³
Z	4
Density (calculated)	1.504 g cm ⁻³
Absorption coefficient	0.673 mm ⁻¹
$F(000)$	3368
Crystal size	0.20 × 0.20 × 0.10 mm
Theta range for data collection	1.59 to 28.68°
Index ranges	$-39 \leq h \leq 40, -16 \leq k \leq 16,$ $-31 \leq l \leq 30$
Reflections collected	42300
Independent reflections	8972 [$R_{\text{int}} = 0.0209$]
Reflections	8466 [$I > 2.0\sigma(I)$]
Completeness to theta = 28.68°	94.4%
Absorption correction	Empirical
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	8972/882/625
Goodness-of-fit on F^2	1.075
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0438, wR_2 = 0.1234$
R indices (all data)	$R_1 = 0.0477, wR_2 = 0.1319$
Largest diff. peak and hole (RMS deviation 0.157 e/Å ³)	3.656 and -2.052 e/Å ³

full-matrix least squares refinement (standard deviation of an observation of unit weight: $[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables) on F^2 was converged. Standard deviation of an observation of unit weight was 0.944 (least squares function minimized: (SHELXL-2013) $\sum w(F_o^2 - F_c^2)^2$, where w = least squares weights).

The nonhydrogen atoms were refined anisotropically. C-bound H atoms in the anion and cation were positioned geometrically and refined by riding model approximation using the bond restraints of 0.99 Å. N-bound H atom in pyridinium cation was also located from the difference Fourier map and refined by riding model approximation using the bond restraints of 0.89 Å.

The crystallographic details are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

3. Results and Discussion

To confirm the structure and photochemical properties of the lanthanum(III) complex, we performed the X-ray structural analysis of the complex. The molecular structure is shown in Figure 2. The main complex moiety including the lanthanum ion was high symmetrical structure (symmetry code (i): $-x + 2, y, -z + (1/2)$), and two of the four CF₃ groups were quite strongly disordered. Therefore, the sum of the C and F atoms of the formula unit was slightly different from that of the theoretical formula, and the disordered C and F atoms of the CF₃ groups are omitted from Figure 2 for clarity. Figure 2 shows the coordination structure around the lanthanum(III) ion. Eight oxygen atoms of the four β-diketonato ligands bind to the lanthanum ion in the center. The distances between the lanthanum ion and the oxygen atoms are between 2.473(2) Å

TABLE 2: Selected bond lengths [Å] and angles [°] of the complex.

Selected bond lengths		Selected bond angles ^a	
La1-O1	2.536(2)	La1-O1-C1	131.75(18)
La1-O2	2.473(2)	O1-C1-C2	129.7(3)
La1-O3	2.489(2)	C1-C2-C3	122.9(3)
La1-O4	2.478(2)	C2-C3-O2	123.4(3)
C1-O1	1.264(4)	C3-O2-La1	138.33(18)
C3-O2	1.259(3)	La1-O3-C21	138.50(17)
C21-O3	1.265(3)	O3-C21-C22	124.4(2)
C23-O4	1.259(3)	C21-C22-C23	122.8(2)
C1-C2	1.390(4)	C22-C23-O4	113.6(2)
C2-C3	1.429(4)	C23-O4-La1	135.26(17)
C21-C22	1.415(4)	O1-La1-O2	68.69(7)
C22-C23	1.379(4)	O1-La1-O3	69.23(6)
		O1-La1-O4	111.31(7)
		O2-La1-O3	115.78(7)
		O2-La1-O4	74.69(7)
		O3-La1-O4	69.23(6)
		O1-La1-O1 ⁱ	71.86(10)
		O1-La1-O2 ⁱ	77.33(7)
		O1-La1-O3 ⁱ	139.07(6)
		O1-La1-O4 ⁱ	147.86(7)
		O2-La1-O2 ⁱ	137.81(9)
		O2-La1-O3 ⁱ	78.73(6)
		O2-La1-O4 ⁱ	143.31(6)
		O3-La1-O3 ⁱ	141.14(8)
		O3-La1-O4 ⁱ	81.81(7)
		O4-La1-O4 ⁱ	83.29(10)

^aSymmetry code: ⁱ = $-x + 2, y, -z + (1/2)$.

