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Hydrothermal synthesis, structure, heterogeneous catalytic activity and photoluminescent properties of a novel homoleptic Sm(III)organic framework



Burak Ay^a, Emel Yildiz^{a,*}, Ashley C. Felts^b, Khalil A. Abboud^b

^a Department of Chemistry, Arts and Science Faculty,Çukurova University, 01330 Adana, Turkey
^b Department of Chemistry, University of Florida, Gainesville, FL 32611, USA

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1. Introduction

In the field of coordination polymers, much work has been focused on metal-organic frameworks (MOFs) based on lanthanides and multifunctional carboxylic acid ligands because of their interesting structures and their many varied of applications. The design possibilities of organic ligands, the coordination tendencies of metal ions, and the variety of possible crystallization conditions have led to a large number of open framework structures, quite often endowed with novel structural features, as well as unique properties [1]. Multidentate N- and O-donor bridging pyridine or pyrazine carboxylic acid ligands have been extensively used for the construction of new MOF systems. Among these ligands, pyridine-2,6-dicarboxylate is suitable for preparing multifunctional MOF properties such as the ability to deprotonate, high symmetry, considerable structural flexibility, and a variety of modes for coordination of metal atoms [2–5]. Lanthanides in particular have an inherent affinity for oxygen-containing ligands over other functional groups and thus provide the potential for recognition or discrimination among a variety of linker and guest species on the basis of, for example, hard-soft acid base considerations [6-8]. The hydrothermal method provides an efficient technique for

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ABSTRACT

A novel metal-organic framework, $(H_2pip)_n[Sm_2(pydc)_4(H_2O)_2]_n$ (1) $(H_2pydc=2,6$ -pyridinedicarboxylic acid, $H_2pip=piperazine)$ has been synthesized under hydrothermal conditions and characterized by the elemental analysis, inductively coupled plasma (ICP) spectrometer, fourier transform infrared (FT-IR) spectra, thermogravimetric analysis (TGA), single crystal X-ray diffraction analysis and powder X-ray diffraction (PXRD). The structure of 1 was determined to be three-dimensional, linked along Sm-O-Sm chains. The asymmetric unit consisted of one singly anionic fragment consisting of Sm(III) coordinated to two H_2 pydc ligands and one water, and one half of a protonated H_2 pip, which sits on an inversion center. 1 exhibited luminescence emission bands at 534 nm at room temperature when excited at 440 nm. Its thermal behavior and catalytic performance were investigated and the selectivity was measured as 100% for the oxidation of thymol to thymoquinone.

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synthesizing MOFs. Factors such as variations in temperature, pH, reactant stoichiometry, the presence or absence of organic cations, and even the fill volume have been shown to influence the product outcome [9,10]. One potential application of transition metal pyridinecarboxylate complexes is the oxidation of organic substrates. Considerable commercial importance is oxidation of thymol to thymoquinone [11].

In this study, we have been exploring MOF containing samarium (III) metal centers due to the ability of the element to have larger coordination sphere compared to transition metals, as well as their unique luminescent properties [12,13], and relevance to spent nuclear fuel issues [14]. Considering all these, we have designed a new metalorganic framework, $(H_2pip)_n[Sm_2(pydc)_4(H_2O)_2]_n$ (1) $(H_2pydc=2,6-pyridinedicarboxylic acid, H_2pip=piperazine)$ incorporating 2,6-pyridinedicarboxylate, aqua ligands, and piperazine as a counter moieties. The catalytic activity and luminescent properties of the synthesized MOF have also been reported. The synthesized catalyst showed high selectivity in the oxidation of thymol to thymoquinone.

2. Experimental

2.1. Materials and methods

 $Sm(NO_3)_3,6H_2O$, 2,6-pyridinedicarboxylic acid, piperazine, thymol, thymoquinone *tert*-Butyl hydroperoxide (~80%) (TBHP)

^{*} Corresponding author. E-mail address: eeyildiz@cu.edu.tr (E. Yildiz).

