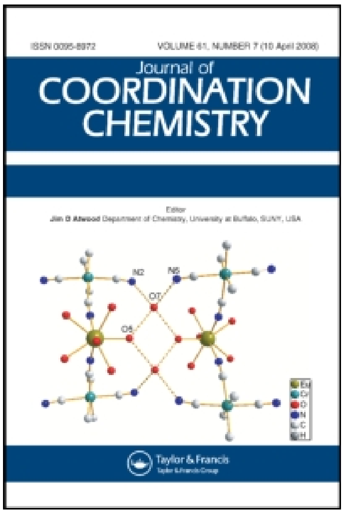

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Synthesis, crystal structure, and characterizations of a 3-D Cu(I) complex with 1,6-bi(benzotriazole)hexane

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Synthesis, crystal structure, and characterizations of a 3-D Cu(I) complex with 1,6-bi(benzotriazole)hexane

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Solvothermal reaction of the flexible ligand 1,6-bi(benzotriazole)hexane (BBTH) with CuCl generated a 3-D hybrid solid, $\{[CuCl]_2(BBTH)\}_n$ (**1**), which was investigated by elemental analysis, FT-IR, X-ray powder diffraction (XRPD), X-ray single-crystal diffraction, TG/DTA, and photoluminescence measurements. Compound **1** crystallizes in the tetragonal system, space group $I4(1)/a$, $a = b = 17.636(2)$ Å, $c = 13.5345(15)$ Å, $V = 4209.6(9)$ Å^3, $Z = 8$. The distorted tetrahedral geometry of Cu(I) is defined by two chlorides and two N donors from different BBTH ligands. Adjacent copper atoms are connected by μ_2-Cl to give a 1-D zigzag inorganic chain, and further linked by BBTH ligands *via* μ_4-bridging, forming the 3-D hybrid structure of **1**. Cu(I) atoms and BBTH ligands can be regarded as two kinds of non-equivalent 4-connected nodes, which lead to an unusual topological network with Schläfli symbol of $(3^2.8.9^2.10)_2(3^2.8^2.9^2)$. Compound **1** exhibits high thermal stability and shows strong red fluorescence emission at 538 nm in the solid state at ambient temperature.

Keywords: Solvothermal reaction; Cu(I); 1,6-Bi(benzotriazole)hexane; Organic–inorganic hybrid solid; Topology

1. Introduction

Organic–inorganic hybrid materials have various architectures and potential application in catalysis, gas storage, non-linear optics, ion-exchange, luminescence, magnetism, and many other fields [1–10]. The diversity in framework structures of such materials depends on the selection of the metal centers and organic spacers, as well as on the reaction pathways [11]. Such materials combine the unique features of the inorganic and organic components in a complementary fashion, resulting in diverse structural chemistry and novel physical properties [12, 13]. The inorganic component is usually based on metal oxides, sulfides, and halides with subnetworks of clusters, chains, or layers, which exhibit rigidity and intriguing physical properties [14–16]. Metal halides or pseudohalides play a critical role as inorganic components. Cu(I) is particularly well-suited owing to its labile coordination modes with coordination numbers 2–5 and associated counter-anion

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X (X = Cl, Br, I, CN, etc.) which can be incorporated as an essential element of the framework. Copper(I) halide or pseudohalide (CuX) skeletons generally exhibit zigzag $[CuX]_n$ chains, rhomboid Cu_2X_2 dimers, double-stranded $[Cu_2X_2]_n$ ladders, $\{Cu_3X_3\}_n$ ladder-like chains, cubane or step-cubane Cu_4X_4 tetramers, hexagonal $[Cu_6X_6]_n$ grid chains, and $\{Cu_8X_8\}_n$ ribbons. Usually, rigid or flexible multidentate nitrogen-donor ligands are organic connectors linking these CuX motifs to form extended organic–inorganic hybrid architectures varying from 1- to 3-D [17–25].