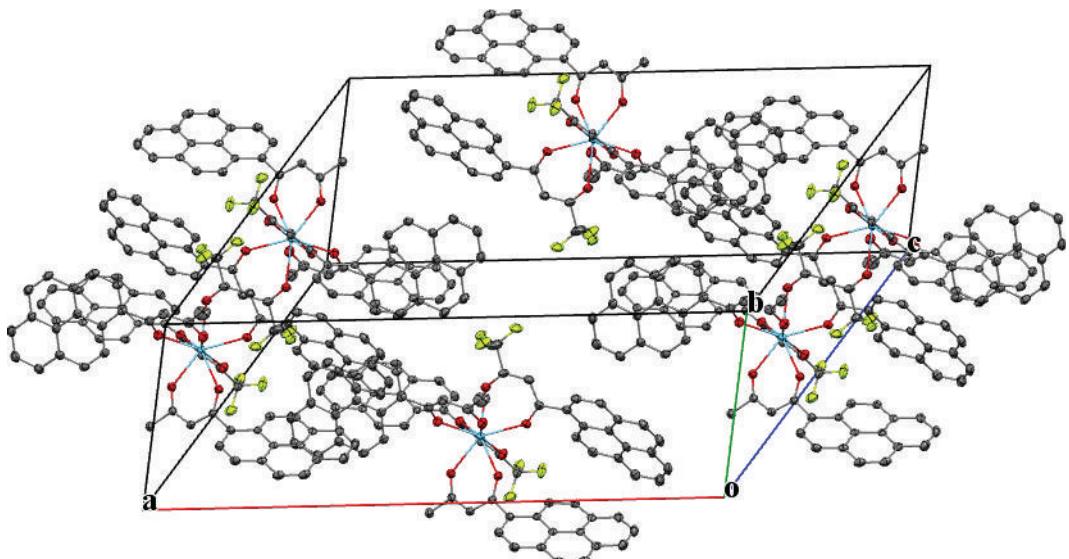


FIGURE 3: Crystal packing of the complex. Thermal ellipsoids are drawn on a 50% probability level. Blue, red, and pale green ellipsoid(s) indicate La, O, and F atom(s), respectively. Hydrogen atoms, the pyridinium counter ions, and toluene molecules are omitted for clarity.

and 2.536(2) Å. On the other hand, the C–O bond lengths are 1.259(3) Å and 1.265(3) Å. These values were quite normal; that is, the bond lengths were not affected by the bulkiness of pyrene moieties and the crystal packing.

The orientation of the four pyrenyl groups on the ligands is shown in Figure 2. Interestingly, the coordination style is similar to the conformation “1,3-alternate structure” of calix[4]arene [17, 18]; therefore, this coordination style is referred to as “1,3-alternate-like structure” in this study. In a recent study, we reported that the structure of the lanthanide complex with four β -diketone ligands having a small aromatic group (phenyl) was the so-called “cone-like structure” [10]. The angles between the pyrene moieties and β -diketonato part of the ligands are listed in Table 2. These results suggest that the structures of the complexes with four β -diketone ligands are affected by the bulkiness of these ligands.

The four pyrene moieties of the complex were not horizontally oriented, and the angle of the two neighboring pyrene moieties was 69.56° (Figure 2). The intramolecular edge-to-face CH $\cdots\pi$ interaction was observed (2.695 Å and 2.959 Å) between the two pyrene protons and the most closely located carbons of neighbor pyrene moiety. Therefore, π -systems on the pyrene moieties exist independently; in other words, intramolecular π - π stacking does not exist between the four pyrene moieties.

