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## Thermodynamically stable MOF showing highly rare four-connected *hxx-d-4-Cccm* net with self-penetration, polyrotaxane, and polycatenane multi-features

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Two different crystals, namely  $Zn_2(L)_2(AzDC)_2 \cdot (H_2O)_2$  (**1**),  $Zn_2(L)_2(AzDC)_2$  (**2**) ( $L=N^2,N^6$ -di(pyridin-4-yl)pyridine-2,6-dicarboxamide,  $H_2AzDC$ =azobenzene-4,4'-dicarboxylic acid) have been co-crystallized in one-pot reaction, where **1** is a thermodynamically stable product, as only few crystal of **2** is observed in this system and after holding in the original solution for more than three hours the crystal of **2** transfers to be **1**. Notably, **1** represents a highly rare *hxx-d-4-Cccm* net with self-penetration, polyrotaxane and polycatenane multi-motifs, whereas common *sql* net with three-fold interpenetration is observed for **2**.

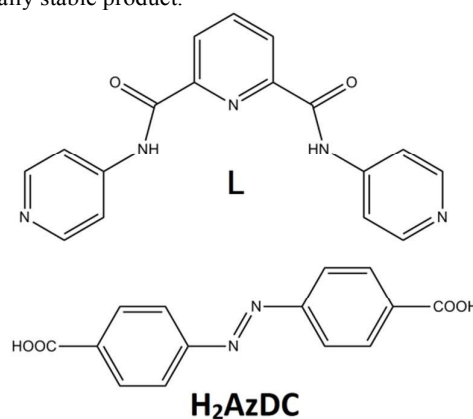
Entangled systems have been receiving great attentions, due to their intriguing topologies and potential applications such as gas separation.<sup>1–3</sup> Several special types with exceptional entangled phenomena, such as polycatenation (e.g. Borromean), polythreading (e.g. polyrotaxane), and polyknotting (e.g. self-interpenetration), are particularly interesting, due to their unique beautiful aesthetics.<sup>4–6</sup> But in this system, to our best of knowledge, a case with the coexistence of multi-features covering self-penetration, polyrotaxane and polycatenane is never reported.

As we know, the self-assembling technique has been used extensively in the design and construction of metal-organic frameworks (MOFs),<sup>7</sup> where the rational selection of organic ligands is crucial to determine the final structure of MOFs. Especially, unusual topology and structural diversity often occurred when mixed N- and O-donor ligands are used to construct MOFs.<sup>8</sup>

Our previous research has revealed that the combination of N-donor acylamide ligand and O-donor carboxylate ligand is facile to construct MOFs, and among them unusual topology, exceptional entangled structures, special coordination mode of

acylamide oxygen atom, tunable luminescence property, selective adsorption of  $CO_2$  molecules, or photo-switching behaviour toward  $CO_2$  were observed.<sup>9</sup> Herein, as an ongoing work in this content, both acylamide ligand of **L** and carboxylate ligand of  $H_2AzDC$  (see Scheme 1) is employed, and two new acylamide MOFs,  $Zn_2(L)_2(AzDC)_2 \cdot (H_2O)_2$  (**1**) and  $Zn_2(L)_2(AzDC)_2$  (**2**), were obtained *via* co-crystallization in one-pot reaction. However, the big difference in both shape and color, *viz.* needle/dark red for **1** vs. block/pale red for **2**, makes the mechanical separation of them very easy.

**1** and **2** were prepared through the co-crystallization in one-pot reaction of  $Zn(NO_3)_2 \cdot 6H_2O$ , acylamide ligand (**L**) and  $H_2AzDC$  ligand in 5 mL DMF and 1 mL water at 160 °C for 60h. The resulted crystalline samples are mainly made up of **1** and contain only few component of **2**. Interestingly, after laying the samples in the original solution for more than three hours, no crystal **2** could be detected but with the outcome of single-crystal-to-single-crystal transformation from **2** to **1**, and finally purity phase of crystal **1** is obtained. This indicates that in this system **1** is of a thermodynamically stable phase, and **2** is a kinetically stable product.



