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Rational Design of MOFs Constructed from Modified Aromatic Amino Acids

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Abstract: Three Phe and Tyr derivatives, 2-amino-3-(4-aminophenyl)-propionic acid (AAP), 3*E*-[5-(2-amino-2-carboxyethyl)-2-methoxyphenyl]-acrylic acid (AMPA) and 3-(4-aminophenyl)-2-(carboxymethyl-amino)-propionic acid (ACP) have been chosen as the ligands to construct four kinds of novel metal-organic frameworks (MOFs) (five structures). These structures are, $[\mathrm{Cd^{II}}\{(R)\text{-AAP}\}(\mathrm{Py})(\mathrm{H_2O})]\cdot(\mathrm{ClO_4})$, (*R*)-**1**; $[\mathrm{Cd^{II}}\{(S)\text{-AAP}\}(\mathrm{H_2O})_2]\cdot(\mathrm{ClO_4})$, (*S*)-**2**; $[\mathrm{Zn_2^{II}}\{(R,S)\text{-AMPA}\}(\mathrm{H_2O})]$, (*R*,*S*)-**3**; $[\mathrm{Zn_2^{II}}\{(R)\text{-ACP}\}(\mathrm{Py})_3]\cdot(\mathrm{ClO_4})_2$, (*R*)-**4**; and the inversion twin of (*R*)-**1**. Rational design to adjust the "depth" and the "width" of ligands can mediate the size and the shape of the grids of these 2D layers. Additionly, among these compounds, three pure chiral coordination polymers are obtained, owing to the inducement of chirality by the modified amino acids. This property makes them potential NLO materials.

Keywords: amino acids · crystal engineering · metal–organic frameworks · nonlinear optics · rational design

Introduction

Research on metal-organic frameworks (MOFs) has been promoted rapidly, as the technologies for the synthesis and property measurement of MOFs have increased and improved over the last two decades.[1] Many studies are focused on the various applications of MOFs, such as catalysis,[2] luminescence,[3] and NLO materials[4]. However, the methods used to mediate the structures of MOFs are still very interesting and challenging for their complexity and uncertainty.[5] The theory on building blocks and spacers is used to explain and design crystal structures.[6] Although, theory and organic synthesis are only two of the facets used to anatomize the essentials of MOFs, both have already been included in "Crystal Engineering".[7]

The relationship between living molecules and materials science has been noted previously, in the design and synthesis of MOFs from biological ligands. In particular, amino acids and their derivatives form a pool of biological ligands that can induce both a chiral and an acentric unit directly into coordination complexes and polymers.[8] Obtaining complexes and frameworks from amino acids and their derivatives is very necessary for promoting the materials chemistry in this domain.[9] In our previous work, several MOFs constructed from heterocyclic amino acids (tryptophan (Trp) and histidine (His)) have been obtained.[10] Herein, we define the $\mathrm{H_2N\text{-}CH\text{-}COO^-}$ groups as the chains and the alkyl, heterocyclic or aromatic groups as the key trunks, as shown in Figure 1. Regarding the three layers contained within the frameworks reported previously,[10] both key trunks of Trp and His are always on two sides of the layers, although they do not act as bridges. The bridges found in these types of MOFs consist of isonicotinic acid or the $\mathrm{H_2N\text{-}CH\text{-}COO^-}$ chain, and the size of the grids in these layers can not be determined by the key trunks of amino acids. Therefore, we assumed that this problem could be conquered if one or two coordinating sites were added into the trunk of the amino acids. The aromatic amino acids phenylalanine (Phe) and tyrosine (Tyr) were chosen as candi-

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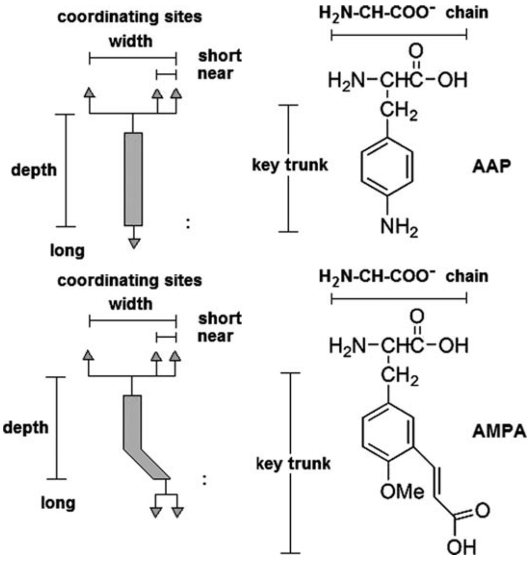


Figure 1. The schematic legend for ligands AAP and AMPA.

dates, because they both have conjugated rings, which may provide rigid trunks in their coordination networks and can be modified easily. In this paper, we report the results of mediating structures, which are constructed from modified aromatic amino acids by means of crystal engineering.

Results and Discussion

Three Phe and Tyr derivatives, 2-amino-3-(4-aminophenyl)-propionic acid (AAP), 3*E*-[5-(2-amino-2-carboxyethyl)-2-methoxyphenyl]-acrylic acid (AMPA) and 3-(4-aminophenyl)-2-(carboxymethyl-amino)-propionic acid (ACP) have been employed, as shown in Figure 1 and Figure 2. Three

