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**Reaction Kinetics, Mechanisms and  
Catalysis**

ISSN 1878-5190

Volume 129

Number 1

Reac Kinet Mech Cat (2020) 129:391-401

DOI 10.1007/s11144-019-01709-3

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# Chemoselective synthesis of drug-like pyrrolo[2,3,4-kl]acridin-1-one using polyoxometalate@lanthanoid catalyst

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Received: 4 November 2019 / Accepted: 9 December 2019 / Published online: 14 December 2019  
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## Abstract

The incorporation of polyoxometalates (POMs) or metal oxides into the metal–organic frameworks opens new research avenues for the synthesis of heterogeneous catalysts. In this project, a catalytic system based on neodymium clusters and Keggin-type of heteropoly acid (HPA) ( $\text{Na}[\text{Nd}(\text{pydc}-\text{OH})(\text{H}_2\text{O})_4]_3$ )[ $\text{SiW}_{12}\text{O}_{40}$ ] was used as heterogeneous catalyst for one pot synthesis of pyrroloacridines, via multi component reactions involving dimedone, isatin and aniline in green condition. The novelty of this work originates from using inorganic–organic hybrids based upon POMs in catalyzing organic transformation. Compared with parent HPA (89.0% yield in 15 min for [ $\text{SiW}_{12}\text{O}_{40}$ ]<sup>4-</sup>), this hybrid catalyst showed higher catalytic activity (94% yield in 8 min) in pyrroloacridines synthesis. The hybrid compound could be reused at least five times without obvious loss of the catalytic activity.

**Keywords** Polyoxometalate · Pyrrolo[2,3,4-kl]acridin-1-ones · Inorganic–organic hybrid catalyst · Chemoselective synthesis · Green chemistry

## Introduction

The antimicrobial chemotherapy is the most important field of medical science in the last century that its advances are essential due to the antimicrobial resistance. In spite of the early breakthroughs obtained by arsenicals, they could associate with considerable side effects. So, scientists announced the idea of synthetic chemotherapy. Ehrlich and Benda employed acridines as antimicrobial agents for the first time in 1912, and the originally medical use of such antibiotics occurred in 1917 [1, 2]. Combination of acridine with different heterocycles is currently

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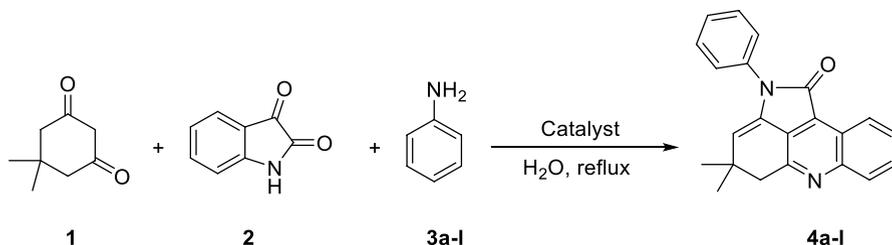
one of the interesting issues in medical sciences. It may give new types of trypanocidal, antibacterial, and antimalarial agents [3].

Further, pyrrole ring presents in the core of many bioactive natural products and new therapeutic compounds. Pyrrole including compounds displayed incredible pharmacological properties such as antimicrobial, antifungal, anti-HIV and antioxidant activities, antagonist effects over the gonadotropin-releasing hormone (GnRH) receptor, cyclooxygenase-2 (COX-2) inhibitory effect, and so on [4–7]. Their optical features make them as potential compounds in optoelectronic tools [8].

It was also found that pyrroloacridines and pyrroloacridones are attractive antitumor [9], anthelmintic [10], and antifungal organic molecules [11]. Some of them may be useful to develop chemotherapy antitumor drugs since they can bind to DNA and inhibit the growth of cancerous cells [12–14]. There are a few synthetic procedures [15] to construct pyrroloacridines and most of discovered pyrroloacridines were isolated as tetracyclic cores from marine metabolites, such as alplakinidines and plakinidines A–C [16].

