以芳香羧酸及双咪唑基化合物为配体的钴配合物的合成和晶体结构

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摘要:以硝酸钴、4,4′-(六氟异丙基)二(苯甲酸)(H₂FBA)和 1,2-二咪唑基二甲苯(OBIX)或 4,4′-二咪唑基二甲联苯(BIMB)为原料,在水热条件下得到 2 个结构不同的配位聚合物[Co(OBIX)(FBA)]ₙ (**1**)和[Co₂(BIMB)₂(FBA)₂]ₙ (**2**)。对它们进行了元素分析、红外光谱分析,并利用 X-射线衍射测定了它们的单晶结构。配合物 **1** 中 2 个钴离子通过 2 个 OBIX 配体桥连成一个 24 元大环,它再通过 FBA 配体连接成一维管状结构,而配合物 **2** 中钴离子通过两种配体连接成一维左右两种螺旋结构,2 种螺旋结构通过交替互锁形成二维层状结构。结果说明了辅助配体在配合物组装过程中起着非常重要的作用。

关键词:钴配合物;双咪唑配体;芳香羧酸配体;晶体结构

Syntheses and Crystal Structures of Two Cobalt(II) Coordination Polymers Derived from 4,4′-(Hexafluoroisopropylidene)bis(benzoate) and Bis(imidazole) Ligands

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Abstract: Two cobalt(II) coordination polymers, $[Co(OBIX)(FBA)]_n$ (**1**) and $[Co_2(BIMB)_2(FBA)_2]_n$ (**2**) (H_2FBA=4,4′-(hexafluoroisopropylidene)bis(benzoic acid), OBIX=1,2-bis(imidazol-1-ylmethyl)benzene and BIMB=4,4′-bis(imidazol-1-ylmethyl)biphenyl), have been synthesized and characterized by IR spectroscopy, elemental analysis and single-crystal X-ray diffraction. Complex **1** crystallizes in monoclinic, space group $P2_1/c$ with a=1.422 43(4) nm, b=1.662 30(4) nm, c=1.234 68(3) nm, β=96.683 (2)°, V=2.899 57(13) nm^3, $C_{31}H_{22}F_6N_4O_4Co$, M_r=687.46, D_c=1.575 $g\cdot cm^{-3}$, $F(000)$=1 396, μ=0.676 mm^{-1} and Z=4. Complex **2** belongs to monoclinic, space group $P2_1/c$ with a=1.416 29(3) nm, b=2.979 64(6) nm, c=1.822 55(5) nm, β=110.716 0(10)°, V=7.193 9(3) nm^3, $C_{74}H_{52}F_{12}N_8O_8Co_2$, M_r=1 527.10, D_c=1.410 $g\cdot cm^{-3}$, $F(000)$=3 112, μ=0.553 mm^{-1} and Z=4. The final R_1=0.061 2 and wR_2=0.124 5 for 6 368 observed reflections ($I>2\sigma(I)$). Structural analyses reveal that complex **1** exhibits a one-dimensional tubular structure consisting of alternating rings and rods, whereas complex **2** possesses a two-dimensional polycatenated framework which is generated by joining both P and M helices by BIMB ligands. The results show that ancillary ligands play a significant role in the structure of the final products. CCDC: 924709, **1**; 924710, **2**.

Key words: Co(II) complex; bis(imidazole) ligands; polycarboxylate; crystal structure

The rational design and controlled synthesis of metal-organic frameworks (MOFs) have attracted tremendous attention owing to their intriguing structural topologies and wide potential applications including gas storage and separation, catalysis, enantioselective separation, luminescent sensing, and

magnetic materials[1-7]. The selection of the special ligand is very important in the construction of these coordination polymers. As an important family of multidentate O-donor ligands, aromatic polycarboxylate ligands have been extensively employed in the preparation of such metal-organic complexes with multidimensional networks and interesting properties [8-14]. Hence, the reported coordination polymers are mostly constructed by rigid polycarboxylate ligands[8-10]. Recently, more and more attention has been paid to the flexible polycarboxylate ligands[11-14], but studies about semirigid V-shaped polycarboxylate ligands are relatively few[15-17].