**Scheme 1.** The acylamide (**L**) and  $H_2AzDC$  ligands involved in this work.

The single-crystal X-ray diffraction shows that **1** crystallizes in monoclinic,  $C2/c$  space group. As shown in Fig. 1, the

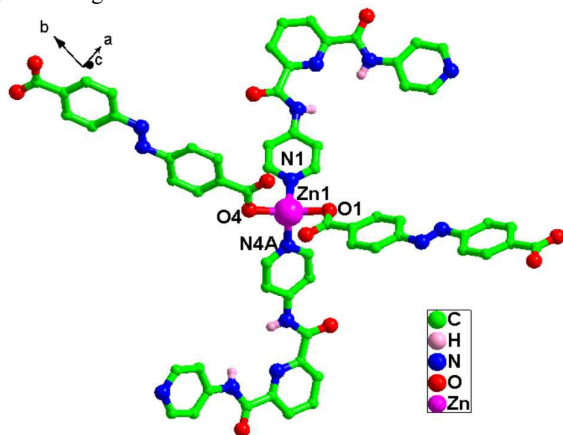
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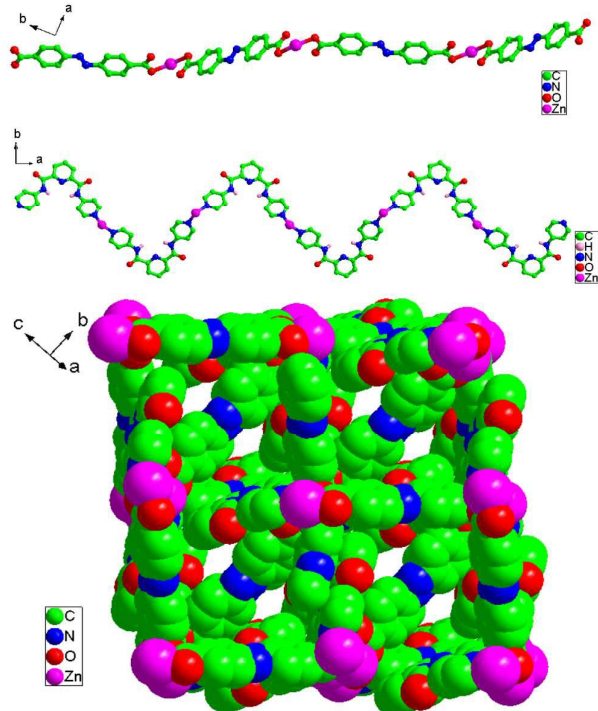
† Footnotes relating to the title and/or authors should appear here.

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asymmetric unit contains one crystallography-unique Zn(II) ion and two half AzDC ligands each lying about independent inversion centres. The Zn(II) site holds the four-coordinated tetrahedral geometry, finished by two AzDC<sup>2-</sup> oxygen atoms (Zn1-O1/2.072(5) Å, Zn1-O4/1.986(5)Å), two L nitrogen atoms (Zn1-N1/2.067(5) Å, Zn1-N4A/2.030(7)Å, symmetry code: A (-0.5+x, 1.5-y, -0.5+z). The Zn-O/N bond lengths of 1.923(2)-2.073(2) Å are in the normal range.<sup>10</sup> The AzDC<sup>2-</sup> ligand takes the bi(monodentate) coordination mode. L ligand takes the *cis*-conformation,<sup>11</sup> where 'cis' means that the two C=O units of acylamide ligand locates on the same side.



**Fig. 1** The coordination surrounding around Zn(II) ion. The hydrogen atoms except on acylamide groups are omitted for clarity. Symmetry transformations used to generate equivalent atoms A:  $-0.5+x, 1.5-y, -0.5+z$ . Color code: Zn/purple, C/green, N/blue, O/red, H/pink.

