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Selective Pyridine Recognition by a Imidazole Dicarboxylate-Based 3D Cadmium(II) MOF

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Supporting information

Experimental Section

Materials and Methods

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The organic ligand 2-(4-chlorophenyl)-1H-imidazole-4,5-dicarboxylic acid (*p*-ClPhH_3IDC) was prepared according to the literature procedure.[1] The C, H and N analyses were carried out on a FLASH EA 1112 analyzer. IR Spectra were recorded on a BRUKER TENSOR 27 spectrophotometer as KBr pellets in the 400-4000 cm^{-1} region. TG-DSC measurements were performed by heating the sample from 20 to 850 °C at a rate of 10 $°C\cdot min^{-1}$ in air on a Netzsch STA 409PC differential thermal analyzer. X-ray powder diffraction measurements were recorded on a Panalytical X'pert PRO X-ray diffractometer.

Synthesis of $\{[Cd_2(p\text{-}ClPhHIDC)_2(4,4'\text{-}bipy)]\cdot H_2O\}_n$ (1):

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (30.8mg, 0.1 mmol), *p*-ClPhH_3IDC (26.6 mg, 0.1 mmol) and CH_3CH_2OH/H_2O (4/3, 7mL), Et_3N (0.014 mL, 0.1 mmol) was sealed in a 25 mL Teflon-lined

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stainless steel autoclave, heated at 155°C for 96 h, and then cooled to room temperature. The colorless cubic blocks crystals of **1** were collected (53% yield based on Cd), washed with distilled water and dried in air. Anal. Calcd. for $C_{32}H_{20}Cd_2Cl_2N_6O_9$: C, 41.37; H, 2.15; N, 9.05%. Found: C, 41.99; H, 1.80; N, 9.24%. IR (cm^{-1}, KBr): 3441 (m), 2925 (w), 1938 (w), 1684 (m), 1607 (s), 1556 (s), 1465 (s), 1416 (m), 1384 (m), 1292 (w), 1256 (m), 1116 (w), 1089 (m), 1003 (m), 855 (m), 841 (m), 809 (m), 785 (w), 749 (m), 628 (m), 558 (w), 453 (m).

Crystal Structure Determinations

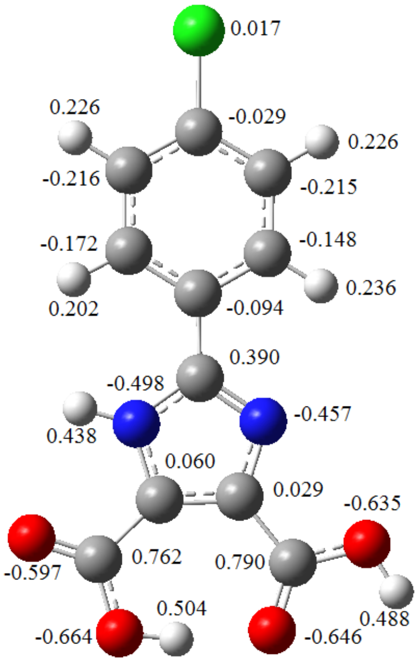
Suitable single crystal of compound **1** was selected for single-crystal X-ray diffraction analyses. The intensity data were measured on a Bruker Smart 1000 diffractometer with a graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). Single crystal of **1** was selected and mounted on a glass fiber. All data were collected at room temperature using the ω-2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The structure was solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 4508 observed reflections and 227 variable parameters. All calculations were performed using the SHELX-97 crystallographic software package.[2]

Quantum-Chemical Calculation.

