Luminescent Zn and Cd Coordination Polymers

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The hydrothermal reactions of $Zn(ClO_4)_2{\cdot}6H_2O$ and $Cd(ClO_4)_2{\cdot}6H_2O$ with 1,3-bis(2*H*-tetrazol-5-yl)benzene in an aqueous ethanol and an aqueous methanol/pyridine medium, respectively, yielded a 3D and a 2D metal-organic coordination framework [Zn(1,3-BTB)] (**1**) and [Cd(1,3-BTB)$_2$(Py)$_2$(H$_2$O)$_2$] [Cd[Cd(Py)(H$_2$O)]$_2$(1,3-BTB)$_2$] (**2**) (1,3-BTB = 1,3-ditetrazolylbenzene, Py = pyridine), respectively. Species **1** possesses an open network structure with no guest molecules residing in its small cavities. The structural characterisation of **2** shows a 2D layered framework consisting of nano-sized polytube structures which are stacked one on top of another in the (110) plane giving small channels along the *b* and *c* axes. Additionally, compounds **1** and **2** exhibit strong fluorescence at room temperature in the solid state.

Introduction

Molecular-based tubular structures have received much attention because of their potential to selectively accommodate ions and molecules and catalyse specific chemical transformations.[1] The potential uses of such architectures largely depend on the size and type of their cavities which are mainly controlled by the ligands and appropriate metal ions.[2] There still remains difficulty in predicting the nature of the cavities in the polymer frameworks because of the frequent occurrence of interpenetration of the networks.[3] This problem could be solved, in principle, by designing organic ligands which disfavour interpenetration. In this respect, the use of a panel-like ligand[4] such as 1,3-ditetrazolylbenzene is promising because its coordination assembly is supposed to give polytube structures[5] without the possibility of interpenetration. Because of the aromaticity and multiple N-donor atoms, tetrazolate is also as excellent an N-donor group as pyridyl[6] and nitrile[7] with potential applications in the construction of coordination frameworks.[8] Most importantly, it is an anionic group like carboxylate which may potentially result in neutral polymeric structures which may not accommodate anions in their cavities, in contrast to those formed from neutral donor ligands. Moreover, it was found that the tetrazole functional group has a wide range of applications as a ligand in coordination chemistry, in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group and in various materials science applications involving high density energy materials and speciality explosives.[9] Here we show, that upon treatment with zinc or cadmium, 1,3-ditetrazolylbenzene can be assembled into a 3D open network structure and a 2D layered framework with a nano-sized polytube structure. No organic guests were found in the small cavities of [Zn(1,3-BTB)] (**1**), while coordinated pyridine molecules resided in the nano-sized tubes of [Cd(1,3-BTB)$_2$Py$_2$(H$_2$O)$_2$][Cd(CdPyH$_2$O)$_2$(1,3-BTB)$_2$] (**2**). Their fluorescence spectra were investigated in the solid state. The present report is concerned with the syntheses, crystal structures and luminescent properties of compounds **1** and **2**.

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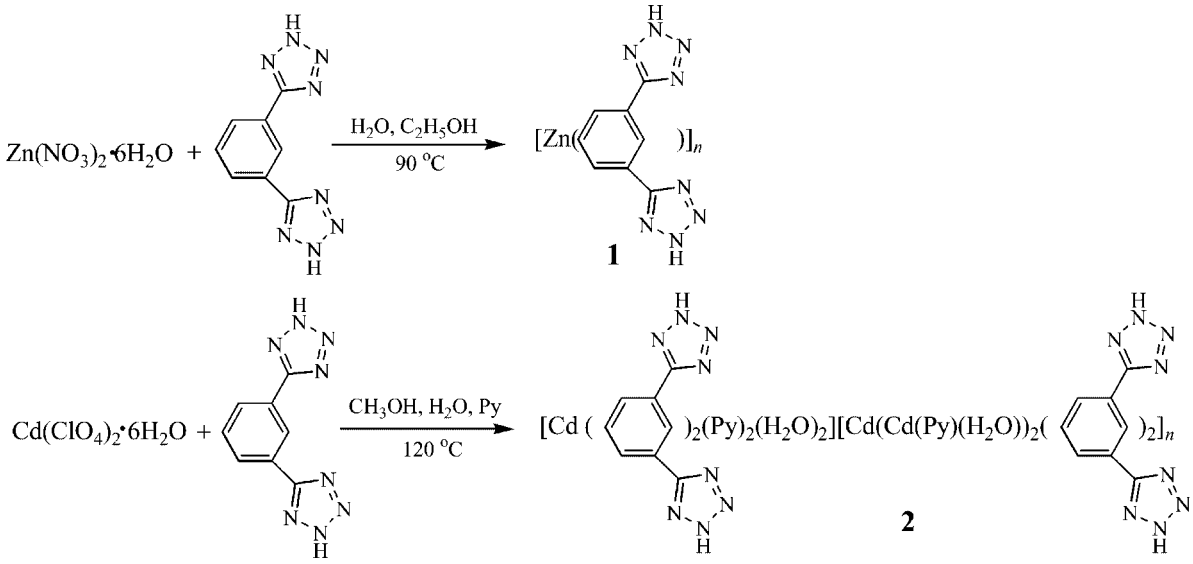
Results and Discussion

