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Three naphthalenedisulfonate polymers with imidazole-containing ligands: Synthesis, structure and heterogeneously catalytic performance in reactions of enamination of β -dicarbonyl compounds



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activity towards enamination of β -ketoesters.

ABSTRACT

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1. Introduction

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Three new naphthalenedisulfonate polymers, $[Cd(2,6-nds)(bib)]_n(1)$, $[Cd(1,5-nds)(bib)]_n(2)$, and $[Cu(2,6-nds)_{0.5}(tpim)]_n(3)$, have been successfully synthesized by hydrothermal reactions of corresponding metal salts with naphthalenedisulfonate (nds) and imidazole-containing ligands 1,4-bis(imidazol-1-yl-methyl)benzene (bib) and 2,4,5-tri(4-pyridyl)-imidazole (tpim). The structures of these polymers were determined by single crystal X-ray diffraction analysis. Polymers 1 and 2 crystallize in the same space group and have similar cell parameters, and thus show same three-dimensional (3D) framework architecture. Complex 3 has the same 2D layer structure. The photoluminescent properties of the complexes

1 and 2 were investigated. Catalytic tests indicate that complex 3 has chemo- and regio-selective catalytic

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The design and synthesis of metal-organic hybrid materials (MOHMs) have attracted much attention not only because of their intriguing structural architectures but also owing to their promising applications in adsorption, guest exchange, magnetism, and heterogeneous catalysis [1-3]. These MOHMs are normally synthesized by mixing metal salts with organic ligands under solvothermal or hydrothermal conditions. The final architecture depends on several factors such as shape and functionalities of the ligands as well as coordination number and geometry of the metal cation. For the organic ligands, the past decade has witnessed the rapid development of various organocarboxylate acid ligands to which great efforts have been devoted due to these ligands having strong coordination capacity and versatile coordination modes [4–7]. In contrast to the flourishing studies of organocarboxylate, the coordination chemistry of organosulfonate remains relatively rare, probably due to their weak coordinating ability, although they have similar structures [8]. In fact, it is noted that the weak coordination nature of SO₃⁻ makes its coordination mode very flexible and sensitive to the chemical environment [9–11]. As a consequence of this, organosulfonates are not only good candidates to provide unique opportunities for the combination of the auxiliary ligands in the construction diverse coordination architectures as multiple H-bonding acceptors by the three oxygen atoms, but also for their functional properties demonstrated by the related complexes [12-15]. For example, Monge's groups have reported a series of thermally stable arenedisufonate lanthanide coordination polymers with CdI₂-like layer structure and bifunctional catalysis properties [15]. Most importantly, Cai et al. have evidenced that the use of auxiliary ligands such as various amines can alter the chemical environment of metal ions, and allow the SO_3^- group compete with water molecules and coordinate to metal ions [16,17]. It is noted that arenedisulfonates have rigid spacers and potential multiple binding sites, which exhibit various coordination modes ranging from μ_1 to μ_6 [18–20] So far, many transition metal complexes with arenedisulfonates, with or without the help of co-ligands have been reported [16–22]. Thus, the efforts of many groups have produced a plethora of organosulfonate structural motifs.

On the other hand, enamination of β -dicarbonyl compounds, which provides important synthetic protocols to build significant subunits in some biologically natural products such as therapeutic agents and antitumour agents, has recently been attracted

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particular attention [23,24]. In this regard, our groups have recently demonstrated that a copper-based metal–organic framework can be used as a promising heterogeneous catalyst for chemo- and regio-selective enamination of β -ketoesters [25]. The interesting result motivated us to further investigate other heterogeneous catalysts for promoting efficiently some organic transformation reactions. In continuation with our ongoing studies on the development of new catalytic system, herein we report our studies on an efficient protocol applicable to enamination of β -dicarbonyl compounds with complex **3** as new heterogeneous catalyst. Further, the syntheses and crystal structures of three polymers, namely, [Cd(2,6-nds)(bib)]_n (**1**), [Cd(1,5-nds)(bib)]_n (**2**), and [Cu(2,6-nds)_{0.5}(tpim)]_n (**3**) will be presented.

