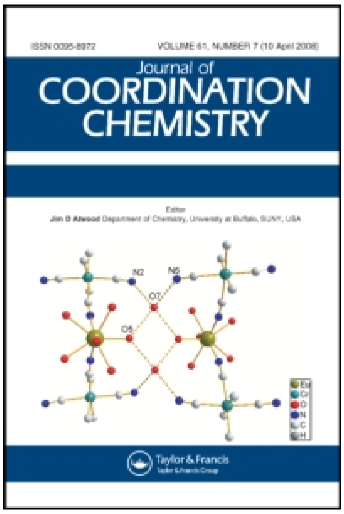

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Synthesis, crystal structures and blue fluorescent properties of two four-coordinate Zinc(II) complexes

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SYNTHESIS, CRYSTAL STRUCTURES AND BLUE FLUORESCENT PROPERTIES OF TWO FOUR-COORDINATE ZINC(II) COMPLEXES

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Two novel complexes, [Zn(deatrz)$_4$](ClO$_4$)$_2\cdot$H$_2$O (**1**) and [Zn(deatrz)$_2$(SCN)$_2$] (**2**), have been prepared and characterized by X-ray crystallography, absorption and luminescence spectroscopy (deatrz = 3,5-diethyl-4-amino-1,2,4-triazole). Complex **1** crystallizes in the monoclinic space group $P2_1/c$, $a = 13.287(8)$, $b = 23.212(14)$, $c = 12.562(8)$ Å, $\beta = 95.926(12)^\circ$, $Z = 4$, $R_1 = 0.0659$, $wR_2 = 0.1494$; **2** crystallizes in the monoclinic space group $P2_1/c$, $a = 9.589(6)$, $b = 24.689(16)$, $c = 18.386(12)$ Å, $\beta = 96.046(11)^\circ$, $Z = 8$, $R_1 = 0.0484$, $wR_2 = 0.1064$. Complex **1** is the first example of zinc(II) coordinated to four triazole ligands in a tetrahedral environment in 3,4,5-alkyl-substituted 1,2,4-triazole complexes. The coordination sphere of the zinc(II) ion in **2** is a distorted tetrahedron completed by two independent nitrogen atoms of two triazole ligands and two thiocyanate ions. Complex **1** displays stronger blue photoluminescence than **2** as the result of extra triazole ligands coordinated to the zinc(II) ion.

Keywords: Zinc(II) complexes; Triazole; Crystal structure; Fluorescence properties

INTRODUCTION

In the past two decades, a variety of coordination compounds containing N^4-substituted-1,2,4-triazoles as ligands coordinated to metal ions has been reported [1–10]. By blocking the N^4 donor position through substitution, only the N^1-monodentate and the N^{1}N^2-didentate coordination modes are possible. Structures and properties of mono- and polynuclear compounds have been described [5–8,10]. Separately, blue luminescent metal complexes have been of particular interest because they are one of the key colour components required for full-colour electroluminescent displays [11–13]. However, there are relatively few reports of luminescent properties of triazole compounds. In this present contribution, we report a triazole ligand (deatrz=3,5-diethyl-4amino-1,2,4-triazole), and two novel zinc(II) complexes, namely [Zn(deatrz)$_4$](ClO$_4$)$_2$ (**1**) and [Zn(deatrz)$_2$(SCN)$_2$] (**2**). Both X-ray crystal structures and their strong blue luminescent properties are noted.

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EXPERIMENTAL

All solvents and chemicals were of reagent grade and used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer 240 instrument. Infrared spectra were measured on a Bruker Vector 22 FT-IR instrument using KBr pellets. Diffuse reflectance absorption spectra were performed with a Shimadzu UV-2101PC spectrophotometer in the range 200–2000 nm at room temperature. The photoluminescence spectra were measured with a MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the source.