Complex **1** was prepared by treating $Zn(NO_3)_2{\cdot}6H_2O$ with 1,3-ditetrazolylbenzene in water and ethanol at 90 °C under hydrothermal conditions (Scheme 1).[10] Complex **2** was prepared by treating $Cd(ClO_4)_2{\cdot}6H_2O$ with 1,3-ditetrazolylbenzene in methanol, water and pyridine at 120 °C under hydrothermal conditions. The observed tetrazolate stretching frequencies (1442 and 1396 cm^{-1} in **1**, and 1448 and 1428 cm^{-1} in **2**) of these compounds are consistent with those of other tetrazolate-based assemblies in previous reports.[8] An IR peak over 3100 cm^{-1} in **2** indicated the presence of coordinated water. The thermogravimetric analysis (TGA) of **1** showed it to be stable up to ca. 300 °C without any weight loss (see Supporting Information; see also the footnote on the first page of this article). The TGA of **2** showed that there were consecutive processes, namely loss of the coordinated water and pyridine molecules as well as ligand pyrolysis.



Scheme 1

Structural Description

[Zn(1,3-BTB)] (1): Compound **1** has a 3D-open network structure. The asymmetric unit comprises one Zn atom and one 1,3-BTB ligand. Each Zn atom is bound to four tetrazoles from four different 1,3-BTB ligands to adopt a highly distorted tetrahedral geometry (Figure 1). The N−Zn−N angles vary from 101.69(7) to 121.31(7)°. All donor atoms form strong bonds with the zinc atom [from 1.986(0) to 2.003(4) Å]. Each 1,3-BTB ligand coordinates through the 1,3 nitrogen atoms (N1, N3) of one tetrazole and the 1,4 nitrogen atoms (N5, N8) of the other tetrazole to four zinc atoms. Zinc atoms are connected by the 1,3 nitrogen atoms of one tetrazole along the *a* axis and by the 1,4 nitrogen atoms of the other tetrazoles along the *c* axis to form 2D sheets (Figure 2). The 1,3-BTB ligands then link parallel sheets together along the *b* axis giving rise to a 3D network (Figure 3). A preliminary inspection of the topology suggests that the zinc centre and the 1,3-BTB ligand both serve as 4-connecting centres. The overall topology appears to be that of the Al net in $SrAl_2$.[11] Small cavities can be seen along the *a* axis. No guest molecules are encapsulated in the cavities because of space restrictions.