2. Experimental section

2.1. Materials and physical techniques

All reagents and solvents were obtained from commercial sources and used without further purification. Elemental analyses of C, H and N were carried out on a Flash 2000 elemental analyzer. Infrared spectra (IR) were recorded as KBr pellets on a Nicolet-6700 spectrometer in the 4000–400 cm⁻¹ region. Thermogravimetric analyses (TGA) were performed by heating the crystalline sample from 25 to 800 °C at a rate of 2 °C/min in a N₂ atmosphere on a SDTQ600 differential thermal analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8-ADVANCE X-ray diffractometer with Cu K α (λ = 1.5418 Å). Luminescent spectra were recorded with a Rigaku RIX 2000 fluorescence spectrophotometer.

2.2. Synthesis of the polymers

All three polymers were synthesized by the same method (Scheme S1, Supporting Information), as follows: a mixture of $M(CH_3COO)_2$ (M = Cd(1), Cd(2), and Cu(3), 0.1 mmol), naphthalenedisulfonate ligand (0.1 mmol), imidazole ligand (0.1 mmol) and $H_2O(10 \text{ mL})$ was adjusted to the special pH values with HNO₃ (1 M) and NaOH (1 M) (the pH values of 4 for 1, and 4.5 for 2 and 3, respectively), stirred for 0.5 h, and then transferred and was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 3 days. Cooling the vessel to room temperature at a rate of 5 °C h^{-1} afforded crystals of **1–3** suitable for a single crystal X-ray diffraction. For 1, yield: 0.497 g, 78% based on Cd. Anal. Calc for C₂₄H₂₀CdN₄O₆S₂: C, 45.25; H, 3.16; N, 8.80. Found: C, 45.39; H, 3.24; N, 8.92%. IR (KBr, cm⁻¹): 2940 m, 2843 m, 1620 w, 1570 m, 1498 m, 1433 m, 1326 m, 1199 s, 1064 s, 1030 s, 987 w, 930 m, 856 m, 831 m, 772 m, 755 m, 718 s, 662 s. For 2, yield: 0.478 g, 75% based on Cd. Anal. Calc for C₂₄H₂₀CdN₄O₆S₂: C, 45.25; H, 3.16; N, 8.80. Found: C, 45.16; H, 3.35; N, 8.97%. IR (KBr, cm⁻¹): 2986 m, 2853 m, 1534 m, 1465 w, 1432 m, 1339 s, 1239 m, 1214 s, 1096 s, 1070 s, 987 w, 920 m, 834 m, 756 m, 753 m, 721 s, 662 s, 631 s. For 3, yield: 0.557 g, 55% based on Cu. Anal. Calc for C₄₆H₃₂Cu₂N₁₀O₆S₂: C, 54.59; H, 3.19; N, 13.84. Found: C, 54.72; H, 3.31; N, 14.12%. IR (KBr, cm⁻¹): 3138 s, 3115 s, 2989 m, 2858 m, 1566 m, 1475 w, 1414 m, 1323 w, 1232 s, 1184 s, 1098 s, 1056 s, 903 w, 830 m, 776 m, 753 m, 718 s, 651 s, 632 s.

2.3. X-ray structural studies

Crystallographic data of **1–3** were collected on a Bruker Smart Apex-II CCD area detector at room temperature (graphitemonochromated, Mo K α -radiation, ω - and θ -scan technique, λ = 0.71073 Å). Intensity data were corrected for Lorenz and polarization effects and a multi-scan absorption correction was

Table 1

Crystallographic data and structure refinement summary for polymers 1-3.

