

The Metal Complex of 2-[2-(4-Cyanophenyl)ethenyl]-8-hydroxyquinoline (2-CEHQ) Ligand: A Novel Trinuclear Zinc(II) Complex with Red Light Emission

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A neutral trinuclear zinc(II) complex containing 2-[2-(4-cyanophenyl)ethenyl]-8-quinolinol (2-CEQH) with strong red light emission was synthesized by hydro(solvo)thermal reaction and its structure was determined by X-ray single crystal diffraction study.

Since the first report of high-efficiency electroluminescence (EL) of a bilayer device using tris(8-hydroxyquinolinato)-aluminum (Alq3) as electron transfer and luminescence material by Tango et al.,¹ much efforts have been made in searching novel metal complexes as EL materials using 8-quinolinol and its derivatives.² Alq3 is a green emitter with peak wavelength around 530 nm. In order to shift the luminescence spectrum of Alq3 to the blue region, a lot of researches have been carried out, for example, introduction of either the electron-releasing substituent at the 2 or 4 position or the electron-withdrawing substituent at the 5 position of the quinoline ligands.³ Meanwhile hydroxyquinoline complexes of all other group 13 elements have also been reported for EL applications.⁴ In those complexes, the emission wavelengths of the Mq3 (M = Al, Ga, In or B) complexes are primarily determined by the covalent nature of the metal–nitrogen bond or the metal–oxygen bond; the weaker the metal–nitrogen or metal–oxygen bonding, the shorter the emission wavelength.^{3a} More recently, Che's group reported a series of blue luminescent zinc(II) complexes with polypyridylamine ligands.⁵ It was pointed out that the emission spectra of these zinc(II) complexes mainly consist of either π - π^* intraligand excited states or π - π aromatic stacking interactions among ligands.^{5a} Our group⁶ also reported a three-dimensional Cd(II) and Zn(II) coordination polymers of which luminescent spectra were assigned to the intraligand emission since weak emission was similarly observed for the free ligand. It is noted that the emission wavelengths of complexes can be tuned by the nature of the ligands such as π - π conjugation and crystal packing. In order to achieve full-color display (red, green and blue), we synthesized a novel 8-quinolinol derivative 2-[2-(4-cyanophenyl)ethenyl]-8-quinolinol and successfully gained its trinuclear Zn(II) complex which exhibits red luminescence. Herein, we report the synthesis, structure and the red luminescent property of $\text{Zn}_3(2\text{-CEQ})_6 \cdot 2\text{H}_2\text{O}$ (2-CEQ=2-[2-(4-cyanophenyl)ethenyl]-8-quinolinolato) **1**.

Complex **1** was synthesized by hydro(solvo)thermal reaction of 2-CEQH ligand with Zn(II) perchlorate in the ethanol/water solution.⁷ The typical procedure is as follows: A heavy-walled Pyrex tube containing a mixture of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1 mmol), 4-CEQH (0.54 g, 2 mmol), ethanol (1.5 mL) and H_2O (0.1 mL) was frozen, sealed under vacuum and placed inside an oven at 110 °C. The yellow prismatic crystals of **1** were harvested after 48 h of heating (0.31 g,

yield: 50%). The presence of uncoordinated cyano groups in **1** was definitely confirmed by an acute peak at 2220 cm^{-1} (CN stretching mode) which is similar to that of the free ligand 2-CEQH (2210 cm^{-1}) in the infrared spectrum. Moreover, there are no strong peaks at about 1100 cm^{-1} , suggesting no perchlorate anions exist in **1**.

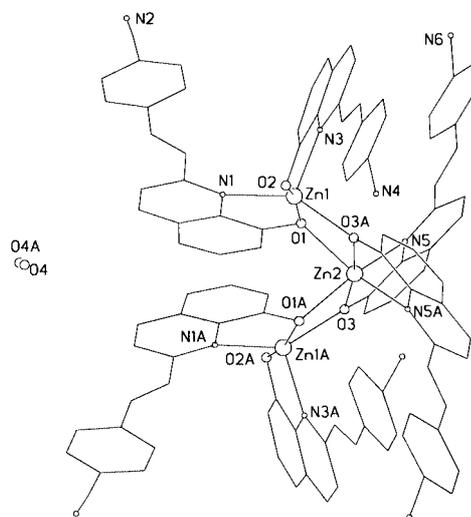


Figure 1. The molecular structure of **1** with labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles(°): Zn1-O1 2.014(2), Zn1-O2 1.980(3), Zn1-O3A 2.160(3), Zn2-O1 2.205(3), Zn2-O3 2.033(2), Zn1-N1 2.222(3), Zn1-N3 2.120(3), Zn2-N5 2.223(3); O2-Zn1-O1 165.53(12), O2-Zn1-N3 82.79(13), O1-Zn1-N3 111.06(12), O2-Zn1-O3A 97.49(11), O1-Zn-O3A 75.44(9), O1-Zn1-N1 79.50(11), N2-Zn1-N1 108.82(12), Zn1-O1-Zn2 104.05(11), Zn1A-O3-Zn2, O1-Zn2-O3A 74.08(9), O3-Zn2-N5 79.05(11), O1-Zn2-O1A 85.88(13),