The ligand 4,4′-(hexafluoroisopropylidene)bis (benzoic acid) as a semirigid dicarboxylate ligand has been investigated in recent years[18-22]. Because of its bent geometry, it can induce porous framework with many characters such as selective adsorption, catalysis, magnetism, fluorescence, and so on. Flexible imidazole ligands have been widely used to construct MOFs. The flexible nature of spacers allows the ligands to bend and rotate when they coordinate to metal centers, which often causes the structural diversity[23-26]. To examine the effect of the flexibility and spacer length of the imidazole ligands on the assembly of supramolecular entities, two bis (imidazole) ligands, namely, 1,2-bis(imidazol-1-ylmethyl)benzene (OBIX) and 4,4′-bis(imidazol-1-ylmethyl)biphenyl(BIMB), were used to react with the Co(II) as ancillary ligands. As expected, we successfully isolated two new coordination polymers [Co(OBIX)(FBA)]$_n$ (1) and [Co$_2$(BIMB)$_2$ (FBA)$_2$]$_n$ (2). Herein, we report their syntheses and crystal structures.

1　Experimental

1.1　Materials and general methods

All reagents for syntheses and analyses were purchased from commercial sources and used as received without further purification. The OBIX and BIMB ligands were synthesized according to the reported method[27]. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region.

1.2　Synthesis of [Co(OBIX)(FBA)]$_n$ (1)

A mixture containing Co(NO$_3$)$_2$·6H$_2$O (59.2 mg, 0.2 mmol), H$_2$FBA (39.2 mg, 0.1 mmol), OBIX (23.8 mg, 0.1 mmol) and LiOH·H$_2$O (8.4 mg, 0.2 mmol) in 15 mL of deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 140 ℃ for 3 d. Purple block crystals of 1 were collected by filtration and washed with water and ethanol several times with a yield of 62% based on OBIX ligand. Anal. Calcd. for C$_{31}$H$_{22}$F$_6$N$_4$O$_4$Co(%): C, 54.16; H, 3.23; N, 8.15. Found(%): C, 54.09; H, 3.25; N, 8.17. IR spectrum: 3 412, 3 089, 1 612, 1 573, 1 522, 1 435, 1 377, 1 287, 1 181, 1 091, 1 019, 973, 861, 779, 695 and 592 cm^{-1}.

1.3　Synthesis of [Co$_2$(BIMB)$_2$(FBA)$_2$]$_n$ (2)

A mixture containing Co(NO$_3$)$_2$·6H$_2$O (59.2 mg, 0.2 mmol), H$_2$FBA (78.4 mg, 0.2 mmol), BIMB (62.8 mg, 0.2 mmol) and LiOH·H$_2$O (16.8 mg, 0.4 mmol) in 15 mL of deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 140 ℃ for 3 d. Purple block crystals of 2 were collected by filtration and washed with water and ethanol several times with a yield of 55% based on BIMB ligand. Anal. Calcd. for C$_{74}$H$_{52}$F$_{12}$N$_8$O$_8$Co$_2$(%): C, 58.20; H, 3.43; N, 7.3. Found (%): C, 58.11; H, 3.47; N, 7.41%. IR spectrum: 3 409, 3 102, 1 613, 1 582, 1 565, 1 519, 1 443, 1 383, 1 293, 1 172, 1 091, 1 007, 971, 843, 752, 692 and 571 cm^{-1}.

1.4　X-ray crystallography

Two purple block single crystals with dimensions of 0.26 mm×0.22 mm×0.20 mm for 1 and 0.22 mm× 0.20 mm×0.12 mm for 2 were mounted on glass fibers for measurement, respectively. X-ray diffraction intensity data were collected on a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) using the φ-ω scan mode at 296(2) K. Data reduction and empirical absorption correction were performed using the SAINT and SADABS program[28], respectively. The structure was solved by the direct method using SHELXS-97[29] and refined by full-matrix least squares

on F^2 using SHELXL-97[30]. All of the non-hydrogen atoms were refined anisotropically. The details of the crystal parameters, data collection and refinement for **1** and **2** are summarized in Table 1, and selected