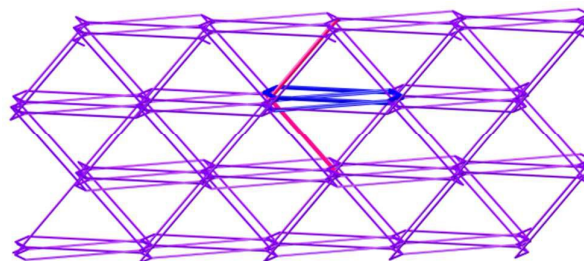


**Fig. 2** View of the 1D chain formed by metal and carboxylate ligands (or L ligands), the 3D framework of **1**.

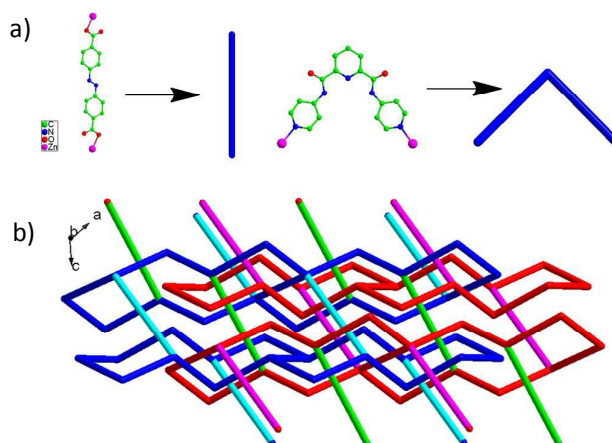
As shown in Fig. 2, the AzDC<sup>2-</sup> ligands connect to two Zn(II)

ions to create infinite 1D chain, while L ligands also connect to two Zn(II) to generate infinite 1D chain. Further, the combination of them constructs a very complicated 3D framework.

To understand this complicated framework presented by **1**, topology analysis by TOPOS program is carried out.<sup>12</sup> With the consideration of each Zn atom as 4-connected node and organic ligands (L and AzDC<sup>2-</sup>) as connectors, a *hxx-d-4-Cccm* net with 6<sup>5</sup>8 short symbol and long symbol of 6.6.6.6.6<sub>2</sub>.8<sub>2</sub> is suggested. As we know, both *dmp* and *cds* nets afford 6<sup>5</sup>8 short symbol, but the long symbol of them is different from the *hxx-d-4-Cccm* net.<sup>13</sup> According to the latest CCDC databases and literatures, only three examples with *hxx-d-4-Cccm* topology have been reported. But careful checking the topology of our case reveals self-penetration, polyrotaxane and polycatenane multi-features. By contrast, any of these features is never observed in the reported cases with *hxx-d-4-Cccm* topology. Thus, our case is unique. Moreover, to our best of knowledge, the motif of self-penetration, polyrotaxane, polycatenane, or coexistence of polyrotaxane and polycatenane has been well realized in the literature,<sup>14</sup> however, the coexistence of multi-features involving in self-penetration, polyrotaxane, and polycatenane in MOFs is never observed.



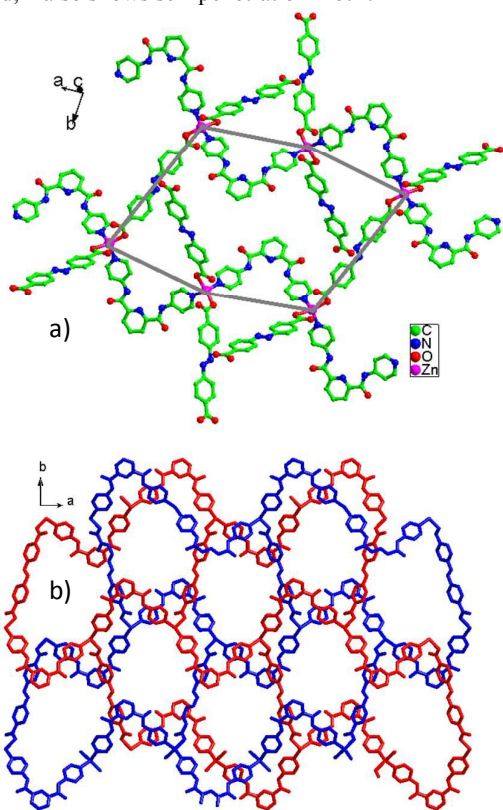
**Fig. 3** Schematic description of the 4-connected *hxx-d-4-Cccm* net with multi-features of self-penetration, polyrotaxane and polycatenane (see the highlighted section)