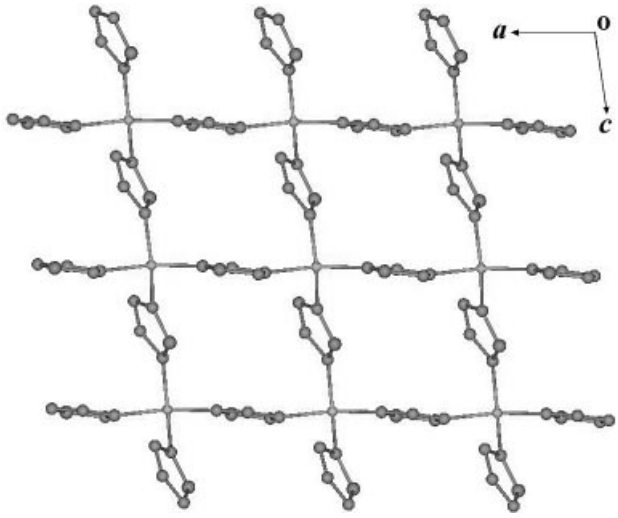


Figure 2. The 2D sheet composed of zinc atoms and tetrazolyl units in **1** (The phenyl ring and the other tetrazolyl ring in the ligand are omitted for clarity)

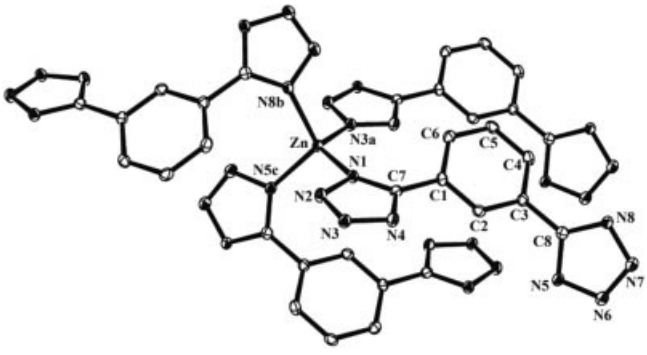


Figure 1. The local coordination geometry around the Zn centre in **1**

[Cd(1,3-BTB)$_2$(Py)$_2$(H$_2$O)$_2$][Cd[Cd(Py)(H$_2$O)]$_2$(1,3-BTB)$_2$] (2): Compound **2** is composed of 2D frameworks, the structure being a little more complicated than that of **1**. The asymmetric unit of **2** consists of one Cd atom and two half Cd atoms, two 1,3-BTB ligands, two water molecules and two pyridines. There are three unique cadmium atoms and all of their coordination geometries may be best described as distorted octahedral. Cd1 is bound to four tetrazoles from four 1,3-BTB ligands, one water molecule and one pyridine, the bond angles around the central Cd1 atom and the *cis* ligands range from 82.5° to 99.4° (Figure 4). Cd2 is

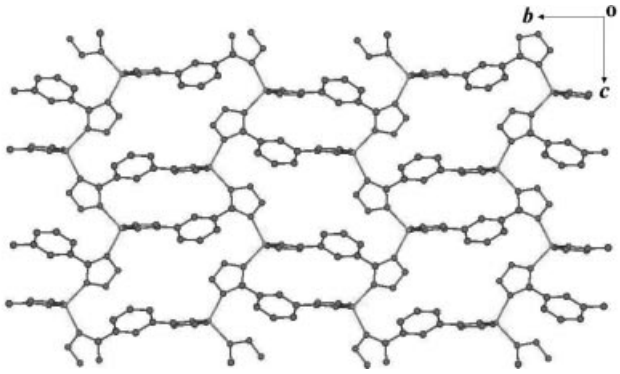


Figure 3. The 3D structure of **1** viewed along the *a* axis

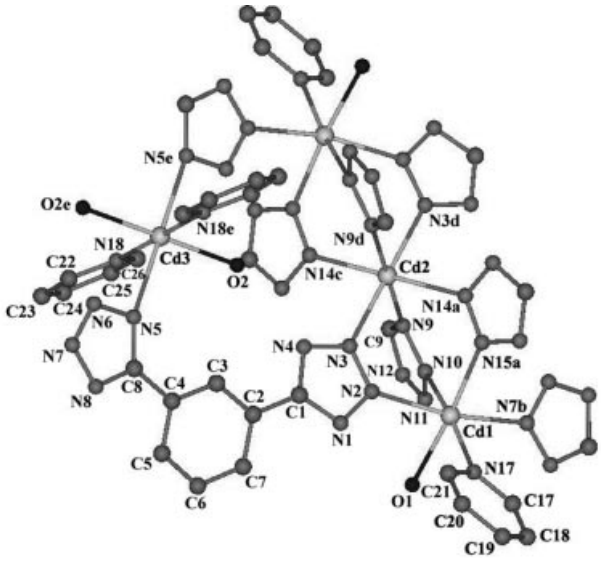


Figure 4. Part of the structure of **2** showing the local coordination geometry around the three unique Cd centres