Among the various catalysts for organic synthesis, heteropoly acid (HPAs), as metal–oxide nanoclusters, are remarkable inorganic materials which have attracted extensive attention [17]. In HPA clusters protons can act as Brønsted acids. Furthermore, the metal ions on the structure of HPAs have unoccupied orbitals that able to accept electrons and act as Lewis acids. Thus, the HPAs are unique acid catalyst for organic reactions. However, the pure bulk HPAs present small specific surface areas that prevent accessibility to the active sites and confine their catalytic activity. Moreover, due to high solubility of HPAs in many polar solvents, separation and recovery of the catalyst is difficult. One of the most promising approaches to improve HPAs catalytic activity is hybridization of HPAs with coordination complexes to build inorganic–organic hybrid structures [18–21]. Inorganic–organic hybrids are usually insoluble and possess good stability and high surface areas. In inorganic–organic hybrid compounds, the Lewis acid properties of metal ions in the metal–organic complex could amplify the acid catalyzed properties of HPAs. In addition, delocalization of negative charge of HPA anions in huge supramolecular hybrid structure could exacerbate the Lewis acid properties of inorganic–organic hybrid catalyst. Due to the interest HPA-based inorganic–organic hybrid architectures, we have successfully synthesized series of these compounds, which demonstrated unusual topologies and improved properties [22–29].

This proves the importance of pyrroloacridine core as the key scaffold of some bioactive molecules. Consequently, to continue our research efforts for developing the efficient approaches in heterocyclic syntheses and heterogeneous catalysis [30–35], herein, preparation of a highly stable  $\{\text{Na}[\text{Nd}(\text{pydc-OH})(\text{H}_2\text{O})_4]_3\}[\text{SiW}_{12}\text{O}_{40}]\cdot 15\text{H}_2\text{O}$  inorganic–organic hybrid catalyst is described and its catalytic role is investigated in the chemoselective synthesis of pyrrolo[2,3,4-*kl*]acridinones. The mentioned inorganic–organic hybrid catalyzed one-pot condensation of dimedone, aniline derivatives and isatin by passing from a ring opening sequence and an intramolecular cyclization (Scheme 1) [36–40].



**Scheme 1** Synthesis of pyrroloacridine derivatives

## Experimental

### Materials and instruments

All chemicals used for synthesis and investigation of the catalytic activity of  $\{\text{Na}[\text{Nd}(\text{pydc-OH})(\text{H}_2\text{O})_4]_3\}[\text{SiW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$  catalyst were purchased commercially and used without further purification. For the synthesis of pyrroloacridine derivatives, dimedone, isatin and different substituted aniline were used. These compounds were obtained from Sigma-Aldrich on analytical grade.

The progress of multicomponent reaction was monitored by TLC silica gel 60 F254, using ultraviolet light.

### Synthesis of hybrid catalyst

$\{\text{Na}[\text{Nd}(\text{pydc-OH})(\text{H}_2\text{O})_4]_3\}[\text{SiW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$  (Nd/HPA hybrid) catalyst was synthesized and characterized and its structure was reconfirmed [23, 31]. This catalyst was synthesized hydrothermally by reacting of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (110 mg, 0.25 mmol),  $\text{H}_2\text{pydcOH} \cdot \text{H}_2\text{O}$  (50 mg, 0.25 mmol),  $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$  (288 mg, 0.1 mmol) and distilled water (15 ml) in Teflon-lined autoclave at 110 °C for 3 days. The pH of the mixture was adjusted to 4 with NaOH solution. After slow cooling to room temperature, yellow prismatic crystals could be isolated.  $\text{C}_{21}\text{H}_{63}\text{N}_3\text{NaN}_3\text{O}_{82}\text{SiW}_{12}$  (4359.70): Calcd. C 5.79, H 1.46, N 0.96; found C 5.84, H 1.35, N 0.89, IR (KBr pellet,  $\text{cm}^{-1}$ )  $\nu$ : 3420 (br.s), 1600 (s), 1753 (s), 1492 (w), 1428 (s), 1338 (m), 1246 (m), 1123 (m), 1028 (s), 973 (s), 924 (s), 881 (m), 795 (s), 701 (w).