and hydrogen peroxide (30%) (H₂O₂) and all other solvents were purchased from commercial sources and used without further purification. 23 mL PTFE-lined stainless steel containers under autogenous pressure were used for the hydrothermal synthesis. Fourier-Transform infrared spectroscopy was performed with KBr pellets on a Perkin-Elmer RX-1 FT-IR spectrometer in the range of 4000–400 cm⁻¹. A Thermo Flash 2000 CHNS Elemental Analyzer was used for elemental analysis. A Perkin-Elmer Optima 2100 DV ICP-OES instrument was used for the ICP analysis. Perkin Elmer Pvris Diamond TG/DTA equipment was used for the TG analysis. A Rigaku Miniflex system with CuK α radiation (λ =1.54059 Å) was used for the PXRD studies. Solid state fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS 55 Luminescence Spectrometer. GC/MS was measured on a Thermo Brand chromatograph with TR5MS capillary columns (60 m \times 0.25 mm i. d.; 25 μ m film thickness). The chromatographic conditions were as follows: Injector temperature: 240 °C, beginning temperature: 50 °C, final temperature: 250 °C and heating rate: 3 °C min⁻¹. For the HPLC analysis, a Shimadzu HPLC system equipped with a reversed phase C8 column ($250 \text{ cm} \times 4.6 \text{ mm}$ column dimensions, 5 μm particle sizes, Ascentis[®]) was used. Methanol: Acetonitrile: Water (50:20:30, v/v) were used for the separation as a mobile phase. The column temperature was 35 °C, detection wavelength was 254 nm, flow rate was 1.0 mL min⁻¹, and retention time was 15 min.

2.2. Synthesis of $(H_2 pip)_n [Sm_2(pydc)_4(H_2O)_2]_n$

A solution of samarium (III) nitrate hexahydrate (0.133 g, 0.30 mmol), 2,6-pyridinedicarboxylic acid (0.150 g, 0.90 mmol), piperazine (0.078 g, 0.90 mmol), and H₂O (5 mL, 278 mmol) with the mole ratio of 1.00:3.00:3.00:927 was stirred before heating to 180 °C and holding for 72 h. The initial and final pH values were 4.80 and 6.20, respectively. The heterogeneous solution mixture was separated from the solid phase and the crystals were washed with water and dried at room temperature. Yellow crystals suitable for X-ray diffraction were isolated in 85% yield (based on Sm). Anal. Calcd. for $C_{32}H_{28}N_6O_{18}Sm_2$: C, 35.38; H, 2.58; N, 7.74. Found: C, 36.67; H, 2.89; N, 7.90%. The ICP analysis (%) showed that 1 contained Sm: 27.44; Calcd.: Sm: 27.71. IR data (cm⁻¹): 3426(s), 3247(m), 3004(m), 2820(m), 1622(s), 1581(m), 1434(s), 1387(m), 1278(m), 1189(w), 1076(w), 1020(w), 764(w), 733(m), 663(w), 582 (w), 415(w).

2.3. X-ray structure determination

X-ray Intensity data were collected at 100 K on a Bruker DUO diffractometer using MoK α radiation (λ =0.71073 Å) and an APEXII CCD area detector [14,15]. Raw data frames were read by program SAINT¹ and integrated using 3D profiling algorithms. The resulting data were reduced to produce *hkl* reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in SHELXTL2014, using full-matrix least-squares refinement [16]. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. Extensive three dimensional hydrogen bonding is present involving all ions. All acidic protons were obtained from a Difference Fourier map and refined freely. In the final cycle of refinement, 3817 reflections (of which 3686 are observed with $I > 2\sigma(I)$) were used to refine 278 parameters and the resulting R_1 , wR_2 and S (goodness of fit) were 1.10%, 2.92% and 1.093, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to

Table 1

Crystal data and structure refinement for the 1.

Empirical formula Formula weight Temperature Wavelength	C ₃₂ H ₂₈ N ₆ O ₁₈ Sm ₂ 1085.30 100(2) K 0 71073 Å	
Crystal system	Triclinic	
Space group	Pī	
Unit cell dimensions	a=6.9138(4) Å	$\alpha = 112.5046(8)^{\circ}$.
	b = 10.8451(6) Å	$\beta = 95.6993(9)^{\circ}$.
	c = 12.2155(6) Å	$\gamma = 94.7594(8)^{\circ}$.
Volume	834.67(8) Å ³	,
Z	1	
Density (calculated)	2.159 Mg/m ³	
Absorption coefficient	3.581 mm^{-1}	
F(000)	530	
Crystal size	$0.237\times0.080\times0.018~mm^3$	
Theta range for data collection	1.823–27.497°.	
Index ranges	$-8 \le h \le 8$, $-14 \le k \le 14$,	
	$-15 \le l \le 15$	
Reflections collected	18715	
Independent reflections	3817 [R(int)=0.0180]	
Completeness to theta=25.242°	100.0%	
Absorption correction	Analytical	
Max. and min. transmission	0.9515 and 0.6647	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints/ parameters	3817 / 0 / 278	
Goodness-of-fit on F ²	1.093	
Final R indices [I > 2sigma(I)]	R1=0.0110, wR2=0.0292 [3686]	
R indices (all data)	R1=0.0117, wR2=0.0293	
Extinction coefficient	n/a	
Largest diff. peak and	0.549 and -0.206 e.Å ⁻³	
hole		