Preparation

The triazole ligand deatrz was prepared as follows: A 80% aqueous solution of 2.6 mol of hydrazine hydrate was added slowly to 2.0 mol of propionic acid. The mixture was heated slowly and kept at 220°C for about 3 h. When the mixture was cooled, the 3,5-diethyl-4-amino-1,2,4-triazole (deatrz) was isolated [14]. A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 0.037 g) or $Zn(SCN)_2$ (0.1 mmol, 0.018 g) was added to a vigorously stirred solution of the ligand deatrz (0.4 mmol, 0.056 g). Stirring was continued until the mixture remained clear. The solution slowly evaporated during a few days and needle-like, 1–2 cm long, colourless and transparent crystals appeared. Anal. Calc. for $C_{24}H_{48}Cl_2N_{16}O_8Zn$ (**1**): C, 34.88; H, 5.63; N, 27.31%; Found: C, 34.91; H, 5.82; N, 27.15%. B.p.: 185–187°C. Yield: 57%. Anal. Calc. for $C_{14}H_{24}N_{10}S_2Zn$ (**2**): C, 36.50; H, 5.18; N, 30.15%; Found: C, 36.37; H, 5.20; N, 30.31%. B.p.: 170–172°C. Yield: 43%.

Structure Determination

Suitable crystals of the title compounds were carefully selected. Single crystal structure determination by X-ray diffraction was performed on a BRUKER SMART 1000 CCD detector with graphite-monochromatized Mo Kα radiation, wavelength 0.71073 Å, at 293(2) K. Refined cell constants and additional relevant crystal data are given in Table I. Intensity data were corrected for absorption using a semi-empirical correction (Ψ-scans). Structure solution and refinement were carried out using SHELXS-97 [15] and SHELXL-97 [16]. Zinc atoms were located first and all the remaining atoms, including hydrogen atoms, were found by difference Fourier maps after least-squares refinement. Hydrogen atoms were introduced in the refinement as fixed contributors. Refinements were performed using anisotropic thermal displacements for all non-hydrogen atoms. Final reliability factors converged to $R_{obs} = 0.0659$, 0.0484 and $wR_{obs} = 0.1494$, 0.1064 for **1** and **2**, respectively. Selected bond lengths and angles are given in Table II for both complexes. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms of **1** and **2** are listed in Tables III and IV, respectively.

RESULTS AND DISCUSSION

Two zinc salts, $Zn(ClO_4)_2$, as a species with non-coordinating anions, and $Zn(SCN)_2$, as a species with coordinating anions, were chosen for reactions with deatrz.

TABLE I Crystal data and structure refinement parameters for **1** and **2**

	$[Zn(deatrz)_4](ClO_4)_2\cdot H_2O$ (*1*)	$[Zn(deatrz)_2(SCN)_2]$ (*2*)
Empirical formula	$C_{24}H_{48}Cl_2N_{16}O_8Zn$	$C_{14}H_{24}N_{10}S_2Zn$
Formula weight (g/mol)	825.05	461.95
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	13.287(8)	9.589(6)
b (Å)	23.212(14)	24.689(16)
c (Å)	12.562(8)	18.386(12)
β (°)	95.926(12)	96.046(11)
Temperature (K)	298(2)	298(2)
Volume (Å^3)	3853(4)	4329(5)
Z	4	8
λ MoKα (Å)	0.71073	0.71073
Density (calculated) (g/cm^3)	1.422	1.428
Absorption coefficient (mm^{-1})	0.840	1.349
F(000)	1728	1944
Crystal size (mm^3)	0.32 × 0.24 × 0.21	0.42 × 0.30 × 0.16
θ range for data collection (°)	2.30–25.03	1.39–25.03
Limiting indices	$-12 \le h \le 15$ $-27 \le k \le 27$ $-13 \le l \le 14$	$-8 \le h \le 11$ $-29 \le k \le 28$ $-12 \le l \le 20$
Reflections collected	19996	21777
Independent reflections	6759 [R(int) = 0.0668]	7600 [R(int) = 0.0667]
Absorption correction	Semi-empirical	Semi-empirical
Max. and Min. transmission	0.8433 and 0.7748	0.8131 and 0.6012
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	6759/0/460	7600/2/487
Goodness-of-fit on F^2	0.832	0.788
R_1, wR_2 [$I > 2\sigma(I)$]	0.0659, 0.1494	0.0484, 0.1064
R_1, wR_2 (all data)	0.1589, 0.1793	0.1742, 0.1415
Largest diff. peak and hole (e Å^{-3})	0.633 and -0.289	0.699 and -0.447