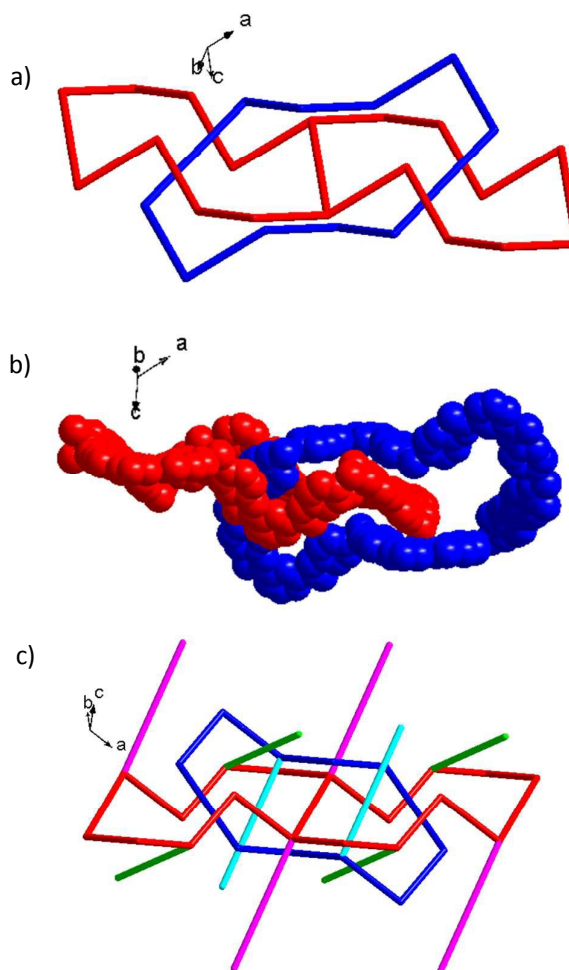
**Fig. 4** View of a) the simplification for this special topology; b) the special topology of coexistence of polycatenane and polyrotaxane.

In order to illustrate the fascinating framework of **1** clearly, the main feature of it is emphasized in Fig. 4. According, the basic component of this framework is the metal-L-AzDC<sup>2-</sup> six-membered rings (Fig. 5a). By sharing two metal ions and one

AzDC<sup>2-</sup> ligands (or L ligands), these six-membered rings create a 2D 6<sup>3</sup> net (Fig. 5b). Then two adjacent identical 6<sup>3</sup> nets intertwine with each other in this way that each six-membered loop from one 6<sup>3</sup> net intertwine with two identical six-membered loops from another adjacent 6<sup>3</sup> net (Fig. 6), thus giving the motif of polycatenane. Meanwhile, another basic component of this framework is the AzDC<sup>2-</sup> ligand that is not the specials used to construct six-membered rings, but acting as pillars locating on each metal site and supporting the aforementioned 6<sup>3</sup> nets. As shown in Fig. 7, for each six-membered loop, six AzDC<sup>2-</sup> pillars locate on it in this way of each three upper and down. Interestingly, each AzDC<sup>2-</sup> pillar penetrates through one six-membered loop of another 6<sup>3</sup> net, while each 6<sup>3</sup> net is penetrated by two AzDC<sup>2-</sup> pillars from another 6<sup>3</sup> net, thus generating the polyrotaxane motif. Note that the present entangled framework is not a common interpenetrating net that is formed by at least two identical or different nets interpenetrating with each other, by contrast, the present framework is only of a single net and could not be isolated, in literature, which is called as self-penetration. In this regard, **1** also shows self-penetration motif.