bound to six tetrazoles from six 1,3-BTB ligands, the bond angles around the central Cd2 atom and the *cis* ligands range from 86.5° to 93.5°. Cd3 is bound to two *trans* tetrazoles from two 1,3-BTB ligands, two *trans* water molecules and two *trans* pyridines, the bond angles around the central Cd3 atom and the *cis* ligands range from 80.9° to 99.1°. The lengths of the majority of the Cd−N bonds vary from 2.265(6) to 2.415(6) Å, while Cd3−N5 is 2.503(6) Å which is a little longer than the ususal value. The two Cd−O bond lengths are 2.317(4) and 2.406(5) Å, while the latter value is somewhat long and indicates weak bonding. The two unique 1,3-BTB ligands have different coordination modes: one coordinates through the 1,3 nitrogen atoms (N5, N7) and the 2,3 nitrogen atoms (N2, N3) of its two tetrazoles, the other coordinates through the 1,2 nitrogen atoms (N9, N10) and the 2,3 nitrogen atoms (N14, N15) of its two tetrazoles.

To clearly understand the 2D framework in **2**, we first consider two Cd1 atoms, one Cd2 atom, two water molecules and two pyridines as a four-connected node. Secondly, we take two 1,3-BTB ligands as one bridge and take one Cd3, two 1,3-BTB ligands, two water molecules and two pyridines as the other bridge. A two-dimensional (4, 4) layer structure is then obtained as can be seen from Figure 5. As a result, the polytube structure is formed with the approximate dimensions of 10.0 × 9.2 Å (Figure 6). Each tube is self-assembled from six units of 1,3-BTB and is mainly lined with phenyl groups which accommodate two coordinated pyridine molecules. The 2D layers pack together in the crystallographic (011)-plane, resulting in channel formation along both the *b*-axis and the *c*-axis (Supporting Information). These 2D frameworks are stabilised by hydrogen bonding (O1···N11, 2.740 Å) (Figure 7).

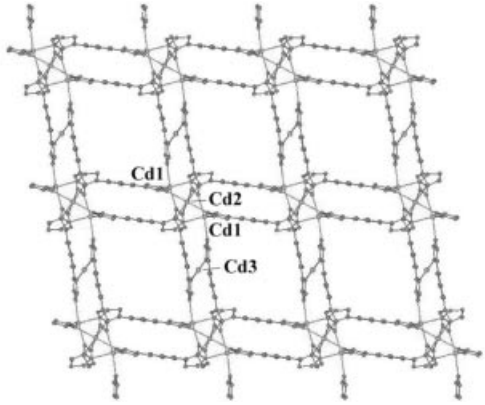


Figure 5. The 2D framework in **2** (coordinated water and pyridine molecules are omitted for clarity)

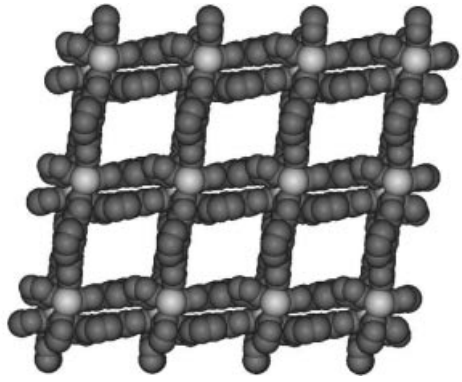


Figure 6. Space filling representation of the nano-sized tubes in the crystal structure of **2** (Coordinated water and pyridine molecules are omitted for clarity)

Fluorescent Properties

Coordination frameworks are promising luminescent materials owing to their higher thermal stability than the pure organic ligand and the ability to affect the emission wavelength of the organic material by metal coordination. The combination of organic spacers and transition-metal centres in the coordination frameworks can be viewed as an efficient method for obtaining new types of electroluminescent materials for potential applications, e.g. as light-emitting diodes (LEDs).[12] The luminescent properties of 1,3-BTB and compounds **1** and **2** were investigated in the solid