Table 1　Crystal data and structure refinement for 1 and 2

Complex	**1**	**2**
Formula	$C_{31}H_{22}F_6N_4O_4Co$	$C_{74}H_{52}F_{12}N_8O_8Co_2$
Formula weight	687.46	1 527.10
Temperature / K	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	1.422 43(4)	1.416 29(3)
b / nm	1.662 30(4)	2.979 64(6)
c / nm	1.234 68(3)	1.822 55(5)
β / (°)	96.683(2)	110.716 0(10)
V / nm³	2.899 57(13)	7.193 9(3)
Z	4	4
D_c / (g·cm⁻³)	1.575	1.410
Absorption coefficient / mm	0.676	0.553
θ range / (°)	1.89~25.05	1.38~25.10
$F(000)$	1 396	3 112
Reflections collected	16 375	45 340
Independent reflections	4 953 (R_{int}=0.046 3)	12 796 (R_{int}=0.081 0)
Reflections observed ($I>2\sigma(I)$)	3 548	6 368
Data / restraints / parameters	4 953 / 0 / 415	12 796 / 0 / 925
Goodness-of-fit on F^2	1.020	1.028
R_1, wR_2 ($I>2\sigma(I)$)	0.036 4, 0.073 9	0.061 2, 0.124 5
R_1, wR_2 (all data)	0.056 9, 0.082 0	0.129 4, 0.141 5
Largest difference peak and hole / (e·nm⁻³)	321 and −259	745 and −554

Table 2　Selected bond lengths (nm) and angles(°) for 1 and 2

1					
Co(1)-O(1)	0.203 05(17)	Co(1)-N(4)ⁱⁱ	0.208 0(2)	Co(1)-N(1)	0.204 77(19)
Co(1)-O(2)	0.233 15(19)	Co(1)-O(3)ⁱ	0.205 7(2)		
O(1)-Co(1)-N(1)	106.66(7)	O(3)#1-Co(1)-N(4)ⁱⁱ	96.13(9)	O(1)-Co(1)-O(3)ⁱ	151.73(9)
O(1)-Co(1)-O(2)	59.92(7)	N(1)-Co(1)-O(3)ⁱ	93.18(8)	N(1)-Co(1)-O(2)	88.09(8)
O(1)-Co(1)-N(4)ⁱⁱ	99.22(8)	O(3)ⁱ-Co(1)-O(2)	101.92(8)	N(1)-Co(1)-N(4)ⁱⁱ	101.69(8)
N(4)ⁱⁱ-Co(1)-O(2)	158.97(7)				
2					
Co(1)-O(2)	0.197 6(3)	Co(2)-N(7)	0.201 9(4)	Co(1)-O(4)ⁱⁱⁱ	0.200 4(3)
Co(2)-O(5)	0.204 5(3)	Co(1)-N(5)ⁱⁱⁱ	0.202 1(4)	Co(2)-N(3)	0.205 8(4)
Co(1)-N(1)	0.202 6(4)	Co(2)-O(6)	0.231 7(3)	Co(2)-O(8)ⁱⁱⁱ	0.200 7(3)
O(2)-Co(1)-O(4)ⁱⁱⁱ	105.60(14)	N(7)-Co(2)-O(5)	109.69(16)	O(2)-Co(1)-N(5)ⁱⁱⁱ	108.19(14)
O(8)ⁱⁱⁱ-Co(2)-N(3)	102.04(15)	O(4)ⁱⁱⁱ-Co(1)-N(5)ⁱⁱⁱ	129.78(16)	N(7)-Co(2)-N(3)	99.59(17)
O(2)-Co(1)-N(1)	96.82(14)	O(5)-Co(2)-N(3)	96.82(15)	O(4)ⁱⁱⁱ-Co(1)-N(1)	108.29(14)
O(8)ⁱⁱⁱ-Co(2)-O(6)	87.84(14)	N(5)ⁱⁱⁱ-Co(1)-N(1)	103.37(16)	N(7)-Co(2)-O(6)	88.87(16)
O(8)ⁱⁱⁱ-Co(2)-N(7)	132.65(17)	O(5)-Co(2)-O(6)	59.41(13)	O(8)ⁱⁱⁱ-Co(2)-O(5)	108.88(16)
N(3)-Co(2)-O(6)	156.22(14)				

Symmetry code: ⁱ $x+1$, y, z; ⁱⁱ $-x+2$, $-y$, $-z$ for **1**; ⁱⁱⁱ $x-1$, y, z for **2**.

bond lengths and angles with their estimated standard deviations are listed in Table 2.