TABLE II Selected bond lengths (Å) and angles (°) for **1** and **2**

$[Zn(deatrz)_4](ClO_4)_2\cdot H_2O$ (*1*)		$[Zn(deatrz)_2(SCN)_2]$ (*2*)	
Zn(1)–N(9)	1.986(5)	Zn(1)–N(2)	1.934(14)
Zn(1)–N(1)	1.992(5)	Zn(1)–N(1)	1.959(13)
Zn(1)–N(5)	1.997(5)	Zn(1)–N(3)	2.005(12)
Zn(1)–N(13)	2.015(5)	Zn(1)–N(7)	2.014(12)
N(9)–Zn(1)–N(1)	114.24(19)	N(2)–Zn(1)–N(1)	108.9(6)
N(9)–Zn(1)–N(5)	110.4(2)	N(2)–Zn(1)–N(3)	109.0(5)
N(1)–Zn(1)–N(5)	103.2(2)	N(1)–Zn(1)–N(3)	115.6.(5)
N(9)–Zn(1)–N(13)	109.1(2)	N(2)–Zn(1)–N(7)	109.7(5)
N(1)–Zn(1)–N(13)	108.03(19)	N(1)–Zn(1)–N(7)	105.3(5)
N(5)–Zn(1)–N(13)	111.7(2)	N(3)–Zn(1)–N(7)	108.2(5)

The structures of **1** and **2** have shown that the coordination behaviour of the anions was as expected [17,18].

The cationic unit of **1** is depicted in Fig. 1. The zinc(II) ion in **1** is located at a slightly distorted tetrahedral centre relating four N-bonded deatrz ligands. The Zn–N (1.986(5)–2.015(5) Å) distances are within the range observed for other tetrahedral complexes [19]. The bond angles around the zinc atom do not deviate much with respect to the value expected for an ideal tetrahedron, 109°; they range from 103.2(2) to 114.24(19)°. Though a few mononuclear compounds are known in which 3,4,5-alkyl-substituted

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for non-hydrogen atoms of **1**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)[a]
Zn(1)	7419(1)	917(1)	189(1)	55(1)
Cl(1)	5365(2)	3949(1)	503(2)	107(1)
Cl(2)	8439(2)	8321(1)	5696(2)	89(1)
N(1)	8509(4)	1496(2)	542(4)	54(1)
N(2)	8199(4)	2008(2)	935(4)	69(2)
N(3)	9854(5)	1988(2)	1006(4)	71(2)
N(4)	10860(5)	2120(3)	1154(5)	108(2)
N(5)	6154(3)	1384(2)	151(4)	59(1)
N(6)	5624(4)	1377(2)	1049(4)	74(2)
N(7)	5025(4)	2051(2)	−99(5)	70(2)
N(8)	4453(4)	2488(3)	−587(5)	104(2)
N(9)	7491(4)	519(2)	−1201(4)	53(1)
N(10)	8232(4)	653(2)	−1850(4)	63(1)
N(11)	7219(4)	5(2)	−2613(4)	67(1)
N(12)	6754(5)	−373(3)	−3369(5)	114(2)
N(13)	7505(3)	327(2)	1372(4)	58(1)
N(14)	7567(5)	−245(2)	1128(5)	84(2)
N(15)	7475(4)	−140(3)	2832(4)	73(2)
N(16)	7406(5)	−261(3)	3895(5)	115(2)
O(1)	5056(11)	3469(5)	967(9)	309(7)
O(2)	5242(7)	3832(5)	−570(7)	239(4)
O(3)	4679(9)	4325(6)	721(9)	296(6)
O(4)	6276(7)	4080(6)	878(9)	296(7)
O(5)	8692(9)	8500(5)	6668(7)	268(5)
O(6)	7908(17)	8713(6)	5349(11)	469(14)
O(7)	9176(8)	8262(5)	5136(10)	314(8)
O(8)	7955(10)	7851(5)	5636(12)	328(8)
C(1)	9015(7)	2302(3)	1201(5)	76(2)
C(3)	9367(7)	2917(4)	2825(9)	143(4)
C(4)	9499(5)	1486(3)	565(5)	63(2)
C(5)	10139(5)	1018(3)	171(6)	86(2)
C(6)	10521(7)	615(4)	1005(7)	133(3)
C(7)	4963(5)	1782(4)	876(6)	83(2)
C(8)	4226(7)	1959(5)	1648(8)	150(4)
C(9)	3267(9)	1772(6)	1451(12)	233(7)
C(10)	5797(5)	1778(3)	−505(6)	65(2)
C(11)	6153(6)	1929(3)	−1575(6)	97(2)
C(12)	6667(7)	2504(4)	−1566(8)	145(4)
C(13)	8046(5)	337(3)	−2692(5)	71(2)
C(14)	8651(7)	343(5)	−3644(6)	142(4)
C(15)	9690(7)	408(4)	−3431(7)	139(4)
C(16)	6900(5)	135(3)	−1670(5)	61(2)
C(17)	6005(6)	−139(3)	−1236(6)	103(3)
C(18)	5045(7)	165(4)	−1634(8)	147(4)
C(19)	7545(6)	−519(3)	2018(7)	95(2)
C(20)	7662(13)	−1183(5)	2197(10)	207(7)
C(21)	7112(17)	−1468(7)	1959(18)	346(14)
C(22)	7463(4)	384(3)	2401(5)	63(2)
C(23)	7449(5)	938(3)	3019(6)	83(2)
C(24)	8479(6)	1114(3)	3506(6)	111(3)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