Organic species with versatile binding modes can be used to adjust the channel size, transfer energy or electron, enhance spin orbital coupling, and impart chemical reactivity or chirality [26]. Many hybrid materials have been synthesized using rigid organic ligands. Recent investigations show that among flexible ligands based on polyazaheteroaromatics such as imidazole, benzoimidazole, and triazole, the flexible benzotriazoles are relatively less studied [25, 27–33]. As an extension of our previous study of the coordination chemistry of 1,2,4-triazole and its derivatives [34], we have embarked on a program to discover new hybrid solids based on α,ω-bis(benzotriazole)alkane ligands. Using the self-assembly of CuX (X = Cl, Br, I, or CN) with 1,2-bis(benzotriazole)ethane, 1,3-bis(benzotriazole)propane, or 1,4-bis(benzotriazole)-butane under hydrothermal or solvothermal conditions, we have synthesized and characterized a series of structurally unique materials of the Cu(I)/X/bis(benzotriazole)alkane organic–inorganic hybrid family [35, 36]. In order to proceed our investigations, 1,6-bi(benzotriazole)hexane (BBTH) with much longer alkane spacer is selected. To the best of our knowledge, no hybrid materials constructed from BBTH have been reported. Herein, using BBTH under solvothermal reaction with CuCl, we obtain a 3-D organic–inorganic hybrid solid $[(CuCl)_2(BBTH)]_n$ (**1**), which has been characterized by X-ray single-crystal diffraction, FT-IR spectrum, elemental analysis, X-ray powder diffraction (XRPD), TGA, and photoluminescence measurements.

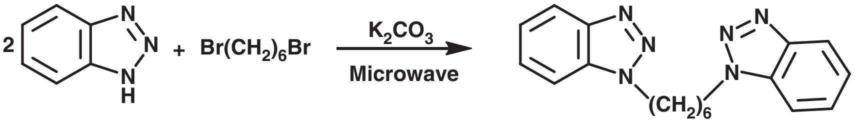
2. Experimental

2.1. *Materials and physical measurements*

Reagents and solvents were commercially available and used without purification. The C, H, and N elemental analyses were performed using an Elementar Vario EL III elemental analyzer. Fourier-transform infrared spectra (KBr pellets) were recorded using a Nicolet Avatar 360 FT-IR spectrometer in the range 4000–400 cm^{-1}. Thermal stability studies were carried out using a NETSCHZ STA–449C thermoanalyzer under a nitrogen atmosphere (40–1000°C range) at a heating rate of 10°C min^{-1}. Fluorescence spectra were measured with a Cary Eclipse fluorescence spectrophotometer at room temperature using powdered crystal samples.

2.2. *Synthesis of BBTH*

A mixture of 3.0 g (25 mmol) benzotriazole, 0.3 g (0.83 mmol) PEG-400, and 15 mL saturated potassium carbonate solution was stirred for several minutes in a 100 mL rockered flask (scheme 1) [37]. Then, 3.2 g (10 mmol) of 1,6-bi(bromine)hexane was added to the solution, mixed, and then set into a microwave oven with condensator at



Scheme 1. The synthesis route for BBTH.

480 W power for 3–6 min. During the process of microwave radiation, a certain amount of 2% sodium hydroxide aqueous solution was added every 1 min until precipitate appeared. After cooling to room temperature, the white precipitate was filtered, washed with water, and recrystallized from ethanol and water three times giving colorless sheet-shaped crystals. IR (KBr pellet (cm^{-1})): 3059 (m), 2937 (s), 2859 (w), 1610 (w), 1571 (w), 1451 (s), 1371 (w), 1321 (s), 1272 (m), 1199 (m), 1161 (m), 1057 (s), 994 (w), 850 (m), 747 (s). Anal. Calcd for $C_{18}H_{20}N_6$ (%): C, 67.48; H, 6.29; N, 26.23. Found (%): C, 67.56; H, 6.04; N, 26.43.