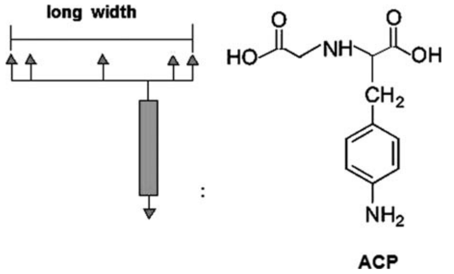
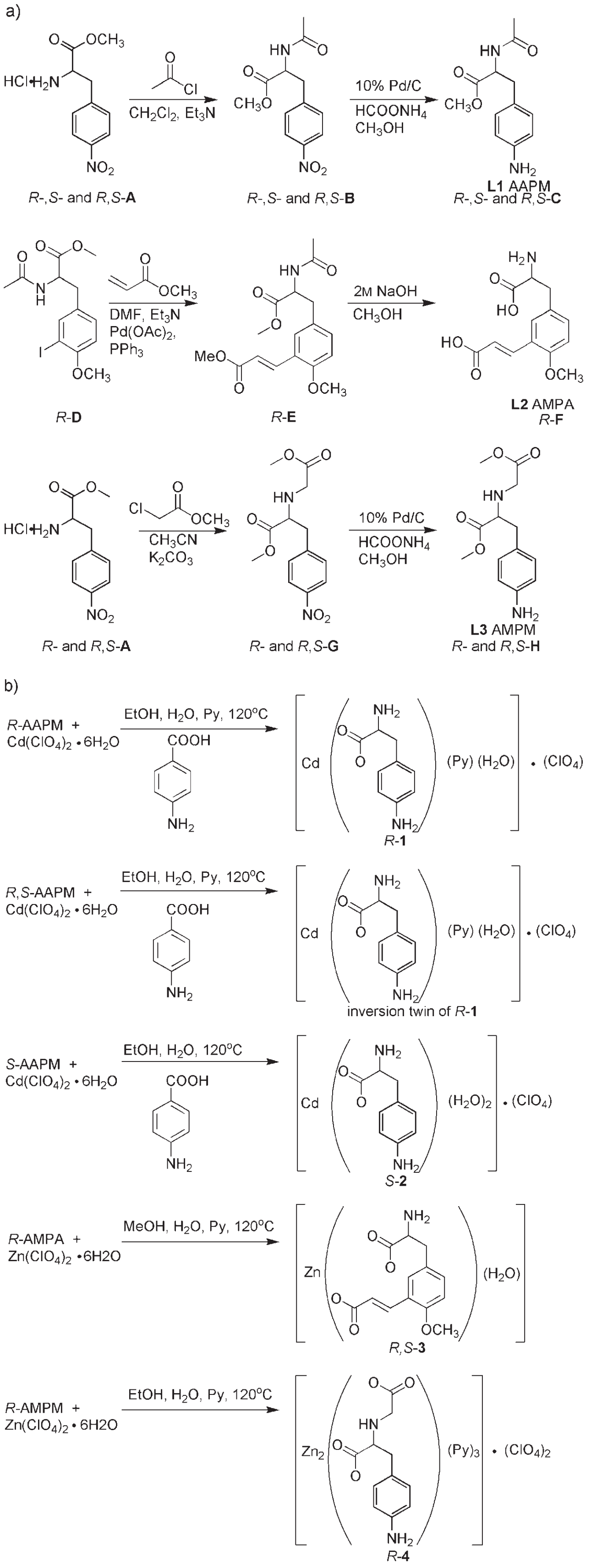


Figure 2. The schematic legend of the ligand ACP.

molecules: 2-acetylamino-3-(4-aminophenyl)-propionic acid methyl ester (AAPM, **L1**), AMPA (**L2**) and 3-(4-amino-phenyl)-2-(methoxycarbonylmethyl-amino)-propionic acid methylester (AMPM, **L3**) were synthesized, as shown in Scheme 1a. The AAP ions and ACP ions were generated in-situ, after hydrolysis. $[Cd^{II}\{(R)\text{-AAP}\}(Py)(H_2O)]\cdot(ClO_4)$, (*R*)-**1**, with a Flack factor of $-0.01(10)$[11] is synthesized by treating (*R*)-AAPM and $Cd(ClO_4)_2{\cdot}6H_2O$ under solvothermal conditions with the buffer 4-aminobenzoic acid and



Scheme 1. a) The reactions forming three ligands: AAPM, AMPA and AMPM. b) The reactions forming MOFs **1**, **2**, **3**, and **4** (4-ABA = 4-Aminobenzoic acid).

alkali pyridine at 120°C. Whereas, $[Cd^{II}\{(S)\text{-AAP}\}(H_2O)_2]\cdot(ClO_4)$, (*S*)-**2**, with a Flack factor of 0.02(9) is obtained from (*S*)-AAPM without pyridine at the same temperature. Additionally, if (*R*)-AAPM is replaced with (*R*,*S*)-AAPM to synthesize **1** and **2**, the inversion twin[12] of (*R*)-**1** with a Flack factor of 0.40(12) and a powder product, which has the same FT-IR as (*S*)-**2** can be obtained. $[Zn_2^{II}\{(R,S)\text{-AMPA}\}(H_2O)]$, (*R*,*S*)-**3**, is synthesized by treating (*R*)-AMPA in an aqueous solution of $Zn(ClO_4)_2\cdot 6H_2O$ and pyridine in methanol at 120°C. Whereas, $[Zn_2^{II}\{(R)\text{-ACP}\}(Py)_3]\cdot(ClO_4)_2$, (*R*)-**4**, with a Flack factor of −0.02(2) is prepared by treating (*R*)-AMPA in an aqueous solution of $Zn(ClO_4)_2\cdot 6H_2O$ and pyridine in ethanol at 120°C. It is noted that the racemization of (*S*)-AMPA occurs in the preparation of (*R*,*S*)-**3**, whereas (*R*)-ACP keeps its chirality in the synthesis of (*R*)-**4.** When (*R*)-AMPM was replaced by (*R*,*S*)-AMPM to synthesize **4**, it was only possible to obtain a product in powder form, the FT-IR spectra of which is the same as that found for (*R*)-**4**. These reactions are shown in Scheme 1b.