1,2,4-triazoles coordinates through N^1 [17–19], this is the first example for a metal ion coordinated by four triazole ligands.

An ORTEP diagram of **2** is shown in Fig. 2 together with the atom labelling scheme. The metal ion is surrounded by two crystallographically independent nitrogen atoms

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{\AA}^2 \times 10^3$) for non-hydrogen atoms of **2**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)[a]
Zn(1)	3442(2)	1225(1)	−233(1)	45(1)
Zn(2)	8445(2)	3774(1)	−235(1)	46(1)
N(1)	5319(14)	1027(6)	−471(8)	68(4)
N(2)	2160(15)	1208(6)	−1118(7)	68(4)
N(3)	2666(12)	767(5)	529(6)	43(3)
N(4)	1261(10)	638(5)	456(6)	41(3)
N(5)	2268(11)	271(5)	1433(5)	39(3)
N(6)	2511(12)	2(5)	2114(6)	70(4)
N(7)	3625(12)	1990(5)	147(6)	42(3)
N(8)	2880(11)	2114(5)	723(6)	48(3)
N(9)	4098(12)	2802(5)	474(7)	44(3)
N(10)	4676(10)	3320(5)	541(7)	72(4)
N(11)	10331(15)	3964(6)	−420(8)	74(5)
N(12)	7134(15)	3781(5)	−1107(7)	62(4)
N(13)	8588(12)	3011(5)	157(6)	42(3)
N(14)	7849(12)	2879(5)	752(6)	49(4)
N(15)	9138(11)	2185(5)	484(6)	41(3)
N(16)	9736(11)	1673(4)	564(5)	54(3)
N(17)	7740(12)	4216(5)	537(6)	42(3)
N(18)	6310(12)	4366(5)	431(6)	48(3)
N(19)	7325(12)	4723(5)	1455(7)	52(3)
N(20)	7569(12)	5007(5)	2104(6)	61(4)
S(1)	7784(5)	1187(2)	−1087(3)	69(2)
S(2)	572(6)	1154(2)	−2466(2)	74(2)
S(3)	12786(5)	3815(2)	−1084(3)	72(2)
S(4)	5573(6)	3850(2)	−2455(2)	73(2)
C(1)	6351(15)	1088(6)	−697(9)	55(5)
C(2)	1475(16)	1199(6)	−1675(10)	61(5)
C(3)	1007(15)	324(6)	983(8)	41(4)
C(4)	−265(14)	52(6)	1114(8)	53(4)
C(5)	−1557(15)	379(7)	858(10)	92(6)
C(6)	3257(14)	557(6)	1136(8)	41(4)
C(7)	4725(15)	627(7)	1475(8)	69(5)
C(8)	4893(18)	1036(7)	2078(10)	116(8)
C(9)	3184(15)	2599(6)	899(8)	51(4)
C(10)	2653(17)	2933(6)	1517(7)	64(5)
C(11)	1890(20)	2632(8)	2025(10)	104(7)
C(12)	4406(14)	2405(6)	0(7)	39(4)
C(13)	5276(16)	2459(6)	−608(9)	62(5)
C(14)	4496(17)	2401(7)	−1347(9)	86(6)
C(15)	11324(17)	3915(7)	−734(8)	56(5)
C(16)	6499(16)	3819(6)	−1674(7)	46(4)
C(17)	8152(15)	2371(6)	947(7)	47(4)
C(18)	7679(18)	2059(7)	1535(10)	93(7)
C(19)	6815(16)	2363(8)	1998(8)	79(6)
C(20)	9320(14)	2581(6)	9(8)	41(4)
C(21)	10256(14)	2531(7)	−584(7)	53(4)
C(22)	9507(16)	2612(7)	−1349(6)	75(6)
C(23)	6117(14)	4660(6)	1007(8)	41(4)
C(24)	4765(14)	4937(6)	1163(8)	53(4)
C(25)	3437(15)	4655(6)	883(8)	61(5)
C(26)	8319(17)	4440(7)	1138(9)	51(4)
C(27)	9765(15)	4380(8)	1469(9)	81(6)
C(28)	9845(18)	3962(8)	2089(9)	103(8)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