Crystal packing and the molecular structure, as shown in Figures 3 and 4, indicate the presence of a one-dimensional intermolecular edge-to-face CH $\cdots\pi$ interaction between all pyrene moieties of the neighboring molecules along the *c*-axes (2.854 Å and 3.016 Å). Therefore, intermolecular π - π stacking was also not observed.

In the case of pyrene and its analogues, concentration quenching or excimer formation occurs in a concentrated solution or a solid [19]. However, the absorption behavior of the complex was quite different because the concentration quenching or excimer formation was not observed at a solution concentration of 10⁻³ mol/dm³ and in the solid (crystal). UV-vis and fluorescence data were strongly supported by the orientation of the intramolecular and intermolecular pyrene moieties. No further ligand was observed to bind with the lanthanum ion in the crystal. In addition, the toluene molecule and the pyridinium ion were located independently in the crystal. These molecules did not form π -stacking or other interactions with the pyrene moieties in the crystal.

4. Conclusion

The novel complex was synthesized in high yield and characterized by IR spectroscopy, ¹H-NMR spectroscopy, elemental analysis, and pos. FAB-MS, and its spectral data were discussed. Single crystals were grown and the crystal parameters were evaluated. The 8-coordinate structure of the complex was confirmed by single crystal X-ray diffraction. One pyridinium counter cation and one toluene solvent molecule were included in the crystal. The lanthanum(III) ion in the center of the complex exhibits an 8-oxygen coordinate environment with four β -diketonato ligands.

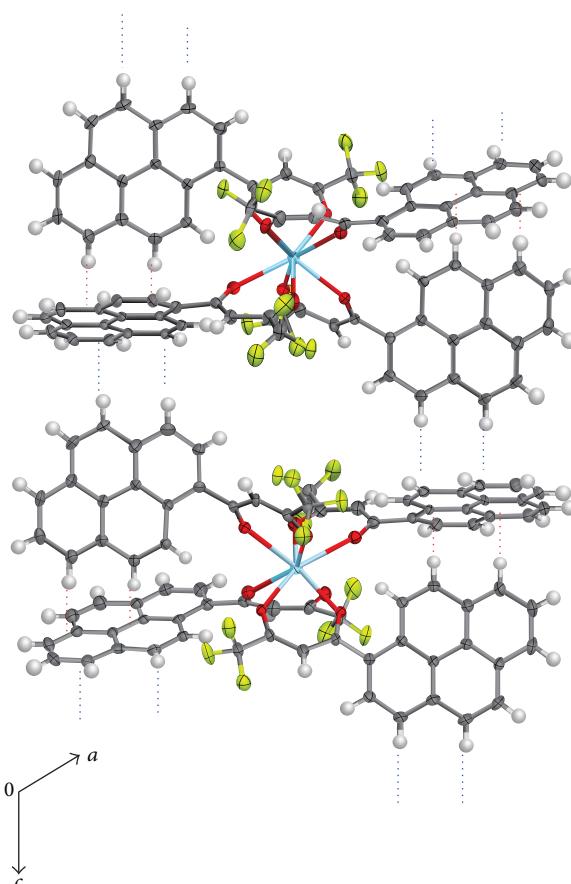


FIGURE 4: One-dimensional edge to face intra- and intermolecular CH $\cdots\pi$ interaction network of the complex in the crystal. Red and blue dotted lines show intra- and intermolecular interaction, respectively. Hydrogen atoms, the pyridinium counter ions, and toluene molecules are omitted for clarity. View along the *b*-axes.

The pyrene moieties on the ligands effectively aggregate via lanthanide multicoordination; however, intramolecular and intermolecular π - π stacking between the pyrene moieties were not observed. These results strongly support the results obtained from UV-vis and fluorescence spectral data.

Additional Material

CCDC number 1006238 contains the supplementary crystallographic data for pyridinium tetrakis{1-trifluoromethyl-3-(1'-pyreno)-1,3-propanedionato}lanthanate(III) complex. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallography Data Centre, 12 Union Road, Cambridge, UK.