Both (*R*)-**1** and (*S*)-**2** are formed as 2D layers and crystallize in the orthorhombic space group $P2_12_12_1$. For (*R*)-**1**, each Cd ion coordinates to one water molecule, to one pyridine molecule, to one amino group of one (*R*)-AAP ligand, to one carboxylate group of another (*R*)-AAP ligand in bidentate fashion, and to one amino and one carboxylate group of a different (*R*)-AAP ligand in monodentate mode. In particular, one bond length of Cd−O is 2.76 Å, which is longer than the other bonds linking the Cd ion. The coordinated water and pyridine molecules are positioned quasi-perpendicularly around the Cd ion. Thus, the central Cd ion adopts a seven-coordinate environment that has decahedral geometry. In every rectangle grid of one 2D layer, the Cd–Cd separations are 4.99 and 11.76 Å, respectively. The trunk of the (*R*)-AAP ligand is on one side of the grid, although the carboxylate group of the ligand is on the other side (Figure 3). The structure of (*S*)-**2** is very similar to that of (*R*)-**1**. The shared feature of these two structures is that the AAP molecules act as spacers and that a full elongation is made, because an amino group is added in the 4-position of Phe. However, there are three major differences that exist. First, in (*S*)-**2** the central Cd ion adopts a six-coordinate environment that has an octahedral geometry (because the longest distance between Cd and O in one asymmetric unit is 2.86 Å, instead of 2.76 Å). Second, there are two coordinated water molecules that are positioned quasi-perpendicularly around the Cd ion and no pyridine exists in (*S*)-**2**, unlike (*R*)-**1**. Third, the two phenyl groups of (*R*)-**1** in one grid adopt a partial face-to-face conformation, although the phenyl groups of (*S*)-**2** in one grid adopt a full face-to-face conformation, as shown in Figure 4.

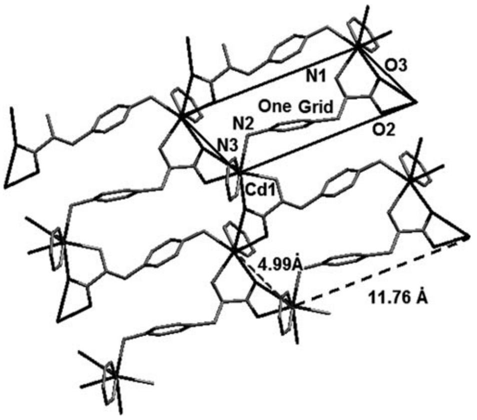


Figure 3. The coordination environment of the atom Cd1 in (*R*)-**1** and the grids formed through the key trunks and carboxylate groups of (*R*)-AAP ligands. The ClO_4^- ions have been removed for clarity.

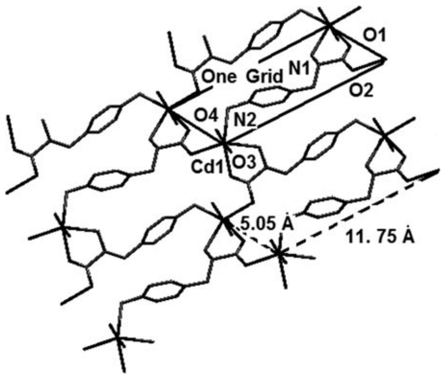


Figure 4. The coordination environment of the atom Cd1 in (*S*)-**2**. Two phenyl groups in one grid adopt a full face-to-face conformation. The ClO_4^- ions have been moved for clarity.

(*R*,*S*)-**3** is a 2D layer and crystallizes in the monoclinic space group $P2_1/c$. Each Zn ion coordinates to one water molecule, to one amino group and one carboxylate group of one (*R*,*S*)-AMPA ligand in a monodentate fashion, and to two carboxylate groups of the other two (*R*,*S*)-AMPA ligands in the monodentate mode. There are two positions (O5 and O7) for one carboxylate oxygen atom in an asymmetric unit as a result of thermo-probability. Thus, the Zn ion adopts a five-coordinate environment that has a hexahedron geometry. In virtue of the carboxylate groups and the major trunk of (*R*,*S*)-AMPA, a 2D layer structure that has special packet-like grids is generated. In every grid, the Zn–Zn separations are 4.25 and 11.42 Å, respectively (Figure 5). Interestingly, because the two trunks of (*R*,*S*)-AMPA in one grid are not in one plane, the layer has a double β-sheet conformation (Figure 6). AMPA molecules can also be used as spacers here, but the addition of a vinyl carboxylate group in the 3-position of the aromatic ring in Tyr makes a partial elongation.

(*R*)-**4** is a 2D layer and crystallizes in the monoclinic space group $P2_1$. In contrast to the simple decahedral coordination of the Cd ions in (*R*)-**1**, the Zn ions in (*R*)-**4** adopt two kinds of coordination environment. Zn1 has a pentahedral geometry and Zn2 a tetrahedral one. Each Zn1 ion coordinates to one pyridine molecule, to one amino group of one (*R*)-ACP ligand, and to one amino and two carboxylate groups of anther (*R*)-ACP ligand in a monodentate fashion. Whereas, every Zn2 ion coordinates to two pyridine mole-

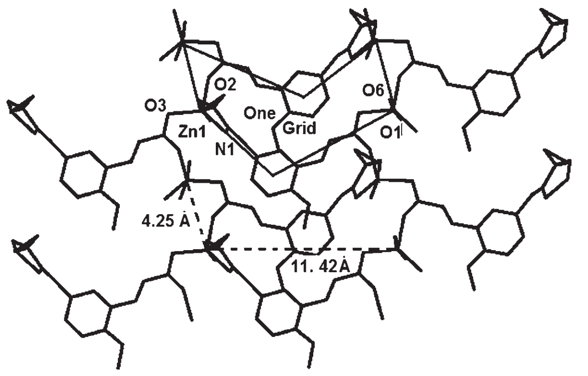


Figure 5. The coordination environment of atom Zn1 in (*R*,*S*)-**3** and the size of one grid.