Complexes	1	2	3
Chemical formula Formula weight Crystal system Space group a (\hat{A}) b (\hat{A}) c (\hat{A})	$\begin{array}{c} C_{24}H_{20}CdN_4O_6S_2\\ 636.96\\ Triclinic\\ P\bar{1}\\ 5.2955(14)\\ 9.241(2)\\ 12.267(3)\end{array}$	$\begin{array}{c} C_{24}H_{20}CdN_4O_6S_2\\ 636.96\\ Triclinic\\ P\bar{1}\\ 5.4578(7)\\ 9.6089(13)\\ 11.2103(15) \end{array}$	$\begin{array}{c} C_{46}H_{32}Cu_2N_{10}O_6S_2\\ 1012.02\\ Triclinic\\ P\bar{1}\\ 8.5300(17)\\ 10.561(2)\\ 13.458(3)\end{array}$
$ \begin{aligned} \alpha & (^{\circ}) \\ \beta & (^{\circ}) \\ \gamma & (^{\circ}) \\ V & (\hat{A}^{3}) \\ Z \\ D_{calc} & (g \text{ cm}^{-3}) \end{aligned} $	89.724(3) 83.419(3) 87.219(3) 595.6(3) 1 1.776	85.756(10) 88.132(10) 80.950(10) 578.87(13) 1 1.827	101.07(3) 103.83(3) 112.72(3) 1029.7(4) 1 1.632
$\mu (mm^{-1})$ T (K) Reflections collected	1.143 296(2) 4307	1.176 293(2) 4406	1.201 293(2) 8535
Unique reflections R_{int} Goodness-of-fit (GOF)	2183 0.0218 1.053	2153 0.0131 1.035	3823 0.0285 1.040
$\frac{K_1(I > 2\sigma)}{wR_2(I > 2\sigma)}$	0.0440 0.1172	0.0186 0.0456	0.0438 0.1367

performed. The structures were solved with direct methods and refined with full-matrix least-squares techniques on F^2 using the SHELXTL program package [26,27]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common isotropic thermal parameter. The 2,6-nds molecules (N3, C16, C17, O9, O10) in 2 are disordered and the occupation of these disordered atoms is 50%, respectively. The crystallographic data for **1–3** are listed in Table 1.

2.4. Typical procedure for the enamination of β *-ketoesters*

The enamination of β -ketoesters were carried out under solvent-free conditions. In a typical enamination reaction, ketone (0.1 mmol) was treated with amine (0.1 mmol) in the presence of complex **3** (0.01 mmol). The reactions were monitored by the thin layer chromatography. After the reaction finished, 10 mL of ethyl acetate was added to the reaction mixture. The mixture was stirred for another 5 min. Then the catalyst was filtered off, and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate mixture (10:1) as the eluent. All isolated pure products were fully characterized by ¹H NMR or otherwise compared with the known compounds. The recovered catalyst was washed with ethyl acetate, dried, and reused without further purification or regeneration. Moreover, the recovered catalysts were characterized by the X-ray powder diffraction and showed identical results to those of the fresh samples.

3. Results and discussion

3.1. Synthesis and IR spectrum

The previous studies have demonstrated that hydrothermal synthesis is a powerful synthetic strategy to prepare polymeric solids with better crystallinity [28]. In the process of hydrothermal synthesis, many factors such as initial reactants, metal-to-ligand ratio, pH value, and temperature have a profound influence on the final crystallization outcome. In this work, parallel experiments show that the pH values of the reaction system are important facts for improving the yield of the tree coordination polymers. The good





Fig. 1. (a) Coordination environment of the Cd atom in 1. The hydrogen atoms are omitted for clarity. Symmetry code: A = -x + 2, -y, -z. B = x + 1, y, z. C = -x + 1, -y, -z. (b) View of 1D infinite chain along the *b* axis generated by the Cd(II) ions and the bib ligands. (c) View of 1D infinite chain along the *c* axis generated by the Cd(II) ions and the 2,6-nds ligands. (d) View of the 3D polymeric framework of **1**.

yields of polymers **1–3** could be obtained in the special pH values of 4 for **1**, and 4.5 for **2** and **3**. When the pH value is lower or higher than that special value, the expected crystals could be obtained in lower yield. The elemental analyses for all the resulting three polymers are in good agreement with the theoretical values.