The trinuclear structure of **1** was revealed by X-ray single crystal diffraction study.⁸ ORTEP drawing of the coordination environment of the Zn(II) center in **1** is shown in Figure 1. The Zn(II) centers have two different coordination environments; the Zn1 and Zn1A centers take five-coordinate distorted trigonal bipyramidal structure in which three different 2-CEQ groups coordinate with Zn(II) ion through two quinolinyl nitrogen atoms, two oxygen atoms of chelating 8-quinolinolato, and one oxygen atom of monodantate 8-quinolinolato while the Zn2 center adopts six-coordinate distorted octahedron structure in which four different 2-CEQ groups bind to Zn(II) ion through two quinoline nitrogen atoms and four oxygen atoms of chelating 8-quinolinolato. Each of two terminal Zn(II) ions (Zn1 and

Zn1A) has a meridional configuration. Two 2-CEQ ligands bridge two Zn(II) ions (Zn1 and Zn2, or Zn1A and Zn2) by their 8-quinolinolato oxygen atoms, resulting in the formation of two four-membered rings in which four atoms of each four-membered ring are almost co-planar (the mean deviation for Zn1, O1, Zn2 and O3A from the plane is 0.0804 Å). The arrangement of three Zn(II) ions is not linear (the angle of Zn1–Zn2–Zn1A is 109.2° and the dihedral angle between two planes of Zn1–O1–Zn2–O3A and Zn1A–O1A–Zn2–O3 is 76.8°), because of the different coordinating environments around three Zn(II) ions. The non-bridging Zn–O distance (1.980 Å) is shorter than that of bridging Zn–O distances (from 2.014 to 2.205 Å). The bond length of Zn1–O1 (2.014(2) Å) is shorter than that of the Zn2–O1 (2.205(3) Å), and the bond length of Zn1–O3A (2.160(3) Å) is longer than that of the Zn2–O3A (2.033(2) Å), which means that the bridging oxygen donor atoms coordinate unequally with both Zn1 and Zn2. Furthermore, O1 and O3A atoms are close to Zn1 and Zn2, respectively. These geometrical features provide distorted octahedral environment around the Zn2 and a distorted trigonal bipyramidal environment around Zn1 or Zn1A.

The most important feature of **1** is that the complex shows strong red light emission in the solid state. The emission of **1**, $\lambda_{\max} = 600$ nm (lifetime $\tau = 2.40$ ns) (shown in Figure 2), is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and can probably be assigned to the intraligand $^1(\pi-\pi^*)$ emission since a similar weak emission (lifetime $\tau = 2.10$ ns) is also observed at $\lambda_{\max} = 570$ nm in the free ligand. It is noteworthy that **1** has a higher emission quantum yield than free ligand in the solid state at room temperature (estimated to be 0.32 vs 0.11). Owing to the red luminescence of **1**, it can be used as an advanced material for red-light emitting diode devices.

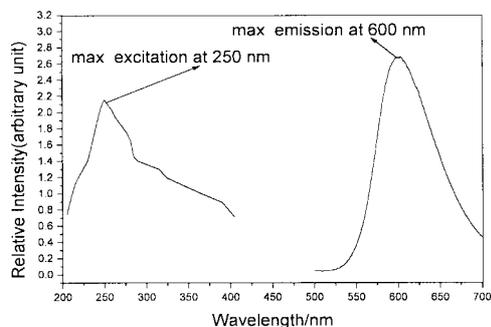


Figure 2. Excitation and emission spectra of compound **1** in the solid state at room temperature.

In conclusion, we have synthesized a novel trinuclear Zn(II) complex with a novel 8-quinolinol derivative, 2-CEQH. This is the first example of any metal complex of 2-CEQH ligand. This new complex exhibits red luminescence spectrum, which is expected to be useful for luminescent device.

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- 7 Physicochemical data for **1**: Anal. Calcd for $C_{108}H_{70}N_{12}O_8Zn_3$: C, 57.45; H, 4.79; N, 6.70%. Found: C, 57.49; H, 4.75; N, 6.77%. IR (KBr, cm^{-1}): 2220(m), 1642(m), 1603(m), 1555(s), 1500(m), 1450(s), 1437(s), 1378(s), 11335(m), 1275(m), 837(m), 742(m).
- 8 Crystal data for **1**: formula = $C_{108}H_{70}N_{12}O_8Zn_3$, fw = 1859.87, monoclinic, space group $C2/c$, $a = 32.8219(9)$, $b = 19.9778(6)$, $c = 15.1486(4)$ Å, $\beta = 116.704(1)^\circ$, $Z = 4$, $V = 8873.6(4)$ Å³, $D_{\text{calcd}} = 1.392$ g cm⁻³, (Mo K α) = 8.47 cm⁻¹, $T = 295(2)$ K, crystal dimensions: $0.17 \times 0.17 \times 0.06$ mm³, 35463 reflections measured ($2\theta_{\text{max}} = 55^\circ$), 10194 ($R_{\text{int}} = 0.090$) used in the refinement, $R_1 = 0.0556$, $wR_2 = 0.109$, GOF = 1.004. Refinement based on F^2 .