### Synthesis of pyrroloacridine derivatives

To a mixture of dimedone (1 mmol), isatin (1 mmol) and aniline (1 mmol) in water (15 ml), Nd/HPA hybrid (0.03 g) as a catalysts was added and the resulting mixture was heated at 80 °C for appropriate reaction time (Table 1). At the end of the reaction (monitored by TLC), the solid was filtered of and recrystallized in

**Table 1** Optimization of the reaction conditions

Entry	Catalyst/amount (mol%)	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	–	H <sub>2</sub> O	80	60	20
2	Sulfamic acid	H <sub>2</sub> O	80	25	80
3	<i>p</i> -TSA	H <sub>2</sub> O	80	20	82
4	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	H <sub>2</sub> O	80	18	89
5	Nd/HPA hybrid/5	H <sub>2</sub> O	80	12	91
6	Nd/HPA hybrid/10	H <sub>2</sub> O	80	8	94
7	Nd/HPA hybrid/15	H <sub>2</sub> O	80	8	95
8	Nd/HPA hybrid/10	H <sub>2</sub> O	r.t	20	80
9	Nd/HPA hybrid/10	H <sub>2</sub> O	50	15	91
10	Nd/HPA hybrid/10	EtOH	70	12	90
11	Nd/HPA hybrid/10	H <sub>2</sub> O/EtOH	80	10	92
12	Nd/HPA hybrid/10	CH <sub>3</sub> CN	80	15	90
13	Nd/HPA hybrid/10	CH <sub>2</sub> Cl <sub>2</sub>	40	25	85
14	Nd/HPA hybrid/10	DMF	80	15	85

EtOH. Nd/HPA hybrid can be recovered and reused with a simple washing up, at least in five consecutive runs without appreciable loss of activity.

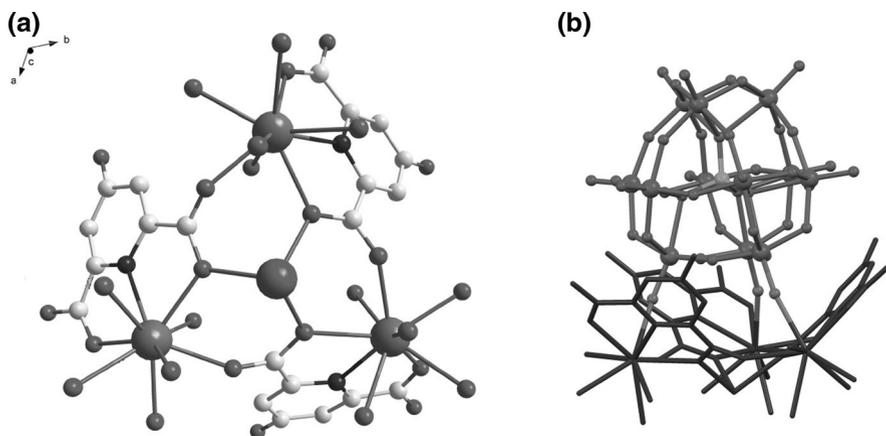
## Result and discussion

### Catalyst characterization

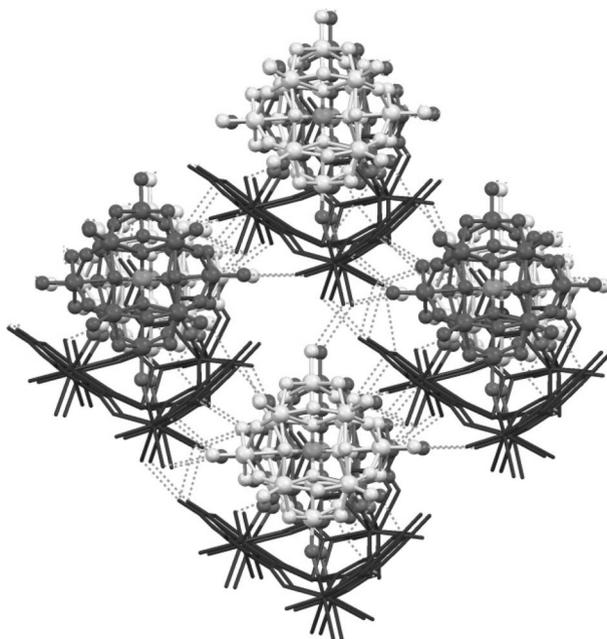
Based on X-ray crystallography, the hybrid catalyst consists of a heterometallic polynuclear cation unit  $\{\text{Na}[\text{Nd}(\text{pydc-OH})(\text{H}_2\text{O})_4]_3\}^+$ , H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> as Keggin-type polyoxometalates (POMs) and 15 lattice water molecules. As shown in Fig. 1a, three Nd<sup>3+</sup> ions are bridged by carboxylate oxygen atoms of the three organic ligands to form an equilateral triangle and central sodium ion is trapped in the center of the trinuclear Neodymium cluster. In this hybrid, trinuclear Nd-organic cluster is bound to three terminal oxygen atoms of the Keggin anion leading to an intriguing flower-like-like structure (Fig. 1b). Notably, all coordinating oxygen atoms of Keggin anion belong to a corner-sharing W<sub>3</sub>O<sub>15</sub> triad, thereby resulting in a discrete molecule. All discrete molecules are further connected to each other by anion– $\pi$  interactions and hydrogen-bonding to construct a 3-D supramolecular network (Fig. 2).