All three coordination polymers are stable in air and insoluble in water and common organic solvents. The IR spectra of complexes of **1–3** show that the aromatic C–H stretching frequencies extend through the region 2804–3078 cm⁻¹. The well-resolved frequencies of the aromatic rings span over the regions of 1250–1750 and 500–980 cm⁻¹. Bands characteristic of the fundamental and split v_3 S–O stretching modes are observed in the range of 1000–1240 cm⁻¹. The IR spectrum of **3**, the broad and strong absorption at 3145–3410 cm⁻¹ is attributed to the N–H stretching vibrations.

3.2. Structure description

3.2.1. Crystal structure of 3D coordination polymers [Cd(2,6-nds)(bib)]_n (1)

The single-crystal X-ray diffraction reveals that polymer **1** crystallizes in the triclinic space group of $P\bar{1}$. The asymmetric unit of **1** consists of half unique Cd(II) ion, half 2,6-nds anion and half bib ligand. As shown in Fig. 1a, each Cd(II) ion is in a slightly distorted octahedral coordination geometry coordinated by two nitrogen from two individual bib ligands, and four oxygen atoms from four individual 2,6-nds anions. The Cd–N distances are 2.256(3) and the Cd–O bonds range between 2.339(3) and 2.368(3) Å. In addition, the bond angles around each Cd(II) range from 84.25(11) to 180.0(8)° (Table 2). They are within the normal range expected for such complexes [29]. In each bib ligand, the two imidazole rings

Table 2 Selected bond distances (A)	Å) and angles (deg) for the po	lymers 1–3 ª.
Complex 1	2.256(2)	Cd(1) O(1)

Complex I					
$Cd(1)-N(1)^{i}$	2.256(3)	Cd(1)-O(1)	2.339(3)	$Cd(1)-O(2)^{ii}$	2.368(3)
Cd(1)-N(1)	2.256(3)	$Cd(1) - O(1)^{1}$	2.339(3)	$Cd(1)-O(2)^{11}$	2.368(3)
$N(1)^{i}-Cd(1)-N(1)$	180.0(2)	N(1)-Cd(1)-O(2) ⁱⁱ	90.40(11)	$O(2)^{i}-Cd(1)-O(2)^{iii}$	180.00(8)
$N(1)^{i}-Cd(1)-O(1)$	84.25(11)	$O(1)-Cd(1)-O(2)^{ii}$	86.94(10)	$O(1)-Cd(1)-O(1)^{i}$	180.00(14)
N(1)-Cd(1)-O(1)	95.75(11)	$O(1)^{i}-Cd(1)-O(2)^{ii}$	93.06(10)	$N(1)^{i}-Cd(1)-O(2)^{ii}$	89.60(11)
$N(1)^{i}-Cd(1)-O(1)^{i}$	95.75(11)	$N(1)^{i}-Cd(1)-O(2)^{iii}$	90.40(11)	$O(1)-Cd(1)-O(2)^{iii}$	93.06(10)
$N(1)-Cd(1)-O(1)^{i}$	84.25(11)	$N(1)-Cd(1)-O(2)^{iii}$	89.60(11)	$O(1)^{i}-Cd(1)-O(2)^{iii}$	86.94(10)
Complex 2					
Cd(1)–N(1)	2.2407(16)	Cd(1)-O(3)#2	2.3279(14)	$Cd(1) - O(1)^{i}$	2.3704(14)
$Cd(1)-N(1)^{i}$	2.2407(16)	Cd(1)-O(3)#3	2.3279(14)	Cd(1)-O(1)	2.3704(14)
$N(1)-Cd(1)-N(1)^{i}$	180.0	$O(3)^{ii}-Cd(1)-O(3)^{iii}$	180.0	N(1)-Cd(1)-O(1)	86.56(6)
$N(1)-Cd(1)-O(3)^{ii}$	94.82(6)	$N(1)-Cd(1)-O(1)^{i}$	93.44(6)	$N(1)^{i}-Cd(1)-O(1)$	93.44(6)
$N(1)^{i}-Cd(1)-O(3)^{ii}$	85.18(6)	$N(1)^{i}-Cd(1)-O(1)^{i}$	86.56(6)	$O(3)^{ii}-Cd(1)-O(1)$	90.34(5)
$N(1)-Cd(1)-O(3)^{iii}$	85.18(6)	$O(3)^{ii}-Cd(1)-O(1)^{i}$	89.66(5)	$O(3)^{iii}-Cd(1)-O(1)$	89.66(5)
$N(1)^{i}-Cd(1)-O(3)^{iii}$	94.82(6)	$O(3)^{iii}-Cd(1)-O(1)^{i}$	90.34(5)	$O(1)^{i}-Cd(1)-O(1)$	180.0(1)
Complex 3					
$Cu(1)-N(3)^{ii}$	1.935(3)	Cu(1)-N(4)	2.031(3)	Cu(1) - O(2)	2.784(4)
$Cu(1)-N(5)^{iii}$	2.004(4)				
$N(3)^{ii}-Cu(1)-N(5)^{iii}$	128.47(15)	$N(5)^{iii}-Cu(1)-N(4)$	106.46(14)	$N(5)^{iii}-Cu(1)-O(2)$	93.89(13)
$N(3)^{ii}-Cu(1)-N(4)$	124.30(15)	$N(3)^{ii}-Cu(1)-O(2)$	98.81(14)	N(4)-Cu(1)-O(2)	84.48(13)