2.3. *Synthesis of* $\{[CuCl]_2(BBTH)\}_n$ *(1)*

A mixture of CuCl (0.0495 g, 0.5 mmol), BBTH (0.161 g, 0.5 mmol), KCl (0.0745 g, 0.5 mmol), and ethanol (6 mL) was stirred for 20 min in a 25 mL Teflon-lined reactor then sealed, heated in an oven to 180°C for 120 h and then cooled to room temperature at a rate of 4°C h^{-1}. Yellow block-shaped crystals of **1** were obtained by filtration, washed with water and ethanol, and dried in air (yield 0.0855 g, 30% based on Cu). IR (KBr pellet (cm^{-1})): 3054 (w), 2920 (s), 2854 (w), 1596 (s), 1494 (w), 1449 (s), 1374 (w), 1313 (s), 1213 (s), 1166 (s), 1102 (m), 997 (w), 741 (s). Anal. Calcd for $C_{18}H_{20}N_6Cu_2Cl_2$ (%): C, 41.70; H, 3.89; N, 16.21. Found (%): C, 41.60; H, 3.81; N, 16.40.

2.4. *Crystal structure determination*

A single crystal of **1** with dimensions $0.40 \times 0.30 \times 0.02\,mm^3$ was carefully selected under an optical microscope and glued to a thin glass fiber. Crystallographic data were collected with a Siemens Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71079$ Å) at $T = 298(2)$ K. Absorption corrections were made using SADABS [38]. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package [39]. All non-hydrogen atoms were refined anistropically. Positions of the hydrogens attached to carbon were fixed at their ideal positions. Crystal data as well as details of data collection and refinement for **1** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of crystal structure*

Single-crystal structure analysis shows that **1** crystallizes in the tetragonal space group *I4(1)/a* and can be described as a 3-D hybrid structure consisting of 1-D inorganic

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{18}H_{20}N_6Cu_2Cl_2$
Formula weight	518.38
Temperature (K)	298(2)
Crystal system	Tetragonal
Space group	*I4(1)/a*
Unit cell dimensions (Å, °)	
a	17.636(2)
b	17.636(2)
c	13.5345(15)
α	90
β	90
γ	90
Volume ($Å^3$), *Z*	4209.6(9), 8
Calculated density ($g\,cm^{-3}$)	1.636
Absorption coefficient (mm^{-1})	2.291
F(000)	2096
θ for data collection (°)	1.90–25.02
Reflections collected/unique	8508/1852
Independent reflections	0.0406
Parameters	127
Goodness-of-fit on F^2	1.123
Final *R* indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0324$, $wR_2 = 0.0680$
R indices (all data)	$R_1 = 0.0601$, $wR_2 = 0.0858$
Largest difference peak and hole ($e\,Å^{-3}$)	0.358 and −0.425

$^aR_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = \left[\Sigma w\left(F_o^2 - F_c^2\right)^2/\Sigma w\left(F_o^2\right)^2\right]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(3)	2.043(3)	N(3)–Cu(1)–N(2)	108.68(11)
Cu(1)–N(2)	2.102(3)	N(3)–Cu(1)–Cl(1)	113.00(9)
Cu(1)–Cl(1)	2.3026(11)	N(2)–Cu(1)–Cl(1)	99.79(8)
Cu(1)–Cl(1)#1	2.3446(11)	N(3)–Cu(1)–Cl(1)#1	101.74(8)
		N(2)–Cu(1)–Cl(1)#1	112.94(8)
		Cl(1)–Cu(1)–Cl(1)#1	120.65(3)

Symmetry transformations used to generate equivalent atoms: #1 $-y+3/4$, $x+1/4$, $z+1/4$.

$[CuCl]_n$ chain subunits and tetradentate bridging BBTH ligands. As shown in figure 1, crystallographically independent Cu(I) is four-coordinate to two chlorides and two nitrogens from two BBTH ligands in a distorted tetrahedron. The Cu–N and Cu–Cl bond lengths are 2.043(3) and 2.102(3) Å, and 2.301(11) and 2.346(11) Å, respectively. The corresponding bond angles are in the range 99.79(8)°–120.65(3)°. Adjacent Cu(I)'s are bridged by μ_2-chlorides along the *c*-axis (figure 2a). In this chain, two neighboring Cu(I)'s are also connected by benzotriazole from BBTH using the pyrazole-like bridging. This linkage separates the coppers at 3.4205(4) Å. One Cl^-, two nitrogen donors, and two coppers generate a $[Cu_2N_2Cl]$ five-membered ring, easing the repulsion of the two metal ions as found for many triazoles for which the *N*4-position is substituted [30, 40]. Since there are four benzotriazoles from different directions, the $[Cu_2N_2Cl]$ rings are arranged in a ... ABCDABCD ... fashion along the *c*-axis. Each BBTH takes the *anti*-conformation to link two adjacent zigzag $[CuCl]_n$ chains, using an unusual μ_4-bidging mode as shown in figure 2(b). Two benzotriazole rings in the same BBTH are parallel to each other. Thus, as depicted in figure 2(c), each $[CuCl]_n$ chain connects four adjacent equivalent inorganic chains *via* BBTH to generate the 3-D