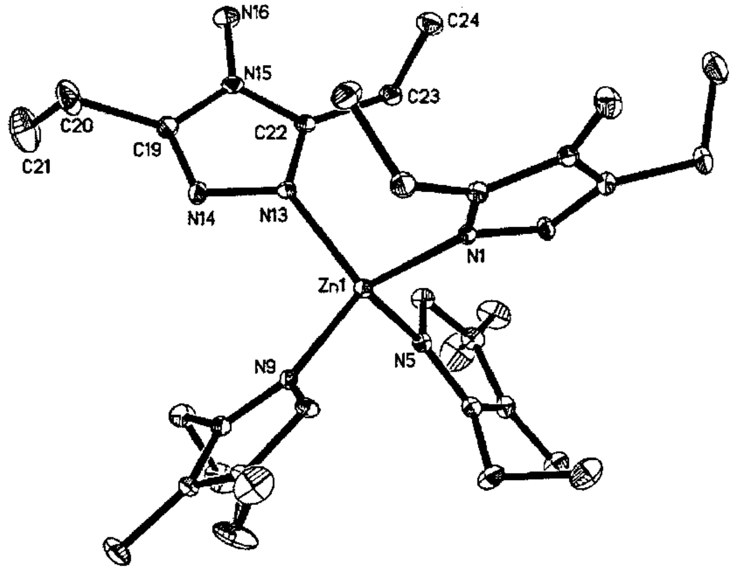

FIGURE 1 ORTEP drawing of $[Zn(deatrz)_4]^{2+}$.

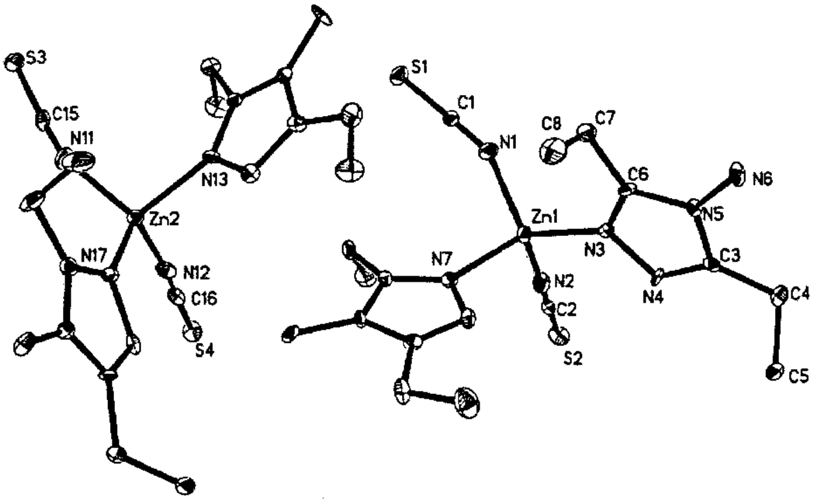

FIGURE 2 ORTEP drawing of $[Zn(deatrz)_2(SCN)_2]$.

belonging to different triazole ligands and two thiocyanate groups. The Zn(II) ion is located on a crystallographic two-fold axis. The coordination sphere of the Zn(II) ion may be described as a distorted tetrahedron, the average Zn–N value being 1.978 Å. SCN groups are N bonded and the Cd–N–C angles are 156.3(14) and 175.1(14)°, respectively. The bond angles around the zinc atom deviate considerably from the value expected for an ideal tetrahedron. Analogously to **1**, complex **2** has similar bond lengths and angles. The nitrogen atoms of two deatrz ligands are connected via hydrogen bonding with a D–A distance of 2.963 Å.