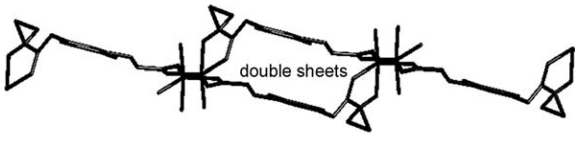


Figure 6. The double β-sheet conformation of one layer in (*R*,*S*)-**3**.

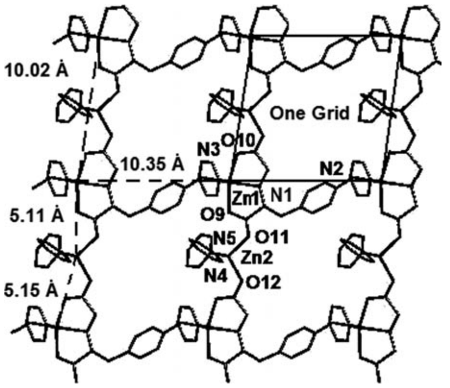


Figure 7. The coordination environment of atoms Zn1 and Zn2 in (*R*)-**4** and the size of the rhombus grid. The ClO_4^- ions have been removed for clarity.

cules, and to two carboxylate groups of neighboring (*R*)-ACP ligands in a monodentate mode. The two coordinated pyridine molecules are positioned at a 115.6° to the Zn2 ion. The lengths of the bonds around central Zn ions are all in a reasonable range. In each rhombus grid of one 2D layer, the Zn1–Zn2 separations are 5.12 and 5.15 Å, and the Zn1–Zn1 separations are 10.35 and 10.02 Å, which is the size of the rhombus grid. The trunk of the (*R*)-ACP ligand is on one side of the grid, although two carboxylate groups of neighboring ligands compose another side with the Zn2 ions. The methoxycarbonylmethyl group added to (*R*)-**A** leads to an increase in the size of the grids of (*R*)-**4**, compared to that of (*R*)-**1**, (*S*)-**2** and, (*R*,*S*)-**3** (Figure 7).

Table 1. Crystallographic data for crystals **1**, **2**, **3** and **4**.

Compound	(*R*)-**1**	Twin of (*R*)-**1**	(*S*)-**2**	(*R*,*S*)-**3**	(*R*)-**4**
formula	$C_{14}H_{18}N_3O_7ClCd$	$C_{14}H_{18}N_3O_8ClCd$	$C_9H_{15}N_2O_8ClCd$	$C_{13}H_{15}NO_6Zn$	$C_{26}H_{27}N_5O_{12}CL_2Zn_2$
M	488.16	488.16	427.08	346.63	803.17
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$P2_1$
a [Å]	9.0030(18)	9.0120(18)	8.8230(18)	11.422(2)	10.021(2)
b [Å]	11.760(2)	11.826(2)	11.746(2)	8.2150(16)	15.540(3)
c [Å]	17.449(4)	17.579(4)	16.791(3)	14.815(3)	10.345(2)
α [°]	90	90	90	90	90
β [°]	90	90	90	100.89(3)	98.24(3)
γ [°]	90	90	90	90	90
V [Å^3]	1847.4(6)	1873.5(7)	1740.1(6)	1365.1(5)	1594.4(6)
Z	4	4	4	4	2
μ [mm^{-1}]	1.368	1.349	1.441	1.827	1.741
ρ_{calcd} [g cm^{-3}]	1.755	1.731	1.630	1.687	1.673
$R_1[I>2\sigma(I)]$[a]	0.0679	0.0766	0.0701	0.0929	0.0511
ωR_2 [all data][b]	0.1846	0.1757	0.1912	0.1804	0.1122
S	1.035	1.000	1.075	1.028	1.017
χ	−0.01(10)	0.40(12)	0.02(9)	N/A[c]	−0.02(2)

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. [b] $\omega R_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] Not available.

Owing to the inducement of the chiral ligands, we could directly obtain chiral structures, which are related to their functional groups. As shown in Table 1, the Flack factors χ help us justify the assignment that the crystal structures of (*R*)-**1**, (*S*)-**2** and (*R*)-**4** are chiral. Additionally, these compounds are all transparent and colorless, so they may respond to the second harmonic generation (SHG) effect. We carried out a preliminary Kurtz powder SHG test,[13] which showed that (*R*)-**1** displays a second-order coefficient (SOC) that is 0.8 times that of potassium dihydrogenphosphate (KDP). (*S*)-**2** was found to have a SOC that is 0.6 times that of KDP. (*R*)-**4** also demonstrates a SOC 1.5 times that of KDP. Additionally, the results of the thermogravimetric analysis (TGA) testify that these three compounds have good thermal stabilities, the decomposition of their main network structures was seen at $T = 280$ (**2** and **4**), 300 (**1**), and 320 °C (**3**), respectively (Figure 8). Furthermore, these compounds all have bad solubility in common solvents. These characteristics imply that (*R*)-**1**, (*S*)-**2** and (*R*)-**4** are good candidates for potential NLO applications.