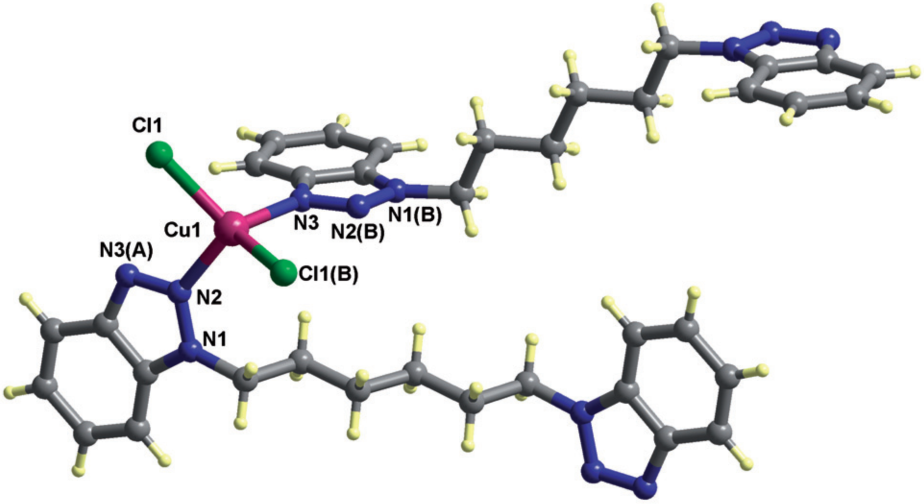


Figure 1. View of the Cu(I) coordination environments in **1** [Symmetry codes: (A) $3/4-x$, $-1/4+y$, $-1/4+z$; (B) $1/4+x$, $3/4-y$, $1/4+z$].

organic–inorganic hybrid architecture of **1**. In order to analyze this 3-D hybrid framework, we define BBTH as a four-connected node and μ_2-Cl as linkers. This means there are two kinds of nodes in the structure of **1**, a four-connected node for Cu(1) and a four-connected node for BBTH. These non-equivalent nodes lead to an unusual network topology depicted in figure 3(a). The node–node distances are of about 3.42, 5.00, and 7.71 Å. The short Schläfli symbol for the network is $(3^2.8.9^2.10)_2(3^2.8^2.9^2)$, representing the nodes Cu(1) and BBTH, respectively. The long Schläfli symbols are $3.3.8.10^2.10.10$ for Cu(1) and 3.3.8.8 for BBTH. Alternatively, Yaghi *et al.* [41] have recently demonstrated a concept of infinite rod-like secondary building units in the design and synthesis of metal–organic frameworks. According to this concept, the 3-D network of **1** exhibits a rather simple topological framework based on 1-D rod-shaped $[CuCl]_n$ building blocks and BBTH linkers (figure 3b).

3.2. *XRPD, FT-IR, and TGA*

As shown in "Supplementary material", **1** was characterized *via* XRPD at room temperature. The XRPD pattern measured for the as-synthesized sample was in good agreement with the XRPD pattern simulated from the single-crystal X-ray data using the free Mercury 1.4 program. On the basis of the XRPD results, it can be established that the single crystal selected is a good representative of the bulk compound. FT-IR spectra of BBTH and **1** are similar. Two absorption bands at 2920 and 2854 cm^{-1} (2937 and 2859 cm^{-1} for BBTH) are attributed to the flex vibration of methylene. The framework vibrations of phenyl and triazole rings are in the range 1200–1600 cm^{-1}. The slight difference in the range 1000–1170 cm^{-1} shows that nitrogens of benzotriazole have coordinated with copper.