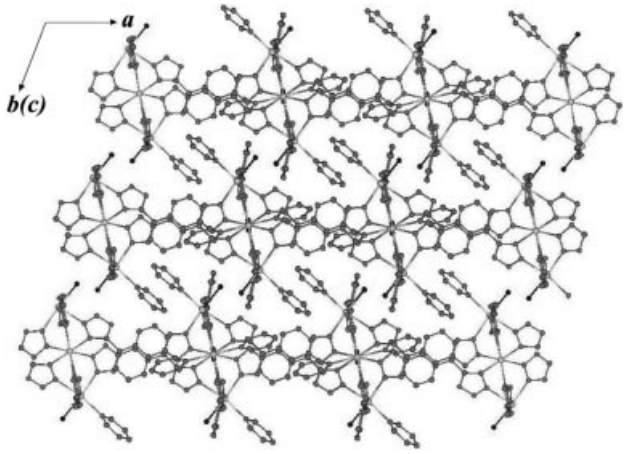


Figure 7. The packing view of the 2D framework in **2**

state. The fluorescence spectrum of 1,3-BTB is shown in Figure 8 and exhibits an emission maximum at 471 nm. The emission spectra of **1** and **2**, also shown in Figure 8, are equally blue-shifted to 323 nm. However, no enhancement in the fluorescence intensity is realised, in fact the fluorescence intensity of **2** is virtually weakened. The emission colour of free 1,3-BTB was significantly affected by its incorporation into the Zn- and Cd-containing polymeric frameworks of **1** and **2**, as evidenced by the large shift in the emission. The emissions that occurred in compounds **1** and **2** can still be assigned to free ligand photoluminescence and the large blue-shift may be due to bad conjugation effects compared with those in the free ligand.[12] In general, compounds **1** and **2** reported herein are unusual examples of room-temperature luminescent Zn- and Cd-containing polymeric compounds.

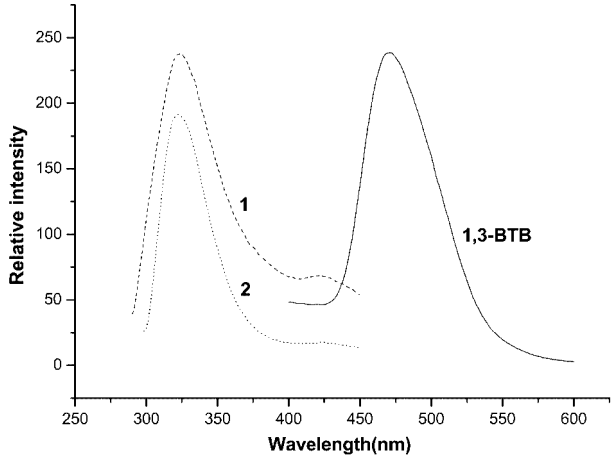


Figure 8. The emission spectra of 1,3-BTB (solid line), **1** (dashed line) and **2** (dotted line) in the solid state at room temperature

Conclusions

In summary, we have prepared two new coordination framework polytube structures from 1,3-ditetrazolylbenzene. The structural features of complexes **1** and **2** demonstrate the coordination flexibility of the tetrazolate group. The luminescent properties of **1** and **2** indicate that the metal coordination and formation of the coordination framework can affect the emission wavelength and the intensity of the organic material.

Experimental Section

General Remarks: 1,3-Ditetrazolylbenzene was prepared from NaN_3 and *m*-dicyanobenzene in 84% yield.[13] Cadmium perchlorate hexahydrate was prepared from the reaction of cadmium hydroxide with perchloric acid.[14] ***Caution:*** $Cd(ClO_4)_2·6H_2O$ is potentially explosive and should be used with care! All other chemicals were of AR grade. Elemental analyses (C, H, N) were performed with an Elementar Vario ELIII elemental analyser. IR spectra as KBr discs were recorded with a Bruker VECTOR-22 FT-IR spectrophotometer. Thermal gravimetric analyses were performed with a Shimadzu TGA-50H Thermal Gravimetric Analyser with a heating rate of 5 °C min^{-1}. Excitation and emission spectra were recorded with a Perkin−Elmer LS55 luminescence spectrometer.

