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Syntheses, Crystal Structures, and Photoluminescence Properties of Three Bis-acylamide Compounds

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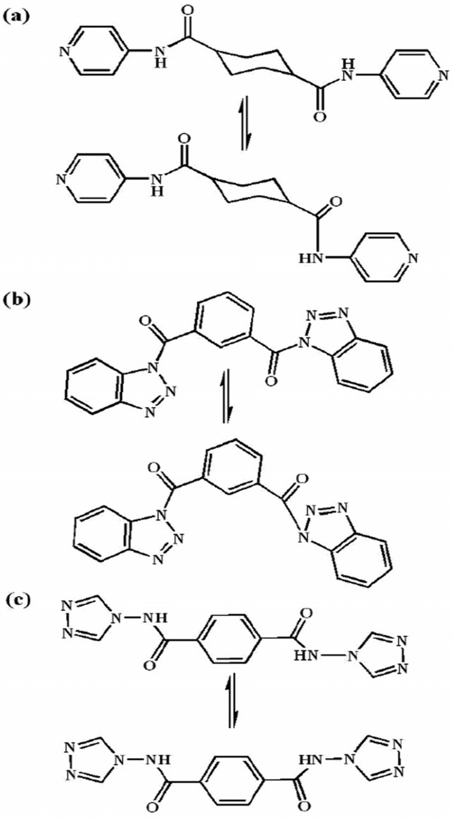
Abstract. Three bis-acylamide compounds, N^1,N^4-bis(pyridin-4-yl)-cyclohexane-1,4-dicarboxamide (**L1**), 1,1′-(1,3-phenylenedicarbonyl-)bis(1H-1,2,3-benzotriazole) (**L2**), and N^1,N^4-bis(1H-1,2,4-triazole) phthalamide (**L3**) were synthesized. **L1**, **L2**, and a Cu^{II} complex based on **L3** formulated as $CuCl_2(\mathbf{L3})_2(en)_2$ (**1**) (en = ethylenediamine) were structurally characterized by single-crystal X-ray diffraction for the first time. **L1**, **L2**, and **L3** exhibit different photoluminescence properties.

Introduction

One of the main goals of molecular electronics is the mastery of intermolecular electron transfer over long distances.[1] This requires the assembly of suitable molecular components into an appropriate supramolecular structure.[2] Compounds containing supramolecular functionalities such as acylamide are useful in self-assembly because they usually give predictable patterns of hydrogen bonds, which can add extra dimensionality.[3–10] Based on the situation, in an attempt to investigate the relationship between the structure and photoluminescence property, herein we synthesized three bis-acylamide compounds, N^1,N^4-bis(pyridin-4-yl)cyclohexane-1,4-dicarboxamide (**L1**), 1,1′-(1,3-phenylenedicarbonyl-)bis(1H-1,2,3-benzotriazole) (**L2**), and N^1,N^4-bis(1H-1,2,4-triazole) phthalamide (**L3**). Among them, the syntheses of **L1** and **L3** were not reported previously. As shown in Scheme 1, the three compounds have different aromatic rings and different bridging units, and all of them exhibit *cis* and *trans* conformations due to the rotation of the flexible C–N single bonds in the structures. In the present work, **L1**, **L2**, and a Cu^{II} complex based on **L3** formulated as $CuCl_2(L3)_2(en)_2$ (**1**) (en = ethylenediamine) were structurally characterized by single-crystal X-ray diffraction for the first time. The photoluminescence properties of the three free compounds, **L1**, **L2**, and **L3** were investigated.



Scheme 1. The *trans* (above) and *cis* (below) conformations of **L1** (**a**), **L2** (**b**), and **L3** (**c**).