^a Symmetry transformations used to generate equivalent atoms for **1**: (i) -x + 2, -y, -z. (ii) x + 1, y, z. (iii) -x + 1, -y, -z. (iv) x - 1, y, z. For **2**: (i) -x + 1, -y + 1, -z + 1. (ii) -x + 2, -y + 1, -z + 1. (iii) x - 1, y, z. For **3**: (ii) x, y, z + 1. (iii) x - 1, y - 1, z.

are mutually parallel, and they form a dihedral angle of 58.425(3)° with the corresponding phenyl ring, respectively.

As depicted in Fig. 1b, the bib ligands adopt the μ_2 -bridging modes to bind adjacent Cd(II) centers forming a 1D zigzag polymeric [Cd(bib)]_n chain along the *b* axis with the adjacent Cd···Cd separation of 15.323 Å. It is also noted that the other one 1D infinite [Cd(2,6-nds)]_n chain along the *c* axis is formed by the connection of 2,6-nds with the Cd(II) ions, as depicted in Fig. 1c. In the latter 1D chains, the distances of two adjacent Cd(II) are 5.295(3) Å. Furthermore, these adjacent 1-D chains are connected through μ_2 -2,6-nds ligands to generate a 2-D sheet in the *ac* plane. Finally, the resulting 2-D sheets are further linked via the μ_2 - η^1 : η^1 2,6-nds ligands in up and down orientation to form a 3D framework structure, as shown in Fig. 1d.

3.2.2. Crystal structure of 3D coordination polymers $[Cd(1,5-nds)(bib)]_n$ (2)

The single crystal X-ray diffraction analysis reveals that **2** and **1** crystallize in the same space group and have similar cell parameters (Table 1), indicating that they have similar structures. The asymmetric unit of **2** consists of half unique Cd(II) ion, half 1,5-nds anion and half bib ligand. As shown in Fig. 2a, each Cd(II) ion is in a slightly distorted octahedral coordination geometry coordinated by two nitrogen from two individual bib ligands, and four oxygen atoms from four individual 1,5-nds anions, similar to those found in **1**. The Cd–N distances are 2.241(2) Å, and the Cd–O bonds range from 2.328(2) and 2.370(2) Å. The bond angles around each Cd(II) range from 85.18(6) to 180.0° (Table 2). They are in good agreement with those reported complexes [30]. In each bib ligand, the two imidazole rings are mutually parallel, and they form a dihedral angle of 70.586(8)° with the corresponding phenyl ring, respectively.