Conclusion

In accordance with the discussion above, the key trunks of the amino acids and the H_2N-CH-COO^- chains in these MOFs act as bridges. Thus, the experimental result is consistent with the assumption that we had envisaged. Both the size and the shape of the grids in the layers are mediated by

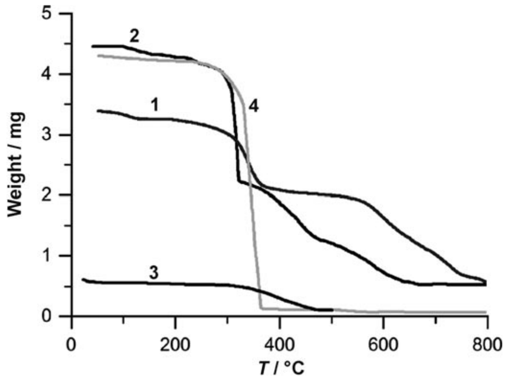


Figure 8. TGA curves of **1**, **2**, **3**, and **4**.

the positions of the coordinating functional groups of the modified amino acids. For convenience, the length of the key trunks is defined as the depth of the ligands, although the length of the H_2N-CH-COO^- chains is defined as the width (Figure 1). In the layers of **1**, **2**, and **3**, the two sides of one grid are key trunks and H_2N-CH-COO^- chains, respectively. Therefore, the size of grid in such layers is determined not only by the depth, but also by the width of ligands (Figure 9). For AAP, the rigidity of the bond between the phenyl ring and the amino group makes the full elongation of the depth and the size of the grids of **1** and **2** to be $\approx$5.0 and 11.8 Å. For AMPA, the flexibility of the vinyl bonding makes a partial elongation of the depth, the resultant straight distances of neighboring corners in the grids of **3** are $\approx$4.3 and 11.4 Å. Thus the sizes of these two kinds of layers are almost same. Furthermore, the key trunk of AAP is almost straight, owing to the addition of the amino group to the 4-position of Phe, resulting in the distorted rectangle shape of the grids in **1** and **2.** Similarly, the key trunk of AMPA is twisted, owing to the addition of an acrylic group to the 3-position of modified Tyr, which lead to the formation of a bend rectangle shape of the grids in **3** (Figure 9).

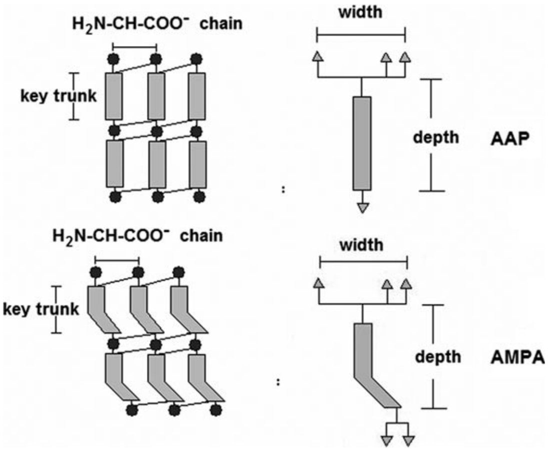


Figure 9. The schematic legend of 2D layers formed from the ligands AAP and AMPA.

In summary, the shared feature of these three kinds of polymers **1**, **2**, and **3** is that the length of the long side is almost two times of that of the short side in the grid if the modified aromatic amino acids are used as spacers. The depth can be extended by adding a coordinating functional group. In the designed structure of ACP, the carboxymethyl group is connected to the amino group of Phe to expand the width, and the other amino group is added at the 4-position of aromatic ring of Phe to extend the depth, as shown in Figure 2. Therefore the shape of the grids in **4** is an approximate rhombus that has a size of about 10.0 and 10.4 Å, which is bigger than those of the grids in the former four structures.

In conclusion, four kinds of 2D MOFs (five structures) are obtained from modified aromatic amino acids. The size and the shape of the grids in these 2D layers can be mediated through rational design by adjusting the "depth" and the "width" of the ligands. More clearly, the key role for mediation of the MOF structures, is the modification of the aromatic amino acids by means of organic synthesis with a clear objective. Additionally, three of these compounds display features that make them potential NLO materials.

Experimental Section

Compound (*R*)-1: A solution of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.060 g, 0.14 mmol), (*R*)-**L1** (0.024 g, 0.10 mmol), 4-aminobenzoic acid (0.020 g, 0.15 mmol), and pyridine (0.050 mL) in ethanol (0.50 mL) and water (0.10 mL) was mixed in a Pyrex tube. The tube was frozen, sealed under vacuum, and placed inside an oven at 120 °C. After 10 days, colorless block crystals were collected and washed with ethanol. Yield: 20.1 % based on cadmium. FT-IR (KBr): $\tilde{\nu}$ = 3467, 3344, 3281, 2923, 1603, 1556, 1518, 1446, 1424, 1358, 1237, 1108, 984, 829, 804, 750, 699, 626 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{18}N_3O_7CdCl$: C 34.45, H 3.72, N 8.61; found: C 34.76, H 3.97, N 8.15. Inversion twin of (*R*)-**1** was obtained if (*R*,*S*)-AAPM was used in place of (*R*)-AAPM.

Compound (*S*)-2: A solution of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.060 g, 0.14 mmol), (*S*)-**L1** (0.024 g, 0.10 mmol), and 4-aminobenzoic acid (0.020 g, 0.15 mmol) in ethanol (0.50 mL) and water (0.10 mL) was mixed in a Pyrex tube. The tube was frozen, sealed under vacuum, and placed inside an oven at 120 °C. After 10 days, colorless block crystals were collected and washed with ethanol. Yield: 16.7 % based on cadmium. FT-IR (KBr): $\tilde{\nu}$ = 3468, 3344, 3286, 2925, 1554, 1517, 1422, 1357, 1235, 1095, 824, 802, 754, 625 cm^{-1}; elemental analysis calcd (%)for $C_9H_{15}N_2O_8CdCl$: C 25.31, H 3.54, N 6.56; found: C 26.04, H 3.94, N 6.69. Only powders which have the same FT-IR with (*S*)-**2** were obtained if (*R*,*S*)-AAPM was used in place of (*R*)-AAPM.

Compound (*R*,*S*)-3: A solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.019 g, 0.050 mmol), (*R*)-**L2** (0.013 g, 0.050 mmol), and pyridine (0.10 mL) in methanol (0.10 mL) and water (0.70 mL) was mixed in a Pyrex tube. The tube was frozen, sealed under vacuum, and placed inside an oven at 120 °C. After 1 day, colorless block crystals were collected and washed with ethanol. Yield: 71.0 % based on zinc. FT-IR (KBr): $\tilde{\nu}$ = 3331, 3283, 2925, 1641, 1525, 1494, 1408, 1261, 1243, 1086, 990, 797, 721, 620 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{15}NOZn$: C 45.05, H 4.36, N 4.04; found: C 44.41, H 4.42, N 4.34.