Since thermal stability is an important quality for the application of organic–inorganic hybrid materials, we also studied **1** by means of thermal analysis under air from 40°C to 1000°C. The TG/DTA curves for **1** are provided in

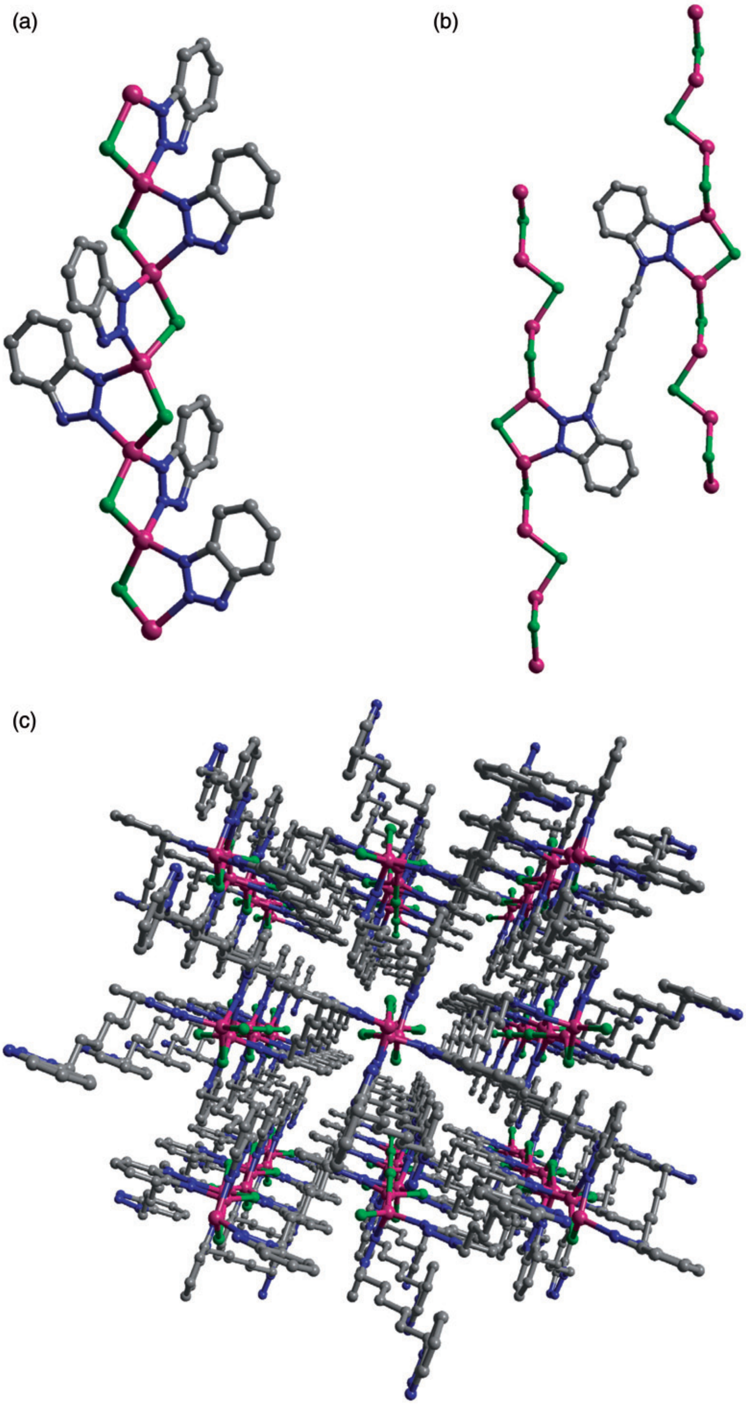


Figure 2. (a) The 1-D inorganic zigzag chain in **1**; (b) the linkage between BBTH and zigzag chains; and (c) the 3-D hybrid structure of **1** viewed along the *c*-axis direction.