In **2**, each bib adopts a μ_2 -bridging mode to bridge Cd(II) ions generating a 1D zigzag polymeric [Cd(bib)]_n chain along the *a* axis with the adjacent Cd···Cd separation of 14.215 Å, as shown in Fig. 2b. Meanwhile, it is noted that all sulfonate groups act as a μ_2 - η^1 : η^1 -bridge through its two O atoms. Thus, each 1,5-nds can also link two adjacent Cd(II) centers to form a 1D infinite chain along the *c* axis, as demonstrated in Fig. 2c. The nearest distance of two adjacent Cd(II) is 5.458(4) Å. Furthermore, the two 1D chains are connected through μ_2 -1.5-nds ligands to generate a 2-D sheet in the *ac* plane, similar to that of **1**. The resulting 2D sheets are further cross-linked via the μ_2 -1,5-nds ligands in different orientation to form a 3D framework, as shown in Fig. 2d.

3.2.3. Crystal structure of 2D coordination polymers $[Cu(2,6-nds)_{0.5}(tpim)]_n$

In polymer **3**, the asymmetric unit consists of one Cu(I) atom, one tpim ligand, and half 2,6-nds, as shown in Fig. 3a. Each Cu(I) atom sits in a tetracoordinate environment defined by three N-donors from three individual tpim ligands and one oxygen atom from one 2,6-nds. The Cu–O bond lengths are 2.784(4), and Cu–N bonds range from 1.935(3) to 2.031(3) Å (Table 1), respectively, typical for bond lengths in similar compounds [31].

In the crystal structure, each tpim adopts a μ_3 - η^1 : η^1 : η^1 bridging mode to bridge Cu(I) ions affording a 2D sheet, as depicted in Fig. 3b. The 2D network structure consists of hexagon grids in which the Cu(I)...Cu(I) distances are 10.710(4), 13.458(3) and 13.651(7) Å, respectively. As shown in Fig. 3c, each 2,6-nds ligand acts as an H-shaped bridge, linking two neighboring Cu(I) ions into 2D layers.

3.3. Fluorescence properties

The photoluminescent properties of **1**, **2**, and bib in solid state at room temperature were studied. The emission spectra of polymers **1**, **2** and ligand bib are very similar, as shown in Fig. 4. Upon excitation at 275 nm, the strongest emission peak for free ligand bib appears at 358 nm, corresponding to the $n \rightarrow \pi^*$ transitions. For **1** and **2**, excitation of the microcrystalline samples at 332 nm and 360 nm leads to the generation of intense fluorescent emissions, with similar maximum peaks observed in the blue region (**1**, 360 nm and **2**, 411 nm). The similarity of the emission and excitation spectra is in agreement with the previous explanation by Chen et al. [32], which indicates that a ligand-centered $\pi \rightarrow \pi^*$ excitation is responsible for emissions in complexes **1** and **2**.

3.4. Thermogravimetric analysis

To investigate their thermal stabilities, thermogravimetric analyses of polymers **1–3** were carried out under nitrogen atmosphere. As shown in Fig. 5, polymers **1–3** show similar thermal behaviors. The three polymers are thermally very stable up to 251 °C, because there are no solvent molecules in the frameworks.



Fig. 2. (a) Coordination environment of the Cd atom in **2**. The hydrogen atoms are omitted for clarity. Symmetry code: A = -x + 1, -y + 1, -z. B = -x + 2, -y + 1, -z + 1. C = x - 1, y, z. (b) View of 1D infinite chain along the b axis generated by the Cd(II) ions and the bib ligands. (c) View of 1D infinite chain along the c axis generated by the Cd(II) ions and the 1,5-nds ligands. (d) View of the 3D polymeric framework of **2**.