The powder X-ray diffraction patterns of hybrid catalyst are all in good agreement with the ones simulated patterns based on the data of the single-crystal structures, indicating the phase purity of the product [23].

The morphology of the catalyst was studied by SEM analyses [31]. SEM analyses clearly indicated that the hybrid catalyst has a regular structure and fine particles.



**Fig. 1** **a** View of the heterometallic cation unit in the hybrid structure and **b** flowerlike-like structure of the hybrid catalyst



**Fig. 2** 3-D supramolecular network in the hybrid catalyst

To confirm the high porosity of the hybrid structures, nitrogen ( $N_2$ ) adsorption was performed at 77 K through simulation study. Grand Canonical Monte Carlo simulation has been employed for predicting the ability of this hybrid catalyst and parent Keggin to capture  $N_2$ . As it has been shown in the already published paper by the authors [31], the  $N_2$  uptake has been increased rather two times over hybrid

**Table 2** One pot, three-component synthesis of pyrrolo[2,3,4-*kl*]acridin-1-one derivatives [36]

<p><b>4a, 8 min, 94 %</b></p>	<p><b>4b, 5 min, 93 %</b></p>	<p><b>4c, 5 min, 96 %</b></p>
M.P.=194-195	M.P.=194-195	M.P.=194-195
<p><b>4d, 5 min, 94 %</b></p>	<p><b>4e, 8 min, 90 %</b></p>	<p><b>4f, 8 min, 94 %</b></p>
M.P.=194-195	M.P.=194-195	M.P.=194-195
<p><b>4g, 10 min, 94 %</b></p>	<p><b>4h, 6 min, 94 %</b></p>	<p><b>4i, 10 min, 94 %</b></p>
M.P.=194-195	M.P.=194-195	M.P.=194-195
<p><b>4j, 12 min, 95%</b></p>	<p><b>4k, 10 min, 93%</b></p>	<p><b>4l, 10 min, 92%</b></p>
M.P. = 180-182	M.P.= 188-191	M.P.= 167-169

structure compared to the parent Keggin. It is worthwhile mentioning  $N_2$  adsorption uptakes over both catalysts imply potential application of the hybrid catalyst in separation and adsorption processes.

### Catalytic activity

In continuation of this research, the catalytic activity of Nd/HPA hybrid was determined in multicomponent reaction. Initially, the reaction of dimedone, isatin and aniline was selected as model reaction. To design an eco-friendly method, water was chosen as a green solvent. At the first several acidic catalysts such as sulfamic acid, *p*-TSA,  $H_4SiW_{12}O_{40}$  and Nd/HPA hybrid were examined in this reaction. The results are shown in Table 1. In the next step, to find the effects of various solvents, different polar and non-polar solvents were examined. Finally, to find the effect of the catalyst amount, this model reaction was performed without catalyst. The uncatalyzed reaction was carried out sluggishly and trace amount of product was obtained, but in the presence of 10 mol% of Nd/HPA hybrid the desired product was isolated in 91% which represented the important role of our hybrid catalyst in the reaction progress.