Results and Discussion

Crystal Structure and Photoluminescence Property of L1

L1 crystallizes in the monoclinic space group $P2_1/n$ with half crystallographically independent **L1** in the asymmetric unit. As we know, 1,4-cyclohexanedicarboxylic acid (1,4-H_2chdc) has three kinds of conformations: *e,a-cis*, *e,e-trans*

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and *a,a-trans*, and the *e,e-trans* is the most stable conformation.[11] As described above, **L1** is obtained by using H_2chdc as starting material. As shown in Figure 1a, the two substituent groups of acylamide in the structure of **L1** are in the stable *e,e-trans*-positions. **L1** exhibits a *trans* conformation (Figure 1a and Scheme 1a) and the two pyridyl rings of **L1** are parallel to each other. Strong intermolecular N–H···N hydrogen bonds are observed in the structure of **L1**, and **L1** shows a three dimensional (3D) supramolecular architecture (Figure 1b). For example: H2–N2: 0.86 Å, H1···N1A: 2.161 Å, N2···N1A: 2.979 Å, and N2–H2···N1A: 158.95° (Figure 1b)[12] (atom with additional label A refers to the symmetry operation: x–1/2, –y+3/2, z+1/2).

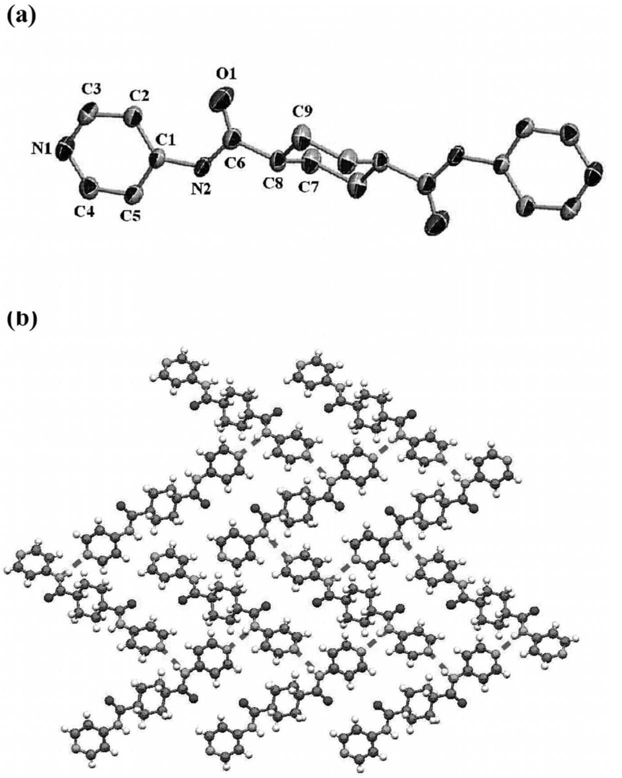


Figure 1. ORTEP view of **L1** with the ellipsoids drawn at the 50 % probability (hydrogen atoms omitted for clarity) (**a**); Strong intermolecular N–H···N hydrogen bonds indicated by dashed lines in the structure of **L1** (**b**).

The photoluminescence property of **L1** in the solid state at room temperature was investigated. The emission spectrum of **L1** (slit width = 5 nm) is shown in Figure 2. **L1** exhibits one emission peak at 461 nm upon excitation at 360 nm, which may be attributable to the intra-ligand electron transitions, such as π→π*, n→π* transitions.[13]

As described above, in the structure of **L1**, the two pyridyl rings are bridged by the nonaromatic cyclohexane ring. If the nonaromatic cyclohexane ring is replaced by the aromatic phenyl ring, and the pyridyl ring is replaced by the benzotriazole ring, it is expected the emission intensity can be improved. In order to prove the expectation, we synthesized compound **L2**.

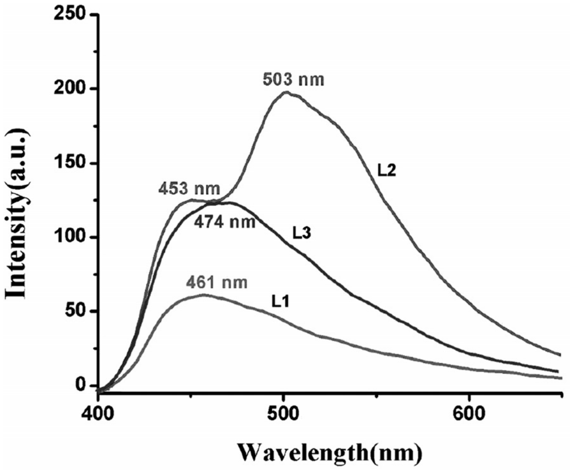


Figure 2. Solid-state emission spectra of **L1**, **L2**, **L3** at room temperature.