Preparation of 1: Hydrothermal treatment of $Zn(NO_3)_2·6H_2O$ (30 mg, 0.1 mmol), 1,3-ditetrazolylbenzene (21 mg, 0.1 mmol), water (0.8 mL) and ethanol (0.2 mL) for 12 h at 90 °C yielded colourless plate crystals (0.012 g, 44%, only one pure phase). $C_8H_4N_8Zn$ (277.56): calcd. C 34.62, H 1.45, N 40.37; found C 35.04, H 1.39, N 40.85. IR spectrum (KBr): $\tilde{\nu}$ = 3444 (w), 1614 (m), 1524 (m), 1441 (s), 1396 (s), 1345 (m), 1251 (m), 1207, 1174, 1127 (m), 1106 (m), 1080 (m), 1064 (m), 1022 (m), 911 (m), 820 (s), 780 (s), 766 (m), 746 (s), 700 (s), 662 (m), 596 (m), 527 (m), 456 (m), 439 (m) cm^{-1}.

Preparation of 2: Hydrothermal treatment of $Cd(ClO_4)_2·6H_2O$ (41 mg, 0.1 mmol), 1,3-ditetrazolylbenzene (21 mg, 0.1 mmol), methanol (0.4 mL), water (0.2 mL) and pyridine (0.1 mL) at 120 °C for 12 h yielded colourless plate crystals (0.029 g, 68%, only one pure phase). $C_{52}H_{44}Cd_4N_{36}O_4$ (1686.79): calcd. C 37.03, H 2.63, N 29.89; found C 37.94, H 2.32, N 30.25. IR spectrum (KBr): $\tilde{\nu}$ = 3384 (w), 1638 (m), 1604 (s), 1447 (s), 1428 (s), 1363 (m), 1327 (m), 1221 (m), 1170 (m), 1155 (m), 1133 (m), 1069 (m), 1040 (m), 1012 (m), 914 (m), 831 (m), 810 (m), 780 (m), 761 (m), 750 (s), 698 (s), 630 (m), 506 (m), 417 (m) cm^{-1}.

X-ray Crystallographic Studies: Crystal data and details of the structure refinements are presented in Table 1. Intensity data were collected using Mo-K_α radiation (λ = 0.71073 Å) at 173 K for compound **1** and 100 K for compound **2**. The structure solutions and refinements were carried out using SHELXS-96[15] and SHELXL-97.[16] All hydrogen atoms were identified from difference maps and were included in the successive refinement cycles. All non-hydrogen atoms (including those of solvent water molecules) were refined anisotropically. CCDC-232821 (for **1**) and -232822 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data and refinement details for **1** and **2**

	1	**2**
Empirical formula	$C_8H_4N_8Zn$	$C_{52}H_{44}Cd_4N_{36}O_4$
M	277.56	1686.79
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / Å	5.6038(10)	11.457(5)
b / Å	18.304(3)	12.210(5)
c / Å	9.9544(17)	12.935(5)
α / °	90	66.206(8)
β / °	98.199(3)	73.384(9)
γ / °	90	82.799(9)
V / Å^3	1010.6(3)	1586.4(11)
Z	4	1
D_c / g·cm^{-3}	1.824	1.472
μ (Mo-K_α) / mm^{-1}	2.419	1.373
F(000)	552	692
T / K	173(2)	100(2)
Total data	5615	6965
Unique data	2372	4533
R_{int}	0.0230	0.0356
Data $I > 2\sigma(I)$	2088	3245
$R1$[a] $[I > 2\sigma(I)]$	0.0301	0.0447
$wR2$[a] $[I > 2\sigma(I)]$	0.0719	0.0762
GOF[b]	1.026	0.863
Residuals / e·Å^{-3}	0.536, −0.366	0.827, −0.723

[a] $R1 = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] GOF $= \{\Sigma[w(F_o^2 - F_c^2)2]/(n - p)\}^{1/2}$.

Acknowledgments

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