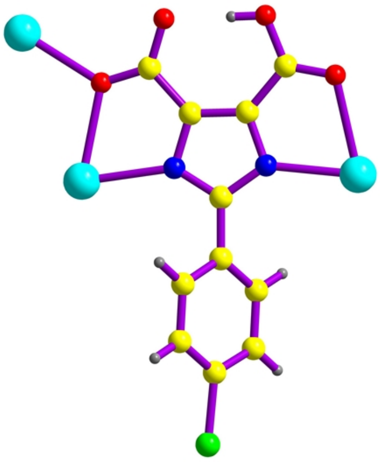
The free ligand *p*-ClPhH_3IDC was fully optimized by employing density functional theory (DFT) using Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)[3] with the 6-31+G* basis set.[4] Harmonic vibrational frequencies were then determined at the same level to confirm that the optimized structures were local minima on the potential energy surfaces. The optimized geometrie was used to carry out natural bond orbital (NBO) analyses[5] at the B3LYP/6-311++G** level of theory. All calculations were performed by using the Gaussian 09 program .The computed result reveals that the NBO charges are -0.635, -0.645, -0.664 and -0.597 for four carboxylate oxygen atoms, -0.457 and -0.498 for two imidazole nitrogen atoms

(Scheme S1). These values indicate that the oxygen and nitrogen atoms of the ligand have potential coordination ability.



p-ClPhH_3IDC

Scheme S1 The optimized geometries and NBO charge distributions of the free ligand *p*-ClPhH_3IDC (the green ball represents Cl atom, the blue balls represent N atoms, the red balls represent O atoms, the gray balls represent C atoms and the white balls represent H atoms).



Scheme S2 Coordination mode of *p*-ClPhHIDC^{2-} anion. (Color scheme: carbon = yellow, nitrogen = navy, oxygen = red, chlorine = green, cadmium = wathet).

Thermogravimetric Analysis

The TG curve of **1** shows that the first weight loss of 2.05% from 107.3 to 367.2 °C (calculated 1.94%) is assigned to the release of one free water molecule. The second weight loss of 38.43% is between 367.2 and 474.1 °C, accompanying the loss of one 4,4′-bipy and four μ-COO$^-$ units (calculated 35.79%). Subsequently, it keeps losing the remaining *p*-ClPhHIDC^{2-} ligands from 474.1 to 672.8°C (observed 31.23%, calculated 34.60%). After the temperature of 672.8°C, a plateau region is observed. The final residue is 2CdO (observed 28.01%, calculated 27.67%).

For **1** immersed in pyridine, a weight loss of 32.59% (calculated 32.42%) is observed from 58.4 to 349.3 °C for the removal of one free water molecule, two pyridine molecule and four μ-COO$^-$ units. It lost the remaining organic ligands (observed 31.27%, calculated 32.76%) from 349.3 to 506.5 °C. Then, it keeps losing weight from 506.5 to 730.0 °C, corresponding with the loss of the 4,4′-bipy ligand (observed 12.40%, calculated 14.38%). Finally, a plateau region is observed above 730.0 °C. The final residue is 2CdO (observed 23.74%, calculated 23.64%).

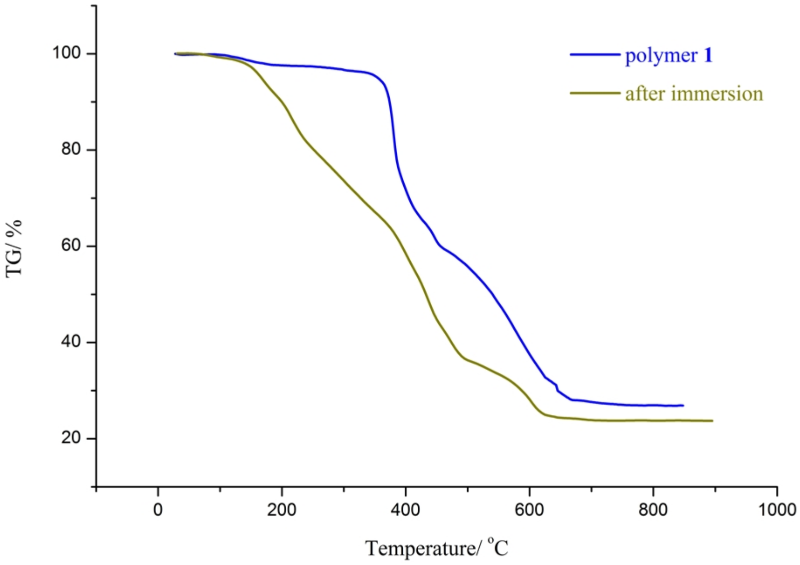


Fig. S1 The TG curve of compound **1** and **1** immersed in pyridine .