Conflict of Interests

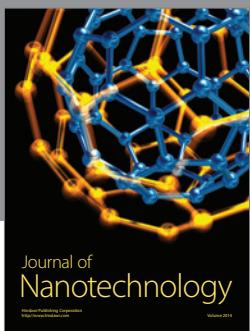
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors are grateful to the Center for Instrumental Analysis, Kyushu Institute of Technology (KITCIA), for elemental analyses, pos. FAB-MS and ^1H -NMR spectral measurements, and X-ray analysis.

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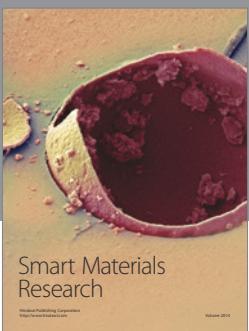
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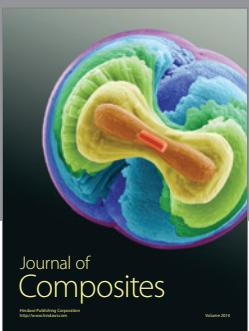
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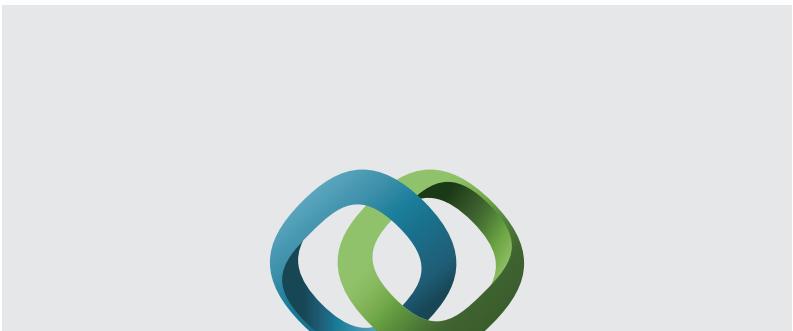
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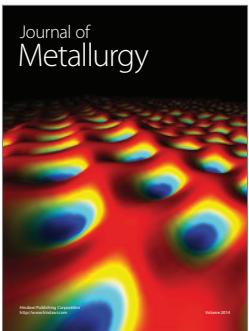


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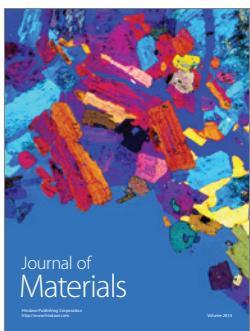
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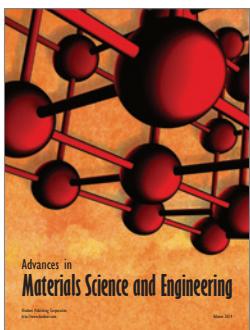
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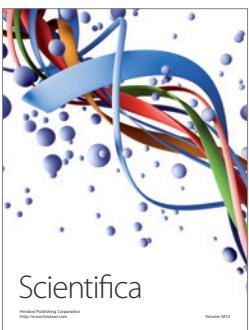
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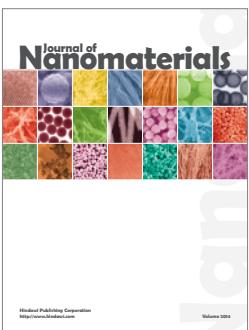
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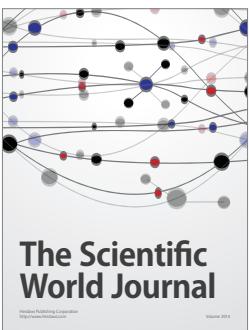
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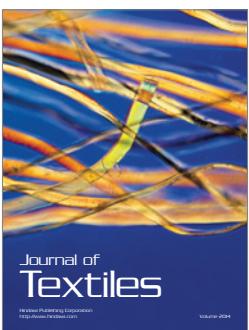
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