Crystal Structure of L2

L2 crystallizes in the monoclinic space group $P2_1/n$, its asymmetric unit contains one crystallographically independent **L2** molecule. As shown in Figure 3a, in the structure of **L2** the phenyl ring and two benzotriazole rings are not coplanar. The dihedral angles between the phenyl ring and two benzotriazole rings are 41.2 and 42.4°, respectively. The dihedral angle between the two benzotriazole rings is 74.5°. **L2** exhibits a *trans* conformation (Figure 3a and Scheme 1b). Strong π···π stacking interactions are observed in the structure of **L2**, for example, plane 1 is constructed by C15, C16, C17, C18, C19, C20, and plane 2 is constructed by C15B, C20B, N4B, N5B, N6B (atom with additional label B refers to the symmetry operation: B 2–x, 2–y, 1–z), the centroid-centroid and perpendicular distances between planes 1 and 2 are 3.821 and 3.485 Å, respectively (Figure 3b). Different **L2** molecules are linked by π···π stacking interactions to form a 3D supramolecular architecture (Figure 3b).

The emission spectrum of **L2** (slit width = 5 nm) is shown in Figure 2. **L2** exhibits an intense emission peak at 503 nm and a shoulder peak at 453 nm (λ_{ex} = 370 nm), which may be attributable to the π→π* or n→π* electron transitions of **L2**.[13] In the structure of **L2**, the phenyl ring and benzotriazole rings are aromatic, and benzotriazole ring has more π-expanded system than the pyridyl ring in the structure of **L1**, so the emission of **L2** is much stronger than that of **L1** (Figure 2).

Crystal Structure of $CuCl_2(L3)_2(en)_2$ (1)

When the benzotriazole ring in the structure of **L2** is replaced by the triazolyl ring, and the 1,3-substituted position of the bridged phenyl ring is changed to be a 1,4-position, we got compound **L3**. We fail to obtain the crystals of **L3** for single-crystal X-ray analysis, but a Cu^{II} complex based on **L3** is obtained instead. Complex **1** crystallizes in the triclinic space group $P\bar{1}$, its asymmetric unit contains one **L3**, one en, half Cu^{II}, and two half uncoordinated Cl^-. As shown in Figure 4a, Cu(1) exhibits a slightly distorted octahedral coordination ar-

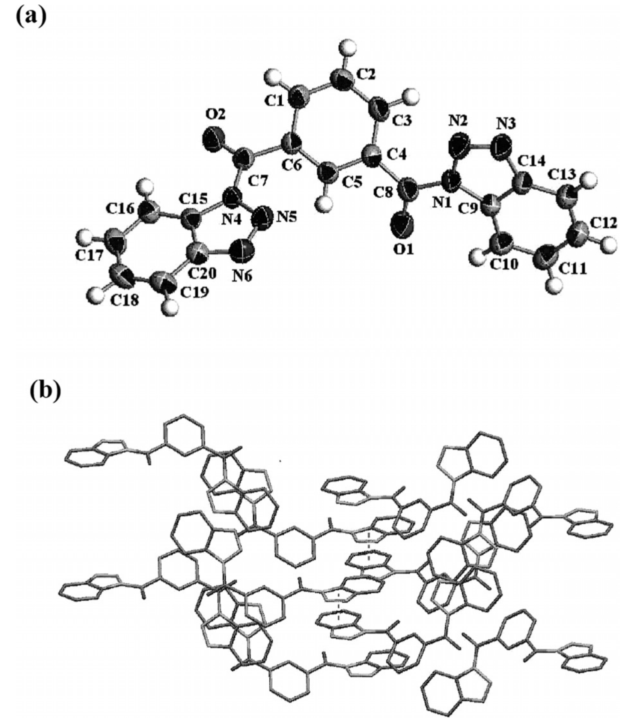


Figure 3. ORTEP view of **L2** with the ellipsoids drawn at the 50 % probability (**a**); Strong intermolecular π···π stacking interaction indicated by dashed line in the structure of **L2** (**b**).

rangement, defined by two nitrogen atoms from two triazolyl of two **L3** in the apical positions and four nitrogen atoms from two en in the equatorial positions [Cu–N 2.011(2)–2.561(3) Å] (Figure 4a and Table S1, Supporting Information). **L3** exhibits a *cis* conformation in the structure of complex **1** (Figure 4a and Scheme 1c). Strong hydrogen bond interactions are observed in complex **1** and it exhibits a 3D supramolecular architecture (Figure 4b and Table 1).