According to the above TGA analyses, we suspect that the formula of **1** immersed in pyridine is $\{[Cd_2(p\text{-}ClPhHIDC)_2(4,4'\text{-}bipy)]\cdot 2py\cdot H_2O\}_n$ (py = pyridine). We check this conjecture by EA analyses, which result is that Anal. Calcd. for $C_{42}H_{30}Cd_2Cl_2N_8O_9$: C, 42.39; H, 2.76; N, 10.31%. Found: C, 42.56; H, 2.38; N, 10.11%.

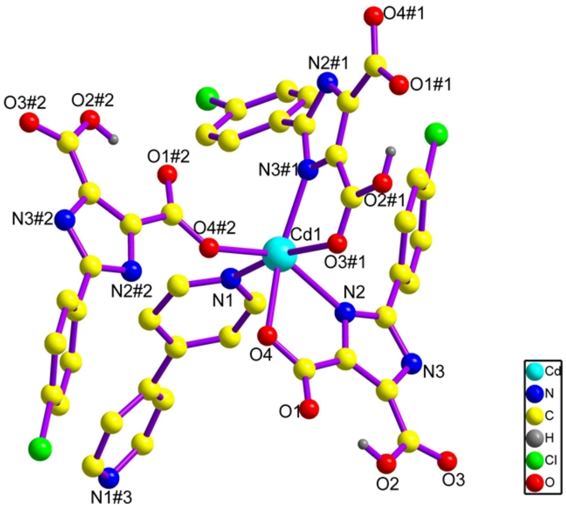


Fig. S2 Coordination environment of Cd(II) atom in **1**(symmetry code: #1: y+1/4, -x+1/4, z+1/4; #2: -x+1, -y, -z; #3: -x+1, -y+1/2, z+0; #4: -y+1/4, x-1/4, z-1/4).

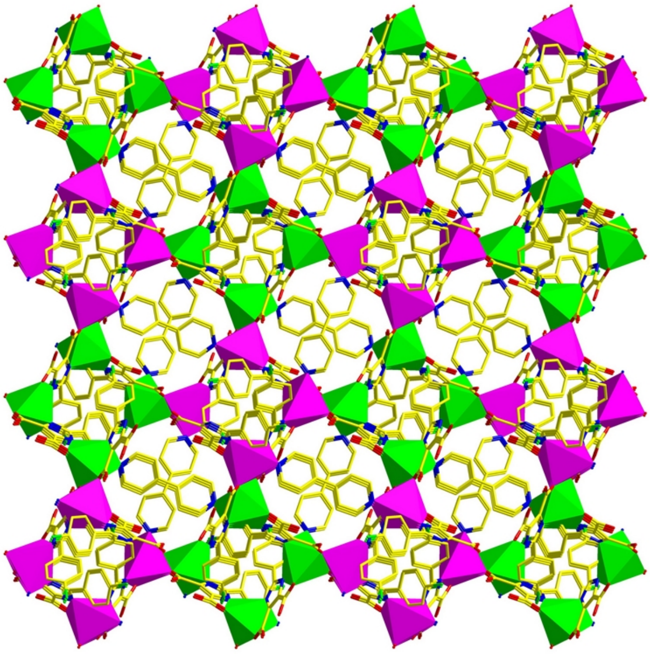


Fig. S3 Features of the exquisite 3D structure along the *c*-axis(Cd(II) in the left-handed helical chains, green; Cd(II) in the right-handed helical chains, violet).

Solid-State Fluorescent Characterization

Herein, the solid-state fluorescent properties of the complex and the free ligand are investigated at room temperature under the same experimental conditions. As shown in Fig. S4, the free *p*-ClPhH$_3$IDC ligand shows luminescence with the emission maximum at 369 nm by selective excitation at 278 nm, which is attributed to the ligand-centered $\pi^* \rightarrow n$ or $\pi \rightarrow \pi^*$ electronic transitions of the aromatic rings. Complex **1** shows an intense fluorescent emission maximum at 468 nm by selective excitation at 367 nm. Comparing with the emission spectrum of free ligand *p*-ClPhH$_3$IDC, the emission peak of complex **1** is red-shifted by 99 nm, which is considered to mainly arise from the increased rigidity of the organic ligand when coordinating to Cd(II). As a result of the Cd(II) ions is difficult to oxidize or reduce because of the d^{10} configuration, the emissions of complex **1** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT). It can probably be attributed to the intraligand fluorescence emission.[6]