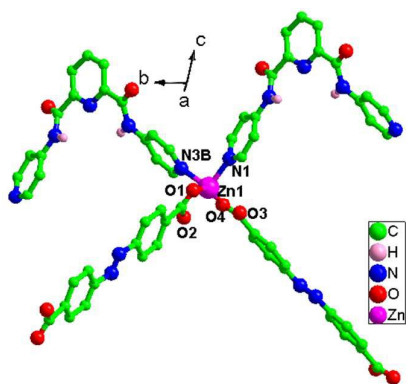


**Fig. 5** a) View of the metal-L-AzDC<sup>2-</sup> six-membered rings; b) of the 2D 6<sup>3</sup> net.



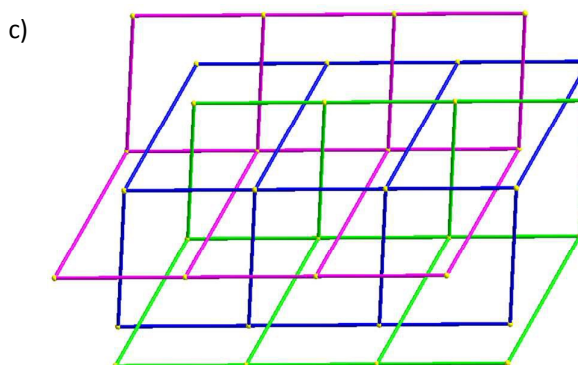
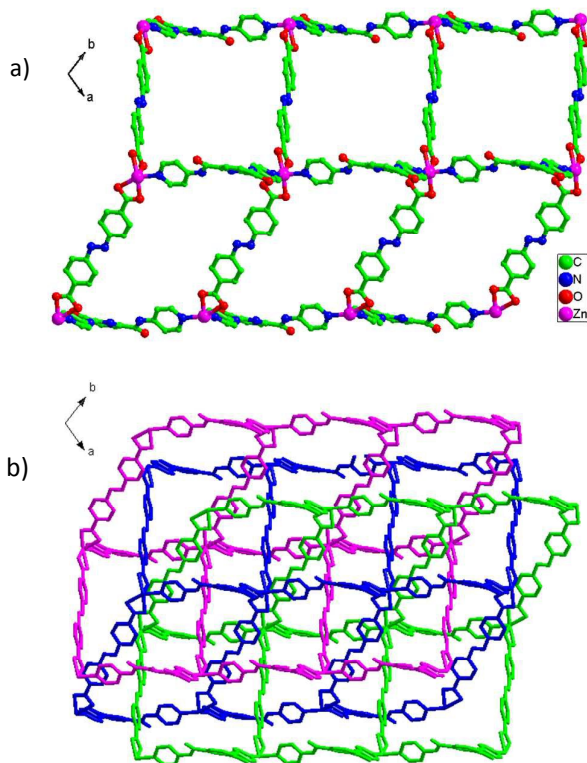
**Fig. 6** View of a), b) the intertwisting mode between six-membered loops; c) the coexistence of polycatenane and polyrotaxane.

The single crystal X-ray diffraction shows that **2** crystallizes in the triclinic *P*-1, space group. In **2** there is also one crystallography-independent Zn(II) site, giving four-coordinated tetrahedral geometry, completed by two oxygen atoms from two AzDC<sup>2-</sup> ligands and two pyridine nitrogen atoms from two L ligands (Fig. 7), and two half AzDC ligands each lying about independent inversion centres. The Zn-O lengths are 2.150(5) Å for Zn1-O1 and 2.106(4) Å for Zn1-O4, while Zn-N length is 2.042(5) Å for Zn1-N1 and 2.060(4) Å for Zn1-N3B (symmetry code: B 1+x, 1+y, z). The Zn-O values are slightly bigger than that observed in **1**, whereas the Zn-N values are comparable. For both L and AzDC<sup>2-</sup> ligands, they show the same coordination mode as observed in **1**.



**Fig. 7** The coordination surrounding around Zn(II) ions. The hydrogen atoms except on acylamide groups are omitted for clarity. Symmetry transformations used to generate equivalent atoms: B  $1+x, 1+y, z$ . Color code: Zn/purple, C/green, N/blue, O/red, H/pink.

As shown in Fig. 8a, the combination of metal ions, L, and AzDC<sup>2-</sup> ligands creates a neutral ‘stairway’-type 2D net. Further, three identical 2D net interpenetrate with each other to form a three-fold interpenetrating framework (Fig. 8b). Topologically, by considering each Zn(II) ion as a 4-connecting node and L, AzDC<sup>2-</sup> ligands as connectors, then **2** can be rationalized as common 4-connected *sql* net (Fig. 8c).



**Fig. 8** View of a) the ‘stairway’-type 2D layer; b) three-fold interpenetrating framework in **2**; c) the simplified three-fold interpenetrating *sql* net. Note that three identical layers are highlighted in blue, green and purple.