Compound (*R*)-4: A solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.060 g, 0.16 mmol), (*R*)-**L3** (0.013 g, 0.050 mmol), and pyridine (0.10 mL) in ethanol (0.50 mL) and water (0.10 mL) was mixed in a Pyrex tube. The tube was frozen, sealed under vacuum, and placed inside an oven at 120 °C. After 15 days, colorless block crystals were collected and washed with ethanol. Yield: 12.9 % based on zinc. FT-IR (KBr): $\tilde{\nu}$ = 3427, 3352, 3243, 2926, 1607, 1578, 1567, 1451, 1425, 1302, 1221, 1093, 760, 699, 625 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{27}N_5O_{12}Zn_2Cl_2$: C 38.88, H 3.39, N 8.72; found: C 38.45, H 3.39, N 8.79. Only powders which have the same FT-IR spectra with (*R*)-**4** were obtained if (*R*,*S*)-AMPM was used in place of (*R*)-AMPM.

X-ray crystallographic data for single crystals: Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). The crystals were collected on a Mar 300 plate scanner, a Enraf–Nonius CAD4 or a Bruker SMART CCD diffractometer with graphite monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) by using the φ and ω scan method at 293(2) K. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 by using the SHELXTL crystallographic software package.[14] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. All hydrogen atoms were placed in the riding model and refined isotropically. Carbon-bound H atoms were constrained to ride on their parent atoms, with C–H = 0.92–0.98 Å. At the same time, nitrogen-bound H atoms were constrained to ride on their parent atoms, with N–H = 0.89–0.91 Å.

CCDC- 638070 (*R*)-**1**, 638071 (inversion twin of (*R*)-**1**), 638072 (*S*)-**2**, 638073 (*R*,*S*)-**3**, and 638074 (*R*)-**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

SHG measurement: Kurtz second harmonic generation measurement for these compounds was performed on powder sample. The Nd: YAG laser ($\lambda = 1064$ nm) was used for the test although potassium dihydrogenphosphate powder was used as the reference.

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[1] a) G. Ballester, E. Corondo, C. Giménez-Saiz, F. M. Romero, *Angew. Chem.* **2001**, *113*, 814–817; *Angew. Chem. Int. Ed.* **2001**, *40*, 792–795; b) M. E. Davis, *Nature* **2002**, *417*, 813–821; c) J. -P. Zhang, S.-L. Zheng, X.-C. Huang, X.-M. Chen, *Angew. Chem.* **2004**, *116*, 208–211; *Angew. Chem. Int. Ed.* **2004**, *43*, 206–209; d) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4823–4827; *Angew. Chem. Int. Ed.* **2005**, *44*, 4745–4749; e) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748–4758; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670–4679; f) X.-M. Zhang, R.-Q. Fang, H.-S. Wu, *J. Am. Chem. Soc.* **2005**, *127*, 7670–7671; g) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; h) T. J. Burchell, R. J. Puddephatt, *Inorg. Chem.* **2006**, *45*, 650–659; i) C. J. Kepert, *Chem. Commun.* **2006**, 695–700; j) L. Pan, B. Parker, X. Huang, D. H. Olson, J. Y. Lee, J. Li, *J. Am. Chem. Soc.* **2006**, *128*, 4180–4181; k) D. Sun, S. Ma, Y. Ke, D. J. Collins, H.-C. Zhou, *J. Am. Chem. Soc.* **2006**, *128*, 3896–3897; l) J. A. Gladysz, *Science* **2006**, *313*, 1249–1250; m) G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **1995**, *374*, 792–795; n) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe, O. M. Yaghi, *Science* **2001**, *291*, 1021–1023; o) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762–1765; p) H. Chun, D. N. Dybtsev, H. Kim, K. Kim, *Chem. Eur. J.* **2005**. *11*, 3521–3529; q) D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey, C. L. Prentice, *Chem. Mater.* **1996**, *8*, 2030–2040; r) X.-M. Zhang, M.-L. Tong, X.-M. Chen, *Angew. Chem.* **2002**, *114*, 1071–1073; *Angew. Chem. Int. Ed.* **2002**, *41*, 1029–1031; s) S.-L. Zheng, J.-P. Zhang, W.-T. Wong, X.-M. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 6882–6883; t) C. Janiak, *Dalton Trans.* **2003**, 2781; u) M. Fujita, *Acc. Chem. Res.* **1998**, *31*, 53–61; v) E. E. Moushi, T. C. Stamatatos, W. Wernsdorfer, V. Nastopoulos, G. Christou, A. J. Tasiopoulos, *Angew. Chem.* **2006**, *118*, 7886–7889; *Angew. Chem. Int. Ed.* **2006**, *45*, 7722–7725; w) C. Y. Su, A. M. Goforth, M. D. Smith, P. J. Pellechia, H. C. ZurLoye, *J. Am. Chem. Soc.* **2004**, *126*, 3576–3586; x) L. Han, M. Hong, R. Wang, J. Luo, Z. Lin, D. Yuan, *Chem. Commun.* **2003**, 2580–2581.