As for the free **L3** ligand, it exhibits one intense emission peak at 474 nm (λ_{ex} = 360 nm, slit width = 5 nm), which may be attributable to the π→π*, n→π* electron transitions of **L3**.[13] The emission is stronger than that of **L1** due to the aromatic phenyl ring and triazolyl ring in the structure of **L3**. The benzotriazole ring in the structure of **L2** has more expanded π system than the triazolyl ring in the structure of **L3**, as a result, the emission of **L3** is weaker than that of **L2**.

Conclusions

Three bis-acylamide compounds, **L1**, **L2**, and **L3** were synthesized. **L1**, **L2**, and a Cu^{II} complex based on **L3** were structurally characterized by single-crystal X-ray diffraction for the first time. **L1**, **L2**, and **L3** exhibit different photoluminescence properties due to different aromatic rings and bridging units in the structures.

Experimental Section

Material Required and Instrumentation: All chemicals were of reagent grade and used without further purication. IR spectra were recorded as KBr pellets with a PerkinElmer spectrometer. C, H, N elemental analyses were performed with an Elementar Vario MICRO E III analyzer. Solid-state photoluminescence spectra of all the compounds were measured at room temperature with an Edinburgh FLS920 fluorescence spectrometer. The instrument is equipped with an Edinburgh Xe900 xenon arc lamp as the exciting light source.

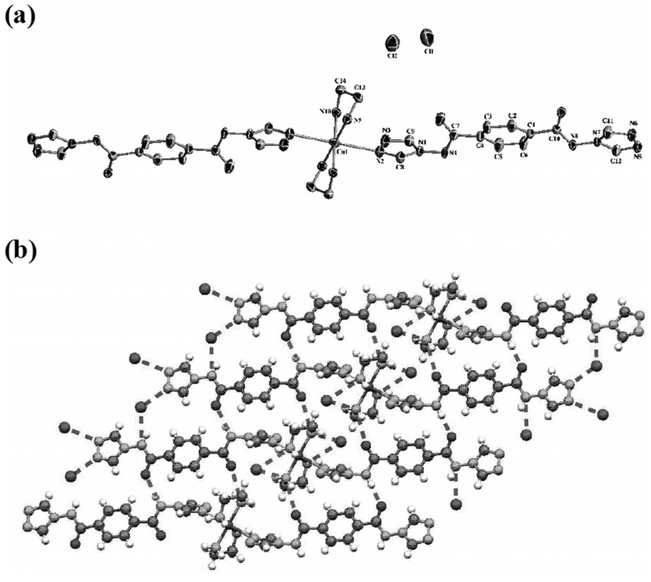


Figure 4. ORTEP view of **1** with the ellipsoids drawn at the 50 % probability (hydrogen atoms omitted for clarity) (**a**); 3D supramolecular architecture of **1** with the strong hydrogen bond interactions indicated by dashed lines (**b**).