IR spectra of compound **1** shows bands as follows: 3410 br, m, 3304 m, 2958 m, 2050 br, vs, 1653 vs, 1615 vs, 1560 w, 1450 m (B band), 1389 s, 938 m, 780 w, 748 m and 660 w cm^{-1}, in which bands at 3410, 1615 and 1450 cm^{-1} correspond to ν_{NH2}, δ_{NH2} and $\nu_{C=N}$, respectively. Bands at 2050 cm^{-1} are attributed to SCN. IR spectra of compound **2** shows bands at 3396 br, m, 3007 m, 1683 vs, 1594 vs, 1558 w, 1453 m, 1397 s, 1050–1140 s, 962 w, 795 w, and 664 m cm^{-1}, in which bands at 3007, 1594 and 1397 cm^{-1} correspond to ν_{NH}, $\delta_{NH2,\ NH}$ and $\nu_{C=N}$, respectively, Bands at 1050–1140 cm^{-1} are attributed to ClO_4^-. IR spectra are consistent with the crystallographic study.

Excitation and emission spectra of pure **1** and **2** in aqueous solution at the same concentration at room temperature are shown in Fig. 3. Blue fluorescence of both complexes can be observed, with maximum emission wavelength at 408 nm for **1** and 412 nm for **2**. The red shift of the emission from the UV region to the blue region is complicated. Emission from a MLCT (metal-to-ligand charge transfer) excited state is excluded, and may involve an excited state of intraligand origin. It is concluded that the dominant factor here is the bonding of the ligand to the metal ion. Structural data have shown that there is no Zn ··· Zn interaction or π–π stacking in **1** and **2**. The molecules must act as separate units in both complexes. It is noticeable that the luminescence efficiency for **1** is stronger than that for **2**. The reason for this may be due to different numbers of triazole ligands around the zinc(II) ion. The high luminescence efficiency in the blue region as well as the high thermal stability indicates the two complexes may be excellent candidates for stable, blue, fluorescent materials. Efforts to further investigate other luminescent metal complexes containing novel ligands are underway in our laboratory.

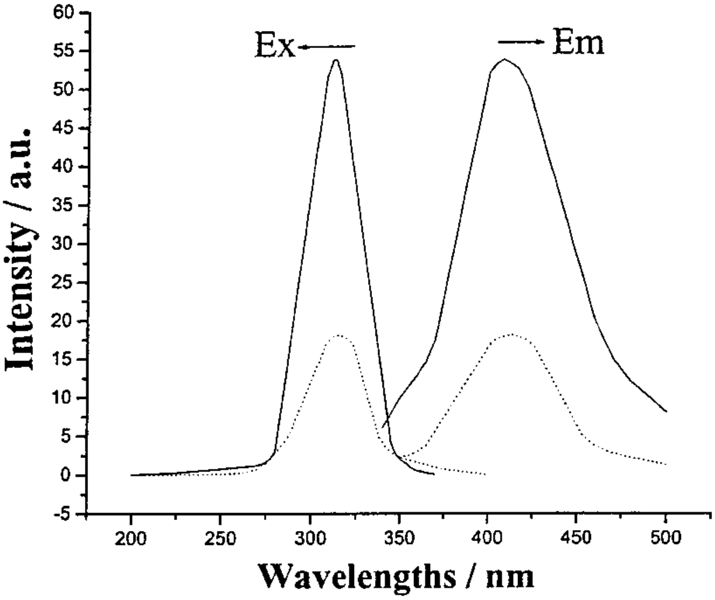

FIGURE 3 The excitation and emission spectra of pure **1** and **2** in aqueous solution at room temperature (**1**, solid line; **2**, dotted line).

Acknowledgements

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Supplementary Data

Full lists of crystallographic data are available from the authors.

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