[2] a) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276–288; b) C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940–8941; c) S. Kitagawa, S.-I. Noro, T. Nakamura, *Chem. Commun.* **2006**, 701–707; d) M. Fujita, Y. J. Kwon, S. Wshizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152; e) O. R. Evans, H. L. Ngo, W. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395–10396; f) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; g) B. Xing, M.-F. Choi, B. Xu, *Chem. Eur. J.* **2002**. *8*, 5028–5032; h) R. Tannenbaum, *Chem. Mater.* **1994**, *6*, 550–555; i) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, doi: 10. 1021/ja067374y; j) T. Sawaki, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 4793–4798; k) T. Sawaki, T. Dewa, Y. Aoyama, *J. Am. Chem. Soc.* **1998**, *120*, 8539–8540; l) J. M. Tanski, P. T. Wolczanski, *Inorg. Chem.* **2001**, *40*, 2026–2033; m) B. Gomez-Lor, E. Gutiérrez-Puebla, M. Lglesias, M. A. Monge, C. Ruiz-Valero, N. Snejko, *Inorg. Chem.* **2002**, *41*, 2429–2432; n) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305–326; o) T. Dewa, T. Saki, Y. Aoyama, *J. Am. Chem. Soc.* **2001**, *123*, 502–503; p) O. Ohmori, M. Fujita, *Chem. Commun.* **2004**, 1586–1587; q) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin, K. Kim, *Angew. Chem.* **2006**, *118*, 930–934; *Angew. Chem. Int. Ed.* **2006**, *45*, 916–920.

[3] a) B. Zhao, X.-Y. Chen, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, *J. Am. Chem. Soc.* **2004**, *126*, 15394–15395; b) Y. A. Lee, R. Eisenberg, *J. Am. Chem. Soc.* **2003**, *125*, 7778–7779; c) T. J. Wadas, Q. M. Wang, Y. J. Kim, C. Flaschenreim, T. N. Blanton, R. Eisenberg, *J. Am. Chem. Soc.* **2004**, *126*, 16841–16849; d) Q.-M. Wang, Y.-A. Lee, O. Crespo, J. Deaton, C. Tang, H. J. Gysling, M. C. Gimeno, C. Larraz, M. D. Villacampa, A. Laguna, R. Eisenberg, *J. Am. Chem. Soc.* **2004**, *126*, 9488–9489; e) Z.-F. Chen, R.-G. Xiong, J. Zhang, J.-L. Luo, X.-Z. You, C.-M. Che, H.-K. Fun, *J. Chem. Soc. Dalton Trans.* **2000**, 4010–4012; f) V. W.-W. Yam, E. C.-C. Cheng, Z.-Y. Zhou, *Angew. Chem.* **2000**, *112*, 1749–1751; *Angew. Chem. Int. Ed.* **2000**, *39*, 1683–1685; g) V. W. -W. Yam, C.-K. Li, C.-L. Chan, *Angew. Chem.* **1998**, *110*, 3041–3044; *Angew. Chem. Int. Ed.* **1998**, *37*, 2857–2859.

[4] a) R. Fu, H. Zhang, L. Wang, S. Hu, Y. Li, X. Huang, X. Wu, *Eur. J. Inorg. Chem.* **2005**, 3211–3213; b) H. E. Katz, W. L. Wilson, G. Scheller, *J. Am. Chem. Soc.* **1994**, *116*, 6636–6640; c) S. Bénard, P. Yu, J. P. Audière, E. Rivière, R. Clément, J. Guilhem, L. Tchertanov, K. Nakatani, *J. Am. Chem. Soc.* **2000**, *122*, 9444–9454; d) C. Janiak, T. G. Scharmann, P. Albrecht, F. Marlow, R. Macdonald, *J. Am. Chem. Soc.* **1996**, *118*, 6307–6308; e) O. R. Evans, W. Li, *Acc. Chem. Res.* **2002**, *35*, 511–522; f) J.-M. Shi, W. Xu, Q.-Y. Liu, F.-L. Liu, Z.-L. Huang, H. Lei, W.-T. Yu, Q. Fang, *Chem. Commun.* **2002**, 756–757; g) Q. Ye, Y.-Z. Tang, X.-S. Wang, R.-G. Xiong, *Dalton Trans.* **2005**, 1570–1573; h) S. P. Anthong, T. P. Radhakrishnan, *Chem. Commun.* **2004**, 1058–1059.

[5] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; b) G. Férey, *J. Solid State Chem.* **2000**, *152*, 37–48.

[6] a) H. Chun, D. Kim, D. N. Dybtsev, K. Kim, *Angew. Chem.* **2004**, *116*, 989–992; *Angew. Chem. Int. Ed.* **2004**, *43*, 971–974; b) P. A. Maggard, C. L. Stern, K. R. Poeppelmeier, *J. Am. Chem. Soc.* **2001**, *123*, 7742–7743; c) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; d) N. W. Ockwig, O. Delgado-friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182; e) G. J. McManus, Z. Wang, M. Zaworotko, *Cryst. Growth Des.* **2004**, *4*, 11–13; f) L. Cario, H. Kabbour, A. Meerschaut, *Chem. Mater.* **2005**, *17*, 234–236; g) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138; h) C. Livage, N. Guillou, J. Chaigneau, P. Rabu, M. Drillon, G.

Férey, *Angew. Chem.* **2005**, *117*, 6646–6649; *Angew. Chem. Int. Ed.* **2005**, *44*, 6488–6491.

[7] a) D. Sun, D. J. Collins, Y. Ke, J.-L. Zuo, H.-C. Zhou, *Chem. Eur. J.* **2006**. *12*, 3768–3776; b) F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2001**, *123*, 7740–7741; c) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; d) W. Li, *J. Solid State Chem.* **2005**, *178*, 2486–2490; e) Y. Cui, O. R. Evans, H. L. Ngo, P. S. White, W. Lin, *Angew. Chem.* **2002**, *114*, 1207–1210; *Angew. Chem. Int. Ed.* **2002**, *41*, 1159–1162; f) K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584–587; *Angew. Chem. Int. Ed.* **1999**, *38*, 492–495; g) D. Braga, L. Brammer, N. R. Champness, *CrystEngComm*, **2005**, *7*, 1–19; h) P. J. Langley, J. Hulliger, *Chem. Soc. Rev.* **1999**, *28*, 279–291.