CCDC: 924709, **1**; 924710, **2**.

2　Results and discussion

2.1　Crystal structure

The crystallographic analysis reveals that **1** is a one-dimensional tubular structure. As shown in Fig.1, the asymmetric unit contains one Co(II) ion, one FBA anion, and one OBIX ligand. Each Co(II) ion is five-coordinated by three oxygen atoms from two different carboxylate groups, and two nitrogen atoms from two OBIX ligands to form a distorted square-pyramidal geometry and its basal plane is occupied by three oxygen atoms, O1, O2 and O3[i], and one nitrogen atom, N4[ii], while the apical position is occupied by the other nitrogen atom, N1. The distortion of tetragonal pyramid can be calculated by the calculated value of the τ parameter introduced by Houser　(τ=0.12)[31].The Co-O　bond lengths are in the range of 0.203 05(17)~ 0.233 15(19) nm,　the Co-N bond lengths are 0.204 77(19)~0.208 0(2) nm and the coordination angles around Co ion are in the range of 59.92(7)°~ 158.97 (7)°. Two Co(II) ions are linked by a couple of OBIX ligands to form 24-membered {Co$_2$(OBIX)$_2$} ring and the distance of neighboring Co(II) ions is about 0.795 34(4) nm as presented in Fig.2. The OBIX ligand adopts a *cis*-conformation with the dihedral angle between the two imidazole rings of 78.21°. Two carboxylate groups of FBA^{2-} ligand adopt monodentate and bidentate chelating coordination mode and link to the neighboring {Co$_2$(OBIX)$_2$}　rings, giving a one-dimen-

Symmetry code: [i] *x*+1, *y*, *z*; [ii] −*x*+2, −*y*, −*z*; Hydrogen atoms are omitted for clarity

Fig.1　Coordination environment of Co(II) in complex **1** with thermal ellipsoids at 30% probability

sional tubular structure. The separation of neighboring Co(II) ions is about 1.122 4 nm as illustrated in Fig.3. The packing structure of **1** shows a three-dimensional supramolecular network derived from chains formed via intermolecular C−H⋯O hydrogen bonds and weak π⋯π stacking interactions　(the centroid-to-centroid distance of 0.401 23 nm between the two adjacent benzene rings of FBA ligands and benzene rings of OBIX ligands, and the dihedral angle is 6.123(5)°).
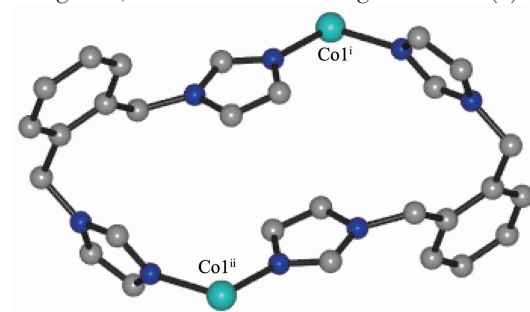
Symmetry code: [i] *x*+1, *y*, *z*; [ii] *x*+2, −*y*, −*z*
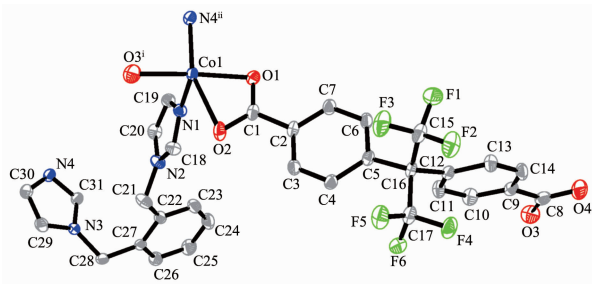
Fig.2　View of 24-membered [Co$_2$(OBIX)$_2$] ring in **1**
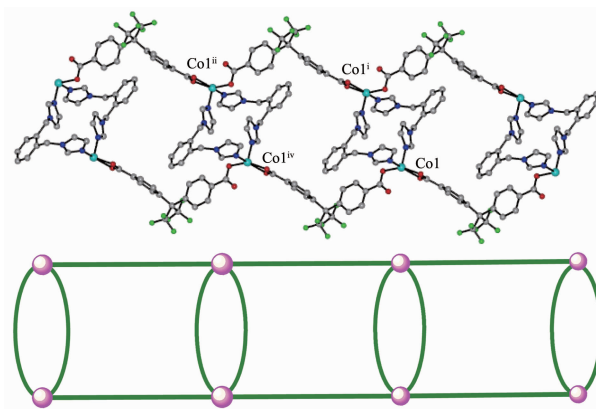
Symmetry code: [i] *x*+1, *y*, *z*; [ii] −*x*+2, −*y*, −*z*; [iv] *x*+1, *y*, *z*