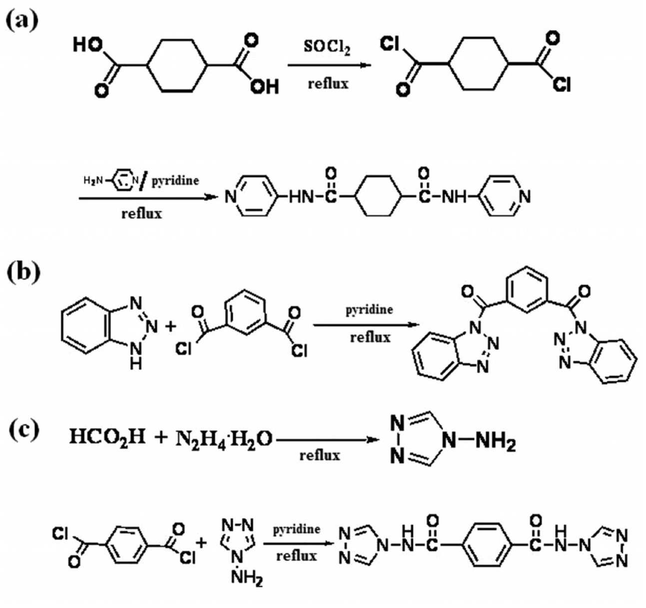
Synthesis of L1: The synthetic routine for **L1** is shown in Scheme 2a. A mixture of cyclohexane-1,4-dicarboxylic acid (0.04 mol, 6.88 g) and thionyl chloride (150 mL) was heated under reflux for 3 h. After completion of the reaction, the excess thionyl chloride was removed under reduced pressure. The yellow residue was washed with benzene (3 × 15 mL), followed by the addition of CH_2Cl_2 (250 mL), pyridin-4-amine (0.04 mol, 3.76 g), and pyridine (4.9 mL). The mixture was stirred overnight at room temperature, and heated at 50 °C for 5 h. After removing the solvent under reduced pressure, the residue was washed with CH_2Cl_2 (2 × 10 mL), H_2O (5 × 10 mL), $NaHCO_3$ (3 × 10 mL, 1 %), and H_2O (3 × 10 mL) and finally dried at 80°C in vacuo to give **L1** as a white solid. Yield ca. 44 % based on cicyclohexane-1,4-dicarboxylic acid. Colorless strip crystals of **L1** were obtained when recrystallized from *N*,*N*-dimethylacetamide (DMA). Elemental data for $C_{18}H_{20}N_4O_2$: calcd. C 66.65; H 6.21; N 17.27 %; found: C 66.71; H 6.18; N 17.23 %. **IR** (KBr): ṽ = 1699 (s), 1598 (s), 1516 (s), 1454 (w), 1419 (w), 1383 (m), 1343 (m), 1298 (m), 1167 (s), 997 (m), 935 (m), 907 (w), 833 s), 586 (m), 539 (m) cm^{-1}.

Synthesis of L2: The synthetic routine for **L2** is shown in Scheme 2b.[14] A mixture of isophthaloyl dichloride (0.05 mol, 10.15 g) and 1H-1,2,3-benzotriazole (0.1 mol,11.9 g) in pyridine (50 mL) was heated at 120 °C for 10 h. After cooling to room temperature, the white precipitate was filtered off, and washed with CH_2Cl_2 (50 mL) and water (3 × 50 mL) to yield crude **L2**. Yield ca. 57 % based on 1H-1,2,3-benzotriazole. Colorless prismatic crystals were obtained when recrystallized from acetonitrile/acetone solution (1:1 v/v). Elemental data for $C_{20}H_{12}N_6O_2$: calcd. C 65.21; H 3.28; N 22.82 %; found: C 65.27; H 3.24; N 22.77 %. **IR** (KBr): ṽ = 3375 (w), 3083 (m), 1697 (s), 1603 (s), 1486 (m), 1451 (m), 1374 (s), 1211 (s), 1047 (s), 973 (s), 878 (m), 758 (s), 635 (m), 590 (w), 472 (w) cm^{-1}.

Table 1. Distances /Å and angles /° involving selected hydrogen bonds for complex **1**.

A	H	*B*	*B*–H distance	*A*···*B* distance	H···*A* distance	*B*–H···*A*
Cl(1A)	H(8)	N(8)	0.86	2.928	2.169	147.01
O(1B)	H(4)	N(4)	0.86	2.753	1.963	152.20
O(2C)	H(92)	N(9)	0.90	2.945	2.227	136.40
Cl(2C)	H(91)	N(9)	0.90	3.066	2.236	153.20
N(3)	H(101)	N(10)	0.90	3.134	2.439	134.23
N(5A)	H(101)	N(10)	0.90	3.277	2.634	129.14
Cl(2B)	H(102)	N(10)	0.90	3.103	2.327	144.41

Symmetry transformations used to generate equivalent atoms: A –*x*, –*y*+1, –*z*+1; B *x*+1, *y*, *z*; C –*x*+1, –*y*+1, –*z*.