the conventional R value but its function is not minimized. Crystal data and structure refinement for the **1** are summarized in Table 1, and selected bond distances, and bond angles are given in Table 2. Hydrogen bonds for **1** are listed in Table 3. Full lists of bond lengths and angles, atomic coordinates and equivalent isotropic displacements parameters, anisotropic displacement and hydrogen coordinates parameters are available in the Supporting Information (Tables S1-S4).

2.4. Catalytic procedure

Thymol oxidation was carried out at room temperature and 60 °C in a three-necked flask (100 mL) equipped with a magnetic

Table 2					
Selected bond lengths	[Å]	and	angles	[°]	for the 1.

Sm(1)–O(7)	2.4056(11)	Sm(1)-O(5)#2	2.5328(10)
Sm(1)–O(1)	2.4382(11)	Sm(1)–N(1)	2.5465(13)
Sm(1)-O(5)	2.5007(10)	O(9)–H(9X)	0.84(3)
Sm(1)-O(3)	2.5047(10)	O(9)–H(9Y)	0.75(3)
Sm(1)-O(9)	2.5108(12)	N(3)–H(3X)	0.93(2)
Sm(1)-O(4)#1	2.5248(11)	N(3)–H(3Y)	0.87(2)
Sm(1)-N(2)	2.5315(12)	C(22)-H(22B)	0.9900
O(7)-Sm(1)-O(1)	79.41(4)	O(1)-Sm(1)-N(2)	138.26(4)
O(7)-Sm(1)-O(5)	127.26(3)	O(9)-Sm(1)-N(2)	121.87(4)
O(1)-Sm(1)-O(5)	149.99(3)	O(5)-Sm(1)-N(1)	133.22(4)
O(7)-Sm(1)-O(3)	84.95(3)	O(9)-Sm(1)-N(1)	121.72(4)
O(1)-Sm(1)-O(3)	126.03(3)	N(2)-Sm(1)-N(1)	116.31(4)
O(7)Sm(1)-O(9)	134.73(4)	C(1) - O(1) - Sm(1)	125.31(9)
O(5)-Sm(1)-O(9)	79.19(4)	C(7) - O(3) - Sm(1)	123.92(9)
O(3)-Sm(1)-O(9)	140.28(4)	Sm(1)-O(9)-H(9X)	111.2(16)
O(7)-Sm(1)-N(2)	63.80(4)	Sm(1)-O(9)-H(9Y)	119.8(19)

Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z #2 -x+1,-y,-z+1 #3 x-1,y,z #4 -x+2,-y,-z+2.

Table 3Hydrogen bonds for 1 [Å and °].

D–HA	d (D–H)	d (HA)	d (DA)	<(DHA)
O(9)–H(9X)O(3)#2 N(3)–H(3X)O(2) N(3)–H(3Y)O(8)#5 C(5)–H(5 A)O(7)#3	0.84(3) 0.93(2) 0.87(2) 0.95	1.80(3) 1.72(2) 1.99(2) 2.53	2.6347(16) 2.6384(18) 2.7804(17) 3.4467(19)	172(2) 171(2) 149(2) 163.5

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 -x+1,-y,-z+1 #3 x-1,y,z #4 -x+2,-y,-z+2 #5 -x+2,-y+1,-z+2.

stirrer, a reflux condenser, and a temperature controller in an oil bath. Thymol (1.5 g, 10 mmol) and 10 mL acetonitrile were added successively into the flask. Then, the appropriate amount of oxidant 30 wt% of the aqueous H_2O_2 (3.5 mL, 34.90 mmol) and 80 wt% aqueous of the *tert*-Butyl hydroperoxide (3.0 mL, 24 mmol) were added in the reaction mixture. After heating this mixture to be 25 °C and 60 °C, the metal complex (0.05, 0.10 and 0.15 g) was joined to start the reaction and stirred constantly for 3, 6, 9, 12 and 24 h. 20 μ L aliquots were collected at given time intervals and were analyzed by HPLC for determining the thymoquinone (Scheme 1).