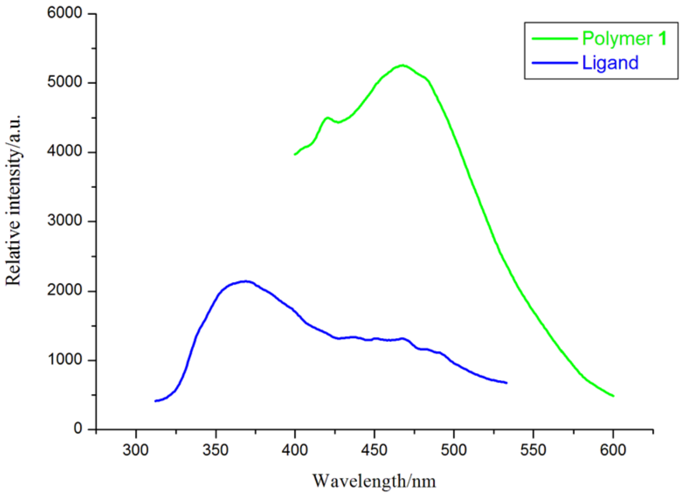
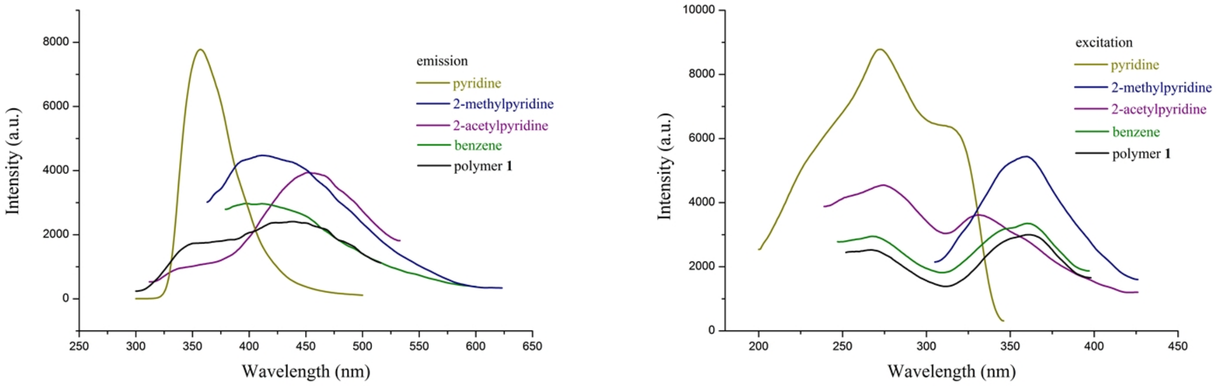


Fig. S4 The solid-state photoluminescent spectra of the free ligand *p*-ClPhH$_3$IDC and polymer **1** at room temperature.

The test samples ware obtained by immersing the powder sample of **1** into different small molecular organic solvents for 10 h, and for the volatile solvents, let them air-dry, while for DMF, THF and pyridine, we added washing samples with ethanol.



(a) (b)

Fig. S5 (a) Normalized solid-state emission and (b) excitation spectra of **1** immersed in different solvents.

References

1 H. K. Fun, S. S. S. Raj, R. G. Xiong, J. L. Zuo, Z. Yu and X. Z. You, *J. Chem. Soc., Dalton Trans*. 1999, 1915; M. R. Grimmett, Product Class 3: Imidazoles. *Org. Chem.*, 2002, **12**, 325.

2 G. M. Shelddrick, SHELX-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany 1997.

3 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785; P. J.Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623.

4 W. J. Hehre, L. Radom, P. R. Schleyer and J. A. Pople, , *Ab initio Molecular Orbital Theory; John Wiley & Sons: New York*, 1987.

