

## Electrophosphorescence from Tetrameric Copper (I)-Amide Cluster

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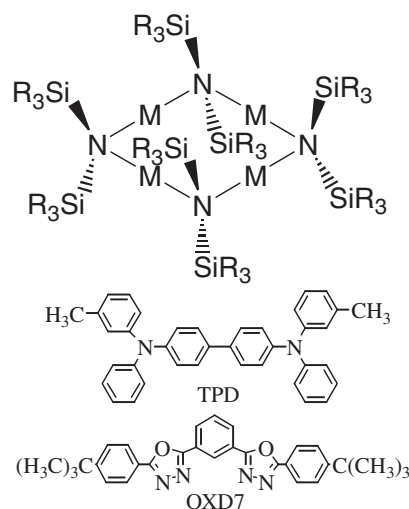
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Green electrophosphorescence from a tetrameric copper (I)-amide cluster  $[\text{CuN}(\text{Si}(\text{CH}_3)_2)_4]$  was successfully observed in the heterostructure device combined with organic carrier transport materials and the copper cluster (peak wavelength = 493 nm, and max. luminance =  $400 \text{ cdm}^{-2}$  at a current density of  $177 \text{ mA cm}^{-2}$  at a drive voltage of 22 V).

In organic electroluminescent (EL) devices, employment of phosphorescent materials is expected to provide very high efficiency of EL. Phosphorescence makes it possible to utilize both singlet and triplet excitons created by recombination of injected electrons and hole, whereas fluorescence is caused mainly from singlet excitons. In 1999, M. A. Baldo and his coworkers have reported that very efficient green electroluminescence was attained in the device using phosphorescent iridium complex as an emissive material.<sup>1</sup> Their electroluminescent (EL) device using the iridium complex exhibited very high external quantum efficiency of 7.5% at a luminance of  $100 \text{ cdm}^{-2}$ , which exceeded the theoretical upper limit of external quantum efficiency of organic EL device using fluorescent material. Their pioneering work demonstrated that development of phosphorescent material was a crucial subject to attain highly efficient organic EL device. At present, research works concerning phosphorescent materials for EL have been performed mainly on heavy metal complexes such as Pt-porphine, Ir-complexes, and so on.<sup>2-5</sup>

In this work, we have focused on a tetrameric metal-amide cluster, whose structural formula is shown in Figure 1, as phosphorescent materials. The metal clusters are a family of organic-inorganic hybrid materials consisting of a tetrameric skeleton formed from nitrogen and heavy metal atoms and organic substituent  $\text{SiR}_3$  bonding to nitrogen atoms. They are expected to exhibit efficient phosphorescence owing to internal heavy atom effect.<sup>6,7</sup> Furthermore, they possess flexibility in emissive material design by replacing metal and organic substituent. For example, one expects to change emissive color by replacing metal (Ag, Sb, Bi, and so on).<sup>8,9</sup> Incorporation of  $\pi$ -conjugated chromophore as organic substituent R may provide the tetrameric cluster carrier-transporting capability. In addition, they have good film processability; one can prepare optically uniform thin films of the metal cluster by using the conventional vacuum-vapor deposition.<sup>6</sup> In this letter, we report electroluminescent properties of organic EL device using a tetrameric copper(I)-amide cluster ( $\text{M} = \text{Cu}$ ,  $\text{R} = \text{CH}_3$ ) with green phosphorescence as the first step for development of electrophosphorescent devices using the tetrameric cluster as emissive layer.

A tetrameric copper cluster ( $\text{M} = \text{Cu}$  and  $\text{R} = \text{CH}_3$ ), which was employed as phosphorescent material, was prepared according to Ref. 6. A solution of  $\text{NaN}(\text{SiMe}_3)_2$  was added dropwise to a



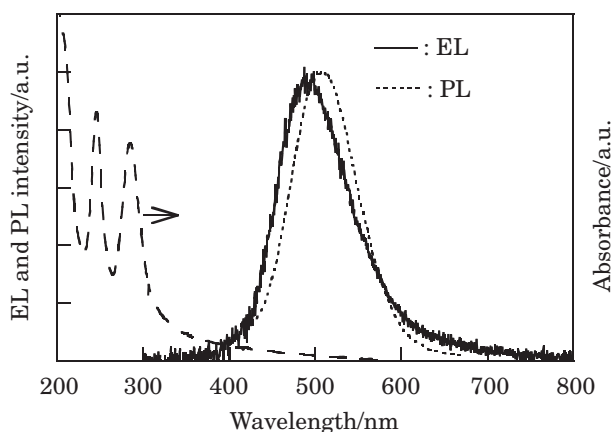
**Figure 1.** Structural formula of tetrameric metal cluster and chemical structures of a diamine derivative TPD and an oxadiazole derivative OXD7.

suspension of  $\text{CuCl}$  in THF, and the mixture was refluxed for 1 hour under  $\text{N}_2$  flow. After evaporation of the mixture, the resulting residue was washed with  $\text{CH}_2\text{Cl}_2$ -pentane (1 : 1 (v/v)). The crude product was purified by the train-sublimation.

Using the copper cluster as emissive material, we prepared the three-layered heterostructure device, Indium-tin-oxide (ITO) anode/a hole-transporting layer of a diamine derivative TPD (45 nm)/the copper cluster layer (20 nm)/an electron-transporting layer of an oxadiazole OXD 7 (45 nm)/ $\text{AlLi}$  cathode, where numerals in parenthesis denote film thickness. The cluster layer, the organic