Fig.3　Schematic representation of the 1D tubular structure in **1**

When　BIMB was reacted with Co(NO$_3$)$_2$ and H$_2$FBA using a preparation procedure similar to that of **1**, complex **2** was isolated. As shown in Fig.4, the asymmetric unit consists of two crystallographically unique Co(II) ions, two individual FBA anions, and two BIMB ligands. Two types of coordination environments exist around the Co(II) ions. Co1 lies in a slightly distorted tetrahedral coordination sphere defined by two oxygen atoms from two different FBA anions and two nitrogen atoms from two different BIMB ligands. The Co-O bond distances are 0.197 4(3)

and 0.199 9(4) nm, respectively. And the Co-N bond distances are 0.202 6(5) and 0.203 0(4) nm, respectively. Co2 is presented in a distorted square-pyramidal geometry formed by two carboxylate oxygen atoms from one FBA anion and two nitrogen atoms from two individual BIMB ligands at the basal positions and one oxygen atom from the other FBA anion at the apical position. The distortion of tetragonal pyramid can be calculated by the calculated value of the τ parameter introduced by Houser (τ=0.397)[31]. The Co-O distances range from 0.200 5(4) to 0.231 7(4) nm and the Co-N distances vary from 0.202 3(5) to 0.206 2(4) nm.
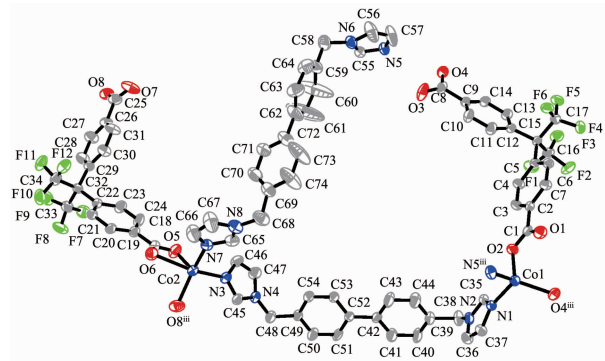
Symmetry code: iii $x-1$, y, z; Hydrogen atoms were omitted for clarity

Fig.4　Coordination environments of the Co(II) atoms in **2** with the ellipsoids drawn at the 30% probability level

It is obvious that the BIMB ligands have two different configurations when coordinated with Co(II) ions contributing to its flexibility. One is named A type including N1 and N3 atoms, in which the biphenyl is nearly planar and the angle between two phenyl rings is 5.611 (2)°. The dihedral angles between imidazole and phenyl are 85.631(2)° and 72.742(2)°, respectively. The other named B type showed no coplanar mode, in which the angle between two phenyl rings is 69.732(2)°. The dihedral angles between imidazole and phenyl are 59.673(2)° and 89.579(3)°, respectively. The two types of BIMB ligands connected adjacent Co(II) ions to form a 1D helix with different chirality as described in Fig.5. The 1D left-handed (M)/right handed (P) helical infinite chain is around the crystallographic 2_1 axis in the direction