For further evaluation of the scope and limitation of this strategy, a variety of functionalized anilines were reacted with isatin and dimedone under the optimal conditions. The corresponding pyrroloacridine derivatives were obtained in excellent yields in short reaction times. The results are summarized in Table 2. All compounds are known and their physical data were compared with those of authentic samples and found being identical.

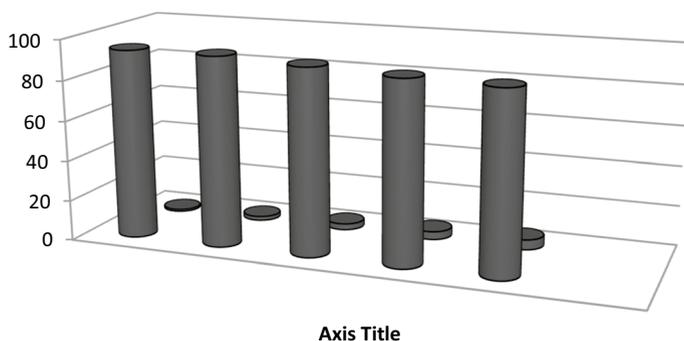
Finally, the efficiency of Nd/HPA for the above mentioned multi-component reaction was compared with some of the previously reported catalysts (Table 3). By comparing the protocols, it can be concluded that the use of Nd/HPA led to higher product yield in shorter reaction times. In addition, use of aqueous media and heterogeneous catalyst make this protocol eco-friendly.

### Catalyst recycling

The important property of a catalyst is its reusability. The highly stable crystalline 3-D supramolecular structure provides hybrid catalyst to be stable and reusable. Moreover, good diffusion of HPAs at the molecular level reduces the conglomeration

**Table 3** Comparison of Nd/HPA hybrid with other heterogeneous catalysts

Entry	Catalyst/catalyst amount	Reaction condition	Time (min)	Yield (%)	References
1	Lactic acid/35 mol%	Solvent free, 80 °C	30	91	[37]
2	[HMI]HSO <sub>4</sub> /0.5 ml	80 °C	35	88	[38]
3	Ag NPs/rGO/4 wt%	EtOH/MW	2	90	[39]
4	[B(HSO <sub>4</sub> ) <sub>3</sub> ]/0.1 g	EtOH, reflux	7	92	[40]
56	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SO <sub>3</sub> H/0.01 g	Solvent free, 80 °C	14	88	[36]
6	Nd/HPA	H <sub>2</sub> O, 80 °C	5	96	This work



**Fig. 3** Reusability of Nd/HPA hybrid in the synthesis of pyrrolo[2,3,4-kl]acridin-1-one

[41], catalyst leaching and deactivation [41], and finally leading to the high immobilization of HPAs.

Lastly, the reusability of Nd/HPA hybrid was investigated. In this regard, the product yield in the model product was studied for five cycles in the presence of fresh and reused Nd/HPA hybrid. It was found that Nd/HPA hybrid can be recycled for five reaction runs while its catalytic activity was not changed (Fig. 3).

## Conclusion

In conclusion, we have developed a green and highly efficient approach for a one-pot three-component synthesis of pyrrolo[2,3,4-kl]acridin-1-one as pharmacologically active compounds using  $(\text{Na}[\text{Nd}(\text{pydc}-\text{OH})(\text{H}_2\text{O})_4]_3)\{\text{SiW}_{12}\text{O}_{40}\}$  hybrid as a reusable heterogeneous catalyst in  $\text{H}_2\text{O}$  as a green solvent. Simple reaction conditions, short reaction time, high to excellent yields of the products, easy isolation of the products and reusability of the catalyst for five reaction runs are the key features of this multicomponent reaction. Catalytic activity of this hybrid compound is much higher than that of parent POM, indicating that the uniform dispersion of POM units into the coordination complex may expose more POMs active centers at the molecular level, thus remarkably improve the catalytic activities. Finally, we provide an outlook at emerging areas, where polyoxometalate@lanthanoid composites could lead to new catalytic reactivity [41–43].

**Acknowledgements** We appreciate partial financial support from Alzahra University, Tehran, Iran. M.M. is thankful to Research Council of Ferdowsi University of Mashhad, Mashhad, Iran.

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