Subsequently, it keeps losing weight at 251-355 °C for **1**, 258-510 °C for **2**, and 256-490 °C for **3**, corresponding to the thermal decomposition of the organic components.

3.5. Enamination of β -ketoesters

Recent studies have shown that some copper coordination complexes exhibit interesting catalytic activities [25,33-35]. To evaluate the catalytic activity of **3**, the reaction of ethyl acetoacetate with aniline was performed in solvent free conditions at room temperature for 1 h, which generated the corresponding product in excellent yield (Table 3, entry 1). To check the generality as well as the effectiveness of our protocol, a number of aromatic and aliphatic amines were screened for this study, and the results are listed in Table 3. The reaction proceeded with equal ease in the case of substituted amines containing electron-donating functionalities or not functionalities. This method is also very efficient for aliphatic amines, such as cyclohexenamine (Table 3, entry 8). However, probably because of steric reasons, *ortho*-chloroaniline and *ortho*-methylaniline reacted slowly and gave a relatively lower yield than the corresponding *para* isomers, respectively (Table 3, entries 2 and 3, entries 5 and 6). It is noted that this reaction



Fig. 3. (a) Coordination environment of the Cu atom in **3** with a labeling scheme and 30% thermal ellipsoids. The hydrogen atoms omitted for clarity. Symmetry operators: A = x, y, z + 1; B = x - 1, y - 1, z. (b) View of a two-dimensional grid in **3**. (c) View of 2D layer structure in **3**.

(c)

displays the excellent chemoselectivity. The nucleophilic reactant amine only reacts with the ketone of the β -ketoesters, in all the cases no reaction with ester was observed to give the corresponding amide, similar to that of our previous report [25].

To prove the heterogeneous mechanism of the condensation catalyzed by polymer **3**, the catalyst was filtered off after 15 min reaction time and stirring of the filtrate continued at the same condition. The reaction was again monitored by ¹HMNR analysis. The



Fig. 4. Fluorescence spectra of bib, 1 and 2 in the solid state at room temperature.

Fig. 5. Thermogravimetric analyses (TGA) curve of polymers 1–3.

Table 3

Synthesis of different β -enaminoesters using complex **3** as catalyst under solvent-free conditions.



Table 3 (continued)



^a Isolated yield.

result confirms the assumption of a heterogeneous mechanism since neither additional ethyl acetoacetate is consumed nor product formed after filtration. Further, for a more comprehensive study of the catalytic activity of **3** in the condensation of β -ketoesters with primary amines, a recycling test with three consecutive runs was performed (see Section 2 and Fig. S1). As mentioned before, a product yield of 96% is achieved in the first run after 1 h. In the second and the third run the product yields, determined after the same reaction time (1 h), decrease to 94% and 92%, respectively. Thus, the recovered materials remained stable with complete retention of reactivity, which is further confirmed by PXRD analysis, although the powder pattern for **3** showed the presence of some minor different peaks in the experimental patterns, such as the positions, intensities, etc., compared with that of the simulated (see Supporting Information, Fig. S1).

4. Conclusions

In this contribution, three new naphthalenedisulfonate polymers with diverse structures were successfully constructed under hydrothermal conditions. With the help of multidentate imidazole-containing ligands, the SO_3^- groups can be acted as potential multidentate ligands and compete with water molecules for metal ion coordination. More importantly, catalytic investigations have revealed the polymer **3** to be excellent catalysts for enamination of β -ketoesters. The polymer **3** shows excellent structural stability, and retains good catalytic activity over several cycles, and display chemo- and region-selectivity in the reaction process.

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Appendix A. Supplementary material

The details of X-ray diffraction, analytical and spectral data collections, the corresponding spectra and Tables are given in the Supplementary material. CCDC 1012200, 1012201, 929895 contain the supplementary crystallographic data for compounds **1**, **2** and **3** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.ica.2015.03.014.

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