3. Results and discussion

3.1. Description of crystal structure of $(H_2 pip)_n [Sm_2(pydc)_4(H_2O)_2]_n$

The asymmetric unit consists of the Sm(III) ion, two pyridine-2,6-dicarboxylate anionic ligands coordinated through the pyridine nitrogen and one of each of the carboxylate oxygen atoms, and a coordinated water. The asymmetric unit also contains a half piperazine dication located on an inversion center. One H₂pip is present for every two samarium. Each nitrogen in piperazine has two hydrogen to establish charge balance (Fig. 1). The Sm complex is situated near an inversion center (on 0.5, 0, 0.5) resulting in dimers through the coordination of Sm1 and O5 (and their symmetry equivalents: 1-x, -y, 1-z). To the best of our knowledge. and after an extensive search of the 2016 version of the Cambridge Structural Database (version 1.18) [17,18], we present here the first pure Samarium coordinated pyridine-2,6-dicarboxylate ladder structure (Figs. 2 and 3). Literature searches reveal reports of many Sm(III) extended structures including 1-D chains, 2-D sheets, and 3-D networks. Published ladder structures of samarium are formed by H-bonding between two adjacent chains. A 1-D chain of dimers was also reported, but it does not fit the ladder description. Rungs of the ladder are formed by the dimers through the two Sm(III) centers and atoms O5 and O5a (1-x, -y, 1-z)(Fig. 4). The ladder structure is formed by simple translation along the a-axis, of the dimers through coordination of the Sm(III) centers with the O4 atoms. The counter piperazine dications pack in columns, also along the a-axis, filling channels between the ladders. The cations are strongly H-bonded to the Sm ladders. The coordinated water shows some H-bonding interaction with one of the coordinated carboxylate oxygens, O3, though it does not



Scheme 1. Oxidation of the thymol to thymoquinone using Sm(III) catalyst.

appear to play a large role in the overall three-dimensional network. The ladder structures are connected by H–bonding through the piperazine solvent cations. Piperazine fills the channels between the samarium ladders (Fig. 5).

3.2. IR spectra

The infrared spectrum of the free H₂pydc shows stretching bands attributed to v(O-H), v(C=O), v(C=N) and v(C-H) at 3063, 1688, 1573 and 1080 cm⁻¹, respectively (Fig. S1). The IR spectrum of the free H_2 pip shows stretching bands attributed to v (N-H), v(C-H) and v(C-N) at 3271, 2936 and 1324 cm⁻¹, respectively (Fig. S2). In the IR spectra of 1 (Fig. S3), O-H stretching vibration of coordinated water molecules was observed at 3247 cm⁻¹ [19]. The band, having medium intensity at 3426 cm⁻¹, can be assigned to the v(N-H) stretching vibrations of H₂pip which is outside the coordination sphere in the structure [20]. C=0stretching frequency appeared at 1688 cm⁻¹ in the spectra of ligand, after coordination, this peak shifted to 1622 cm^{-1} in the spectra of **1**. This shift indicates that the oxygen atoms in the carbonyl groups were coordinated to samarium ions. The new bands between 764–433 cm⁻¹, can be assigned to the v(Sm-O)and v(Sm-N) stretching vibrations [21,22]. These new bands also indicate that O and N atoms of H₂pydc coordinate the samarium ions.

3.3. PXRD patterns and thermal analysis

The powder X-ray diffraction data of the **1** was obtained and compared with the corresponding simulated single-crystal diffraction data. PXRD pattern (Fig. 6) indicates that the MOF synthesized under hydrothermal condition is highly crystalline and is in good agreement with the simulated pattern. However, the differences in intensity may be due to the preferred orientation of the microcrystalline powder sample. Thermal analysis was performed in the temperatures range of 50-800 °C under N₂ atmosphere at 1 atm with a heating rate of 10 °C min⁻¹. The TGA curve of **1** is shown in Fig. S4, which indicates that it decomposes in main two steps. The slight slop could be moisture in initiate. The first stage between 290 and 340 °C were attributed to the loss of H₂pip and 2 mol coordinated water molecules per formula unit with weight loss percentage of 13.71% (Calcd.:11.25%). The third weight loss of 45.49%, which occurred between 398 and 548 °C, corresponds to the decomposition of remaining H₂pydc ligands (Calcd. 46.20%). The fact that H₂pydc ligands are lost at a higher temperature suggests that they are coordinated with the samarium atoms. The remaining weight of 29.70% corresponds to the final product Sm₂O₃. The observed weight was in good agreement with the calculated value (28.80%). Thermal results fundamentally agree with the single crystal structure of the 1, and the observed thermal behavior reflects the structural features.