5 E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, *NBO Version 3.1*. 1985.

6 F. H. Zhao, Y. X. Che and J. M. Zheng, *Inorg. Chem. Commun.* 2012, **17**, 99; F. H. Zhao, Y. X. Che and J. M. Zheng, *Inorg. Chem. Commun*. 2012, **24**, 200; W. Q. Kan, J. Yang, Y. Y. Liu and J. F. Ma, *Cryst. Eng. Comm.* 2012, **14**, 6271; L. Liang, C. Yang, Y. Ma and H. Deng, *Cryst. Eng. Comm*. 2013, **15**, 365; J. G. Lin, S. Q. Zang, Z. F. Tian, Y. Z. Li, Y. Y. Xu, H. Z. Zhu and Q. J. Meng, *Cryst. Eng. Comm*. 2007, **9**, 915.

Table S1. Crystallographic data for compound **1.**

	1
formula	$C_{16}H_9CdClN_3O_4$
fw	455.11
crystal system	Tetragonal
crystal size, mm	0.25 × 0.24 × 0.21
space group	I4(1)/a
a, Å	22.0734(10)
c, Å	16.1233(14)
V, Å^3	7855.8(8)
Dc, Mg m^{-3}	1.539
Z	16
μ, mm^{-1}	1.270
reflns collected/unique	24463 / 4508 [R(int) = 0.0414]
data/restraints/parameters	4508 /6 / 227
R^a	0.0467
$R_w{}^b$	0.1275
GOF on F^2	1.111
$\Delta\rho_{min}$ and $\Delta\rho_{max}$, e Å^{-3}	-2.074 and 3.184

Table S2. Selected bond distances (Å) and angles (deg) for compound **1**.

1			
Cd(1)-N(1)	2.324(5)	Cd(1)-N(2)	2.272(4)
Cd(1)-N(3)#1	2.232(4)	Cd(1)-O(3)#1	2.464(4)
Cd(1)-O(4)	2.418(4)	Cd(1)-O(4)#2	2.280(4)
N(3)#1-Cd(1)-N(2)	112.56(16)	N(3)#1-Cd(1)-O(4)#2	99.73(15)
N(2) -Cd(1)-O(4)#2	139.87(15)	N(3)#1-Cd(1)-N(1)	115.80(17)
N(2)-Cd(1)-N(1)	91.25(17)	O(4)#2-Cd(1)-N(1)	95.67(16)

N(3)#1-Cd(1)-O(4)	145.73(15)	N(2)-Cd(1)-O(4)	71.18(15)
O(4)#2-Cd(1)-O(4)	68.73(16)	N(1)-Cd(1)-O(4)	97.78(16)
N(3)#1-Cd(1)-O(3)#1	71.87(15)	N(2)-Cd(1)-O(3)#1	80.71(16)
O(4)#2-Cd(1)-O(3)#1	87.72(15)	N(1)-Cd(1)- O(3)#1	170.77(16)
O(4)-Cd(1)-O(3)#1	75.42(14)		

Symmetry transformations used to generate equivalent atoms for **1**: #1: y+1/4, -x+1/4, z+1/4; #2: -x+1, -y, -z; #3: -x+1, -y+1/2, z+0; #4: -y+1/4, x-1/4, z-1/4.