As discussed above, significant structural diversity between **1** and **2** is observed, although similar coordination surrounding/geometry for metal ion, coordination mode for both L and AzDC<sup>2-</sup> ligands is observed in **1** and **2**. Then, one question that what kind of factor causes this difference arises. To reply this, we further checked both L and AzDC<sup>2-</sup> ligands and found that there is no detectable distortion for two phenyl rings of AzDC<sup>2-</sup> ligand in **1** and **2**, which is accompanied by almost the same value of the span for adjacent metal pair linked by AzDC<sup>2-</sup> ligand (**1**/17.02(2)Å, **2**/17.04(2)Å). However, the span for adjacent metal pair linked by L ligand in **1** is ca. 12.35 Å, clearly shorter than that of ca. 13.86 Å observed in **2**. This can be further reflected in the opening degree for this V-shaped ligand of L, *viz.* 78.33(2)° in **1** vs. 89.60(2)° in **2**. The main reason is due to various degree of distortion for L ligand, such as smaller dihedral angle of 6.61(2)° and 10.09(2)° in **1** and relatively bigger dihedral angle of 27.10(2)° and 46.09(2)° in **2** (the dihedral angle is defined between terminal pyridine ring and middle phenyl ring of one L ligand). Accordingly, we also found significant difference in the O-Zn-O and N-Zn-N angles for each ZnO<sub>2</sub>N<sub>2</sub> tetrahedron in **1** and **2**. For **1**, the corresponding values are 153.92(2)°, 111.20(2)°, respectively, whereas in **2** these values become to be 149.56(2)° and 98.15(2)°. In this regard, it is believed that the various degree of distortion for L ligand between **1** and **2** should be responsible for the difference in structure between them. Moreover, the potential solvent-accessible volume estimated by Platon program is 42.2% in **1** and 48.8% in **2**, which also indicates more stable phase of **1**.<sup>15</sup>

As the phase of **2** was very few during the preparation of **1**, thus, we could not collect enough sample to carry out thermogravimetric and X-ray powder diffraction (PXRD) tests for this phase. The thermostability of **1** is explored by TG studies at 30–800°C. The weight loss at 30–150°C corresponds to release of guest water molecules (calc. 2.68%, exp. 2.70%) (Fig. S1). The PXRD patterns of **1** were recorded at room temperature in order to test the purity of the bulk samples (Fig. S2), where the simulated PXRD patterns from the crystal data match well with experimental PXRD patterns.

In summary, two different crystals have been successfully co-crystallized *via* one-pot reaction. But only one is thermodynamically stable, as the other one would transfer to be the thermodynamically stable phase after several hours. Moreover, the outstanding structure feature of coexistence of self-penetration, polyrotaxane and polycatenane in **1** is also very interesting, and should represent the first case in MOFs.

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## Notes and references

‡**The synthesis of 1 and 2.** They were co-crystallized in one-pot reaction under solvo(hydro)-thermal conditions. An DMF:H<sub>2</sub>O (5:1) solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, L and H<sub>2</sub>AzDC in a ratio of 1:1:1 was sealed in a Teflon reactor, and heated at 160°C for 60 h, and then cooled to room temperature at 3°C·h<sup>-1</sup>. The yield based on Zn for **1** and **2** is ca. 85% and 0.2%, respectively. For **1**, EA (%): calc. C 55.49, H 3.46, N 14.61; exp. C 55.48, H 3.47, N 14.60.

§**Crystal data for 1:** C<sub>62</sub>H<sub>46</sub>N<sub>14</sub>O<sub>14</sub>Zn<sub>2</sub>, formula weight=1341.87, T=120K, Monoclinic, space group C2/c, a =30.8851(18)Å, b=17.4665(10)Å, c=20.3272(14)Å, β=127.705(6)°, V=8675.6(9)Å<sup>3</sup>, Z=4, D<sub>calcd</sub>=1.027gcm<sup>-3</sup>, reflections collected/ unique=31872/7625, R<sub>int</sub>=0.0457, for all data: R<sub>1</sub>=0.1388, R<sub>w2</sub>=0.344, GOF =1.089. The disordered solvent molecules could be exactly determined by single crystal X-ray diffraction, thus they are treated by Platon Squeeze program.<sup>15</sup> The CCDC number is 1441331.

**Crystal data for 2:** C<sub>31</sub>H<sub>21</sub>N<sub>7</sub>O<sub>6</sub>, formula weight=652.92, T=120K, ZnTriclinic, space group P-1, a =10.882(3)Å, b=11.386(3)Å, c=20.627(5)Å, α=100.75(2)°, β=103.307(16)°, γ=103.024(18)°, V=2345.3(11)Å<sup>3</sup>, Z=2, D<sub>calcd</sub>=0.925gcm<sup>-3</sup>, reflections collected/unique=29219/8223, R<sub>int</sub>=0.0457, for all data: R<sub>1</sub>=0.1348, R<sub>w2</sub>=0.2046, GOF=0.912. The disordered solvent molecules could be exactly determined by single crystal X-ray diffraction, thus they are treated by Platon Squeeze program.<sup>15</sup> The CCDC number is 1441332.

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