3.4. Luminescence property

The luminescence properties of the ligand and its polymeric complex containing Sm(III) were performed in solid state at room temperature, and in the same conditions to understand the nature of the luminescence of **1**. As shown in Fig. 7, the free ligand exhibited broad emission band (λ_{max} : 370 nm) when excited at 320 nm in the solid state. The observed emission band may be related to the π - π * transition of aromatic/pyridine rings [23,24]. **1** showed one maximum and sharp emission band at 534 nm upon excitation with a wavelength of 440 nm, which is mainly caused by the ligands and Sm(III) ions. The wavelength of maximum emission peaks of **1** is largely red shifted as 164 nm compared with that of H₂pydc. The red-shift emissions are likely related to



Fig. 1. Displacement ellipsoids of entire fragments (drawn at 40% probability).



Fig. 2. A packing diagram shows extensive hydrogen bonding between piperazine and the molecule to create a three-dimensional network.

the intraligands luminescence emission [24,24-26]. The emission bands of lanthanides with aromatic pyridine carboxylate ligands have shown between 450 and 550 nm compared with that of previous studies [27,28].

3.5. Catalytic activity

One of the most important advantages of heterogeneous catalysts is the easy recovery from the reaction medium and their high thermal stabilities. In comparison, homogeneous catalysts usually have low thermal stability, and the catalyst cannot be easily recovered from the reaction medium by filtration. In this catalytic reaction, acetonitrile was used as a solvent and hydrogen peroxide and *tert*-Butyl hydroperoxide were used as oxidant agents. The conversion values in different catalytic conditions are given in Table 4. The oxidation product, thymoquinone, was characterized by using GC/MS (Fig. S5). HPLC analysis was performed for the determination of the catalytic performance of **1**. Hydrogen peroxide has mostly been used as an oxidant in the investigation of the catalytic efficiency of lanthanide complexes towards oxidation reactions in a heterogeneous medium but TBHP has seldom been used [29]. These oxidant agents are known to be inexpensive and



Fig. 3. A packing diagram shows the samarium complex forming a two-dimensional ladder structure, with the rungs being the samarium dimers.



Fig. 4. A packing diagram shows the diamond-like structure where the Sm(III) complexes form a two-dimensional ladder structure via O5 and equivalent atoms.

environmental friendly oxidant reagents. It is worth mentioning that there were no oxidation products (trace amounts) using only oxidant agents without catalyst (Figs. S6-S7). Thymol was only oxidized to thymoquinone while using the catalyst **1** (Fig. S8). To

determine the catalytic performance of **1**, thymol conversion was plotted as a function of temperature in 25 and 60 °C. Other variables were 0.05, 0.10 and 0.15 g catalyst amounts, *tert*-Butyl hydroperoxide (3.0 mL), and hydrogen peroxide (3.5 mL) as oxidants



Fig. 5. The ladder structures are connected by H-bonding through the piperazine solvent cations.



Fig. 6. X-ray powder diffraction patterns of complex 1: (a) Simulated; (b) Experimental.

for 3, 6, 9, 12 and 24 h reaction times. The obtained maximum conversion values were 16.73% with TBHP and 35.21% with H_2O_2 . Their selectivities were approximately 100% (Figs. S9–S10) for this reaction. The catalyst activities were optimized with 0.15 g (0.14 mmol) of complex using H_2O_2 and TBHP as oxidants. The maximum thymol conversion was 35.21% after 24 h with nearly 100% selectivity at 60 °C. Maximum conversion values were observed when the amount of catalyst and reaction time increased for both oxidants. To determine the effect of H_2 pydc on catalytic performance, the same catalytic conditions were performed in this



Fig. 7. Photoluminescent spectra of the free ligand (red) and compound **1** (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

oxidation process. No product was observed using H_2 pydc as a catalyst in the HPLC analysis results (Fig. S11). Similarly, the reaction was carried out with solely Sm(III) salt, and the product was obtained only trace amount (Fig. S12). These tests supported that ligand and metal salt were not showed any catalytic activities in that oxidation process without catalyst. According to HPLC analysis, any by-product was not observed except thymoquinone by using both oxidants at the end of the catalytic studies (Figs. S13-

Table 4

% Thymol conversion values under different reaction conditions.