Table S3. Hydrogen bonds distances (Å) and angles (deg) for **1.**

1			
D-H...A	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(1)	1.67	2.490(6)	174.9

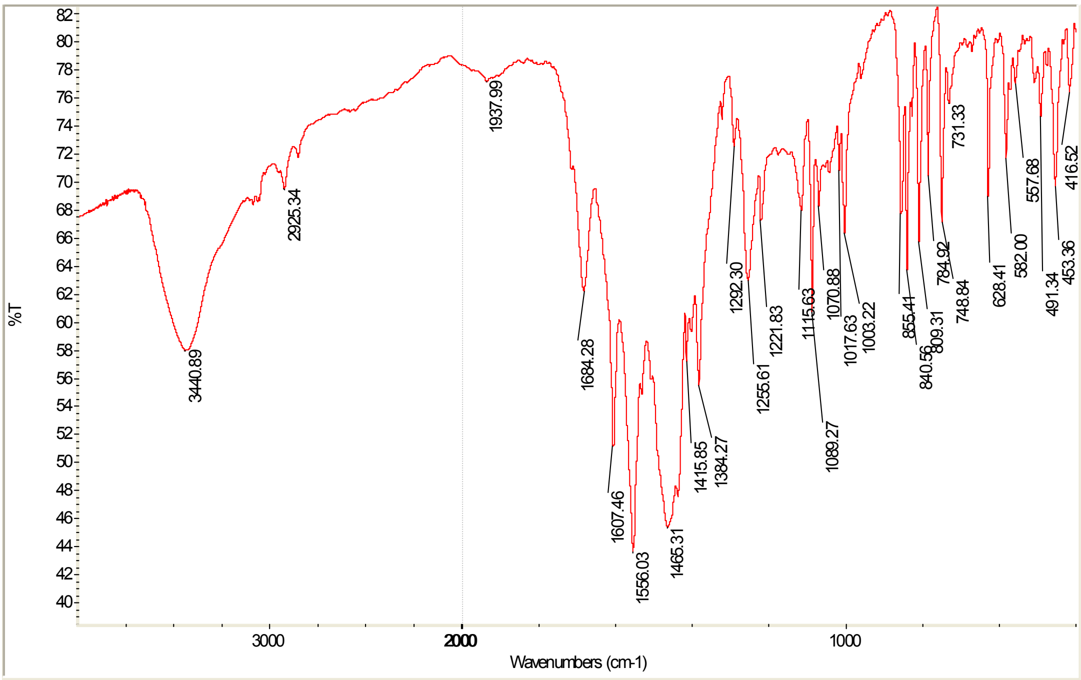


Fig. S6 The IR spectrum of **1** before immersion in pyridine

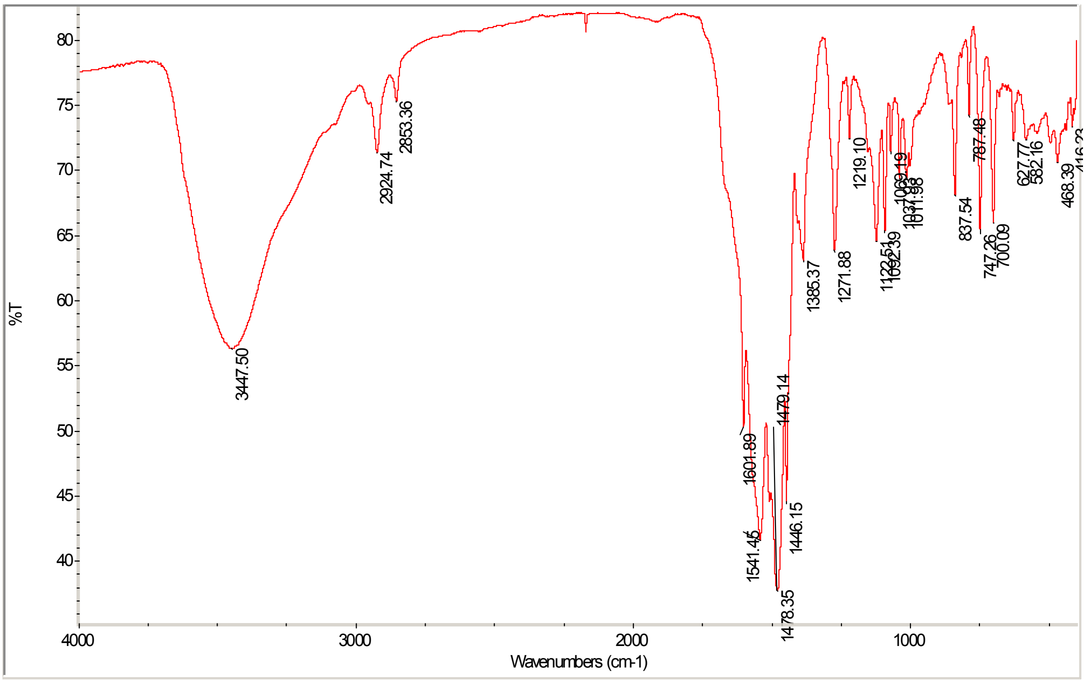


Fig. S7 The IR spectrum of **1** after immersion in pyridine