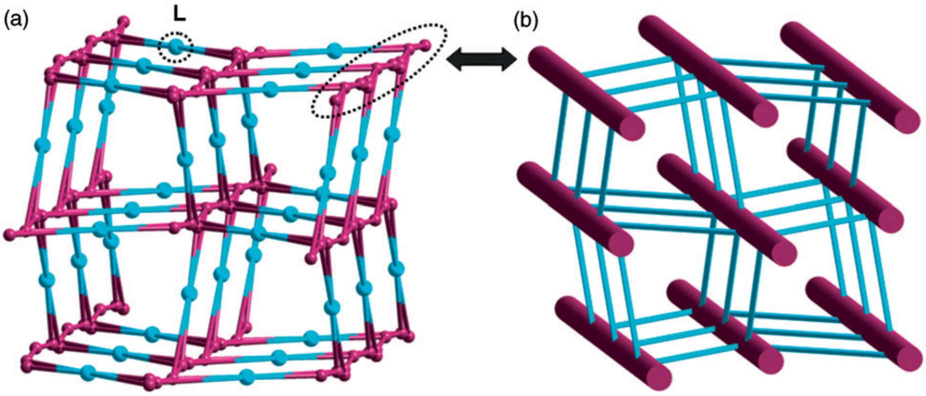


Figure 3. The topological representations of **1** constructed from two non-equivalent 4-connected nodes (a) and 1-D rod-like building subunits (b).

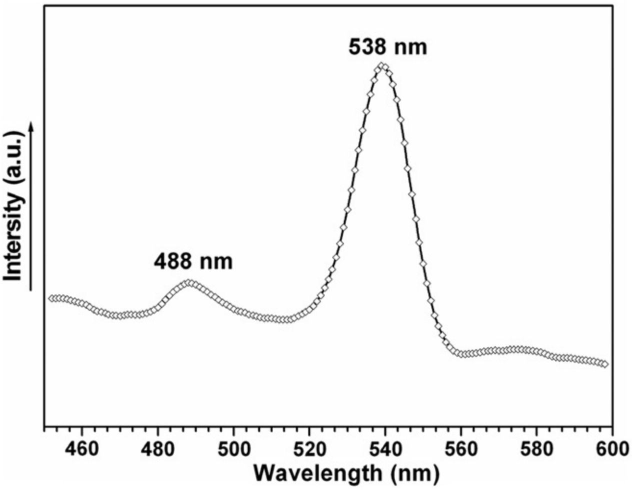


Figure 4. Solid-state emission spectrum of **1** at ambient temperature.

"Supplementary material". The weight loss curve shows that it is stable to *ca* 300°C. Over the range 300–600°C, a sharp weight loss was due to the decomposition of BBTH (Experimental: 59.0%, Calcd: 61.8%). In the temperature range 600–950°C, a mild weight loss is ascribed to the sublimation of CuCl. This conclusion is supported by the value of the second weight loss (Experimental: 38.7%, Calcd: 38.2%) [35].

3.3. *Photoluminescence properties*

Copper(I) halide complexes with both discrete and multi-dimensional structures show excellent luminescence properties [42, 43]. As shown in figure 4, upon excitation of solid **1** at 305 nm, intense emission was observed at 538 nm together with a weak band at 488 nm. To understand more thoroughly the nature of this emission band, the luminescence of BBTH was also investigated. The intraligand emission of free BBTH was observed at 442 nm along with a shoulder band at 420 nm ($\lambda_{ex} = 290$ nm). In our opinion, the weak emission band at 480 nm may be attributed to the intraligand emission of BBTH modified by the coordinated Cu–N bonds. Due to the clear red shift of the emission band at 538 nm compared to that of the free BBTH, it is tentatively assigned to ligand-to-metal charge transfer (LMCT) between Cu(I) and the ligands [10, 30, 31, 44, 45].

4. Conclusion

We have synthesized and characterized a 3-D organic–inorganic hybrid solid constructed from zigzag inorganic $[CuCl]_n$ chains and unique μ_4-BBTH ligands. Based on this work, further investigations of hybrid solids consisting of other flexible polyazaheteroaromatic ligands are under way in our lab.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC reference number for **1** is 733912.

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