H ₂ O ₂			tert-Butyl hydroperoxide				
Temperature (°C)	Catalyst amount (g)	Reaction time (hour)	Thymol conversion (%)	Temperature (°C)	Catalyst amount (g)	Reaction time (hour)	Thymol conversion (%)
25	0.05	3	2.04	25	0.05	3	0.47
		6	3.17			6	0.67
		9	5.16			9	0.85
		12	6.53			12	1.02
		24	9.51			24	1.21
	0.10	3	7.73		0.10	3	1.40
		6	10.73			6	1.59
		9	13.28			9	1.83
		12	14.70			12	1.90
		24	17.95			24	2.52
	0.15	3	14.95		0.15	3	2.95
		6	15.93			6	3.75
		9	16.86			9	4.55
		12	18.62			12	5.29
		24	19.44			24	7.07
60	0.05	3	25.17	60	0.05	3	5.61
		6	26.76			6	6.79
		9	27.94			9	7.26
		12	28.01			12	9.54
		24	30.25			24	12.09
	0.10	3	26.32		0.10	3	10.40
		6	26.85			6	12.94
		9	27.53			9	13.18
		12	28.07			12	13.97
		24	33.52			24	15.74
	0.15	3	27.92		0.15	3	12.40
		6	28.87			6	14.07
		9	30.24			9	14.25
		12	31.01			12	16.49
		24	35.21			24	16.73

(Catalyst: (H₂pip)_n[Sm₂(pydc)₄(H₂O)₂]_n; Solvent: Acetonitrile).

S14). Under the optimized reaction conditions, maximum conversion 35.21% was observed by using H_2O_2 . This value is higher than the corresponding and our previous catalytic studies [30–32]. We believe that the synthesized catalysts under hydrothermal conditions could show high selectivity because of their very high purity and crystallinity properties.

3.6. Separation and reusability of the catalyst

To determine the reusability of the catalyst, we performed under maximum thymol conversion conditions (See Table 4). Five sequential reactions were performed for 0.15 g catalyst, using both hydrogen peroxide and tert-Butyl hydroperoxide as oxidant agents for 24 h at 60 °C. After every reuse, the catalyst was separated from the reaction mixture, filtered off, and washed with hexane (5 mL), water (25 mL), and acetone (20 mL) then dried in a vacuum oven at 50 °C and reused. The conversion values did not decrease significantly after four tests using hydrogen peroxide and two tests using tert-Butyl hydroperoxide (Table S5). These results showed that the catalyst has long usability in the oxidation reaction by using hydrogen peroxide as an oxidant (Fig. 8). Also, the higher conversion was recorded by using hydrogen peroxide. After five tests, by-product formation began to form in the catalytic reaction medium. The samarium content of the filtrate was determined by ICP analysis after the separation of the catalyst by filtration. At the end of the four runs, only 1.2% of samarium was lost into the solution during the reaction.

4. Conclusions

We have successfully synthesized and characterized a recoverable heterogeneous catalyst, $(H_2pip)_n[Sm_2(pydc)_4(H_2O)_2]_n$, by



Fig. 8. The effect of oxidant on the oxidation of thymol by the 1 catalytic system.

using the hydrothermal method as an environmental friendly route. The structure of this MOF, which contains the samarium (III) ion has been reported for the first time. The compound consists of $[Sm_2(pydc)_4(H_2O)_2]_n^{2n-}$ anionic chains linked by $\{H_2pip\}^{2+}$ cations. H_2pip ligands are situated outside the coordination sphere, and are mainly dependent on the pH value of the solution. The photoluminescent spectra show that complex is a potential luminescent material at the maximum emission at 534 nm as a bathochromic shift as compared to that of the ligand.

Thymoquinone is a compound with a commercial value considerably higher than its precursor thymol. Thymoquinone can be easily obtained by catalytic oxidation of this precursor using environmentally cheap oxidizing agent, hydrogen peroxide and the title compound as a heterogeneous catalyst [11]. The catalyst shows high selectivity in the oxidation of thymol to thymoquinone in acetonitrile at 60 °C. No by-product was observed in the HPLC chromatograms. The catalyst could be reused for four successive cycles without noticeable loss of its catalytic activity, and it was eligible for the oxidation of thymol.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2016.09.018.

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