Scheme 2. The synthetic routines for compounds **L1**–**L3**.

Synthesis of L3: The synthetic routine for **L3** is shown in Scheme 2c. 4H-1,2,4-triazol-4-amine was prepared according to the literature method.[15] A mixture of terephthaloyl dichloride (0.1 mol, 20.3 g) and 4H-1,2,4-triazol-4-amine (0.2 mol, 16.8 g) in pyridine (100 mL) was heated at 120 °C for 10 h. After cooling to room temperature, the white precipitate was filtered off, washed with CH_2Cl_2 (3 × 30 mL), CH_3OH (2 × 25 mL), H_2O (3 × 10 mL) and finally dried at 80 °C in vacuo to give **L3**. Yield ca. 44 % based on terephthaloyl dichloride. Elemental data for $C_{12}H_{10}N_8O_2$: calcd. C 48.32; H 3.38; N 37.57 %; found: C 48.43; H 3.41; N 37.52 %. **IR** (KBr): $\tilde{\nu}$ = 3381 (w), 3168 (m), 3111 (m), 3077 (m), 3026 (w), 2928 (s), 2814 (s), 1694 (s), 1569 (s), 1524 (w), 1463 (m), 1384 (s), 1323 (s), 1278 (s), 1201 (s), 1211 (w), 1107 (s), 1073 (s), 1020 (w), 978 (m), 948 (m), 888 (s), 859 (w), 736 (m), 681 (w), 649 (m), 617 (s), 544 (w) cm^{-1}.

Synthesis of $CuCl_2(L3)_2(en)_2$ (1): $CuCl_2·2H_2O$ (0.1 mmol, 0.017g) and ethylenediamine (0.3 mmol, 0.02 mL) were dissolved in H_2O (8 mL), afterwards the mixture was carefully layered on a aqueous solution (2 mL) of **L3** (0.1 mmol, 0.030 g) and $NH_3·H_2O$ (0.5 mmol, 0.02 mL). Upon slow evaporation at room temperature for several days, blue prismatic crystals of complex **1** were filtered off and washed with water. Elemental data for $C_{28}H_{28}Cl_2CuN_{20}O_4$: calcd. C 39.85; H 3.32; N 33.21 %; found: C 39.90; H 3.35; N 33.30 %.

X-ray Crystallography: Single-crystal X-ray data for **L1**, **L2**, and complex **1** were collected with an Oxford XCalibur Eos diffractometer using graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation at room temperature. Empirical absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL-97 software.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of

Table 2. Crystal data and structure refinements for **L1**, **L2**, and complex **1**.

	L1	**L2**	**1**
Empirical formula	$C_{18}H_{20}N_4O_2$	$C_{20}H_{12}N_6O_2$	$C_{28}H_{36}Cl_2CuN_{20}O_4$
M	324.38	368.36	851.22
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a /Å	5.7275(5)	7.561(4)	7.882(3)
b /Å	16.0459(1)	29.585(2)	9.131(4)
c /Å	8.8893(8)	8.467(5)	13.732(6)
α /°	90	90	84.721(1)
β /°	102.238(9)	114.750(5)	77.358(1)
γ /°	90	90	75.745(1)
V /Å³	798.39(2)	1720.0(2)	933.9(7)
Z	2	4	1
D_{calcd} /g·cm⁻³	1.349	1.422	1.514
No. of unique reflcns	3102	3014	5970
reflections used [$I > 2\sigma(I)$]	1412	2675	3138
F(000)	344	760	439
Goodness-of-fit on F^2	1.036	1.274	1.054
R_1 a)	0.0409	0.0735	0.0437
wR_2 a)	0.0722	0.1425	0.1143

a) $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $wR_2 = \Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2.}$

L2 were located in the Fourier difference maps. All of the other hydrogen atoms were placed in the calculated positions. The crystal data and structure refinements for **L1**, **L2**, and complex **1** are summarized in Table 2. Selected bond lengths and angles for the ligands and the complex are listed in Table S1 (Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-822077 (**L1**), CCDC-822078 (**L2**), and CCDC-767851 (**1**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): Selected bond lengths /Å and angles /° for **L1**, **L2**, and **1**.

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