[8] a) H. Imai, K. Inoue, K. Kikuchi, Y. Yoshida, M. Ito, T. Sunahara, S. Onaka, *Angew. Chem.* **2004**, *116*, 5736–5739; *Angew. Chem. Int. Ed.* **2004**, *43*, 5618–5621; b) E. V. Anokhina, A. J. Jacoboson, *J. Am. Chem. Soc.* **2004**, *126*, 3044–3045; c) E. V. Anokhina, Y. B. Go, Y. Lee, T. Vogt, A. J. Jacobson, *J. Am. Chem. Soc.* **2006**, *128*, 9957–9962; d) H.-Y. An, E.-B. Wang, D.-R. Xiao, Y.-G. Li, Z.-M. Su, L. Xu, *Angew. Chem.* **2006**, *118*, 918–922; *Angew. Chem. Int. Ed.* **2006**, *45*, 904–908; e) Q. Ye, Y.-H. Li, Q. Wu, Y.-M. Song, J.-X. Wang, H. Zhao, R.-G. Xiong, Z. Xue, *Chem. Eur. J.* **2005**. *11*, 988–994; f) J.-J. Zhang, T.-L. Sheng, S.-M. Hu, S.-Q. Xia, G. Leibeling, F. Meyer, Z.-Y. Fu, L. Chen, R.-B. Fu, X.-T. Wu, *Chem. Eur. J.* **2004**. *10*, 3963–3969; g) J. D. Ranford, J. J. Vittal, D. Wu, X. Yang, *Angew. Chem.* **1999**, *111*, 3707–3710; *Angew. Chem. Int. Ed.* **1999**, *38*, 3498–3501; h) A. D. C.-V. Noord, J. W. Kampf, V. L. Pecoraro, *Angew. Chem.* **2002**, *114*, 4861–4864; *Angew. Chem. Int. Ed.* **2002**, *41*, 4667–4670; i) X. Shi, G. Zhu, S. Qiu, K. Huang, J. Yu, R. Xu, *Angew. Chem.* **2004**, *116*, 6644–6647; *Angew. Chem. Int. Ed.* **2004**, *43*, 6482–6485; j) B. Sreenivasulu, J. J. Vittal, *Angew. Chem.* **2004**, *116*, 5893–5896; *Angew. Chem. Int. Ed.* **2004**, *43*, 5769–5772; k) R. Vaidhyanathan, D. Bradshaw, J.-N. Rebilly, J. P. Barrio, J. A. Gould, N. G. Berry, M. J. Rosseinsky, *Angew. Chem.* **2006**, *118*, 6645–6649; *Angew. Chem. Int. Ed.* **2006**, *45*, 6495–6499; l) M. A. Alam, M. Nethaji, M. Ray, *Angew. Chem.* **2003**, *115*, 1984–1986; *Angew. Chem. Int. Ed.* **2003**, *42*, 1940–1942.

[9] a) L. P. Battaglia, A. B. Corradi, G. Marcotrigiano, L. Menabue, G. C. Pellacani, *J. Am. Chem. Soc.* **1980**, *102*, 2663–2669; b) O. Yamauchi, A. Odani, *J. Am. Chem. Soc.* **1987**, *109*, 5938–5945; c) Z.-R. Qu, H. Z, Y.-P. Wang, X.-S. Wang, Q. Ye, Y.-H. Li, R.-G. Xiong, B. F. Abrahams, Z.-G. Liu, Z.-L. Xue, X. Z. You, *Chem. Eur. J.* **2004**, *10*, 53–60; d) C.-T. Yang, M. Vetrichelvan, X. Yang, B. Moubaraki, K. S. Murray, J. J. Vittal, *Dalton Trans.* **2004**, 113–121; e) U. Mukhopadhyay, D. Choquesillo-Lazarte, J. Niclós-Gutiérrez, I. Bernal, *Cryst. Eng. Comm.* **2004**, *6*, 627–632; f) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273–282; g) O. Yamauchi, A. Odani, M. Takanl, *J. Chem. Soc. Dalton Trans.* **2002**, 3411–3421; h) C. Kremer, J. Torres, S. Dominguez, A. Mederos, *Coord. Chem. Rev.* **2005**, *249*, 567–590; i) B. Wisser, Y. Lu, C. Janiak, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1189–1192; j) B. Y. Lou, X. Huand, X. Lin, *Z. Anorg. Allg. Chem.* **2007**, *633*, 372–374; k) J. Weng, M. Hong, Q. Shi, R. Cao, A. S. C. Chan, *Eur. J. Inorg. Chem.* **2002**, 2553–2556.

[10] a) Y. Xie, Y. Yan, H.-H. Wu, G.-P. Yong, Y. Cui, Z.-Y. Wang, L. Pan, J. Li, R. Fan, R.-P. Li, Y.-C. Tian, G.-Q. Pan, L.-S. Sheng, X. Li, *Inorg. Chim. Acta* **2007**, *360*, 1669–1677; b) Y. Xie, H.-H. Wu, G.-P. Yong, Z.-Y. Wang, R. Fan, R.-P. Li, G.-Q. Pan, Y.-C. Tian, L.-S. Sheng, L. Pan, J. Li, *J. Mol. Struct.* **2007**, *833*, 88–97; c) Y. Xie, H.-H. Wu, G.-P. Yong, Z.-Y. Wang, *Acta Crystallogr. Sect. E* **2006**, *62*, m2089–m2090.

[11] H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143–1148.

[12] a) H. D. Flack, G. Bernardinelli, *Acta Crystallogr. Sect. A* **1999**, *55*, 908–915; b) H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881.

[13] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1986**, *39*, 3798–3813.

[14] SHELXT97, G. M. Sheldrick, Program for Crystal Structure Refinement, University of Göttingen, Germany, **1997**.

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