with a long pitch of 1.416 3 (21) nm. The FBA occupied the remaining coordination sites of Co(II) within the chain as bridging ligands with the monodentate and bidentate-chelating coordination mode. Because left-handed and right-handed helical chains coexist in the crystal structure, the whole crystal is racemic and does not exhibit chirality. The occurrence of helical structure may contribute to the flexibility of the BIMB ligand. As shown in Fig.6, the M and P helical chains are marked by blue and red colors, respectively. The neighboring helical chains polycatenated to each other and formed a 2D layers. All the helical chains are arranged in "-P-M-P-M-" model both in the b and c
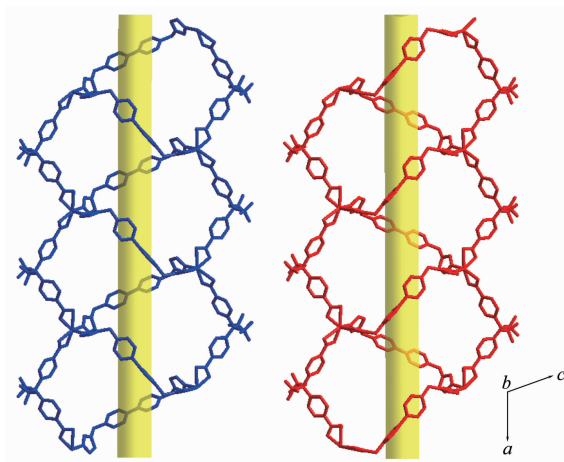

Fig.5　Illustration of left-handed helix (M helix) and right-handed helix (P helix) constructed by BIMB ligands along the a direction
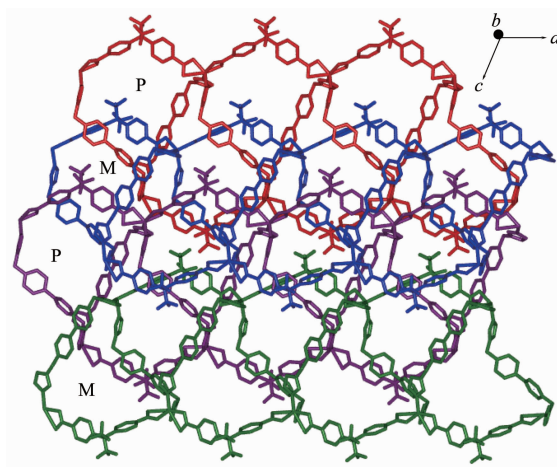

Fig.6　View of the 3D supramolecular structure formed by polycatenation (along the c direction) and π-π interactions (along the b direction) of neighboring helices

directions as illustrated in Fig.6. While in the *b* direction, the adjacent 2D layers give rise to a 3D supramolecular structure by π-π interactions between the rings of symmetry-related pairs of BIMB ligands (the centroid-to-centroid distance between the two adjacent benzene rings of BIMB ligands is 0.372 8 nm, and the dihedral angle is 4.265(3)°).

Reactions of Co(NO$_3$)$_2$, 4,4′-(hexafluoroisopropyli-dene)bis(benzoic acid), and two different flexible linear bis(imidazole) ligands under hydrothermal cond-itions afford two different frameworks. The results clearly indicate that the flexibility and spacer length of the bis(imidazole) ligands have important influence on the structure of the final products. Obviously, the two bis(imidazole) ligands involved in the construction of two complexes have the same imidazole group and a similar bis(monodentate) bridging coordination mode. The length and flexibility of the two ligands is different, which cause different configuration of the two ligands when coordinating to the Co(II) ions and finally result in two distinct frameworks.

2.2　IR spectra

The IR spectra of **1** and **2** show the absence of the characteristic bands at around 1 700 cm^{-1} attributed to the protonated carboxylate group indicates that the complete deprotonation of H$_2$FBA ligand upon reaction with Co ion. The presence of vibrational bands 1 613 ~1 565 cm^{-1}, which are characteristic of the asymmetric stretching of the deprotonated carboxylic groups of FBA^{2-} anion. The symmetric vibrations of the complete deprotonated carboxylic groups are the absorptions at 1 443~1 377 cm^{-1}, and the values of $\Delta(\nu_{as}(COO^-)-\nu_s(COO^-))$ indicate the presence of different coordina-tion modes. The bands in the region 640~1250 cm^{-1} are attributed to the -CH- in-plane or out-of-plane bend, ring breathing, and ring deformation absorptions of benzene ring, respectively. Weak absorptions observed at 3 089~3 102 cm^{-1} can be attributed to ν_{CH} of benzene ring. The IR spectra exhibit the characteristic peaks of imidazole groups at *ca.*1 520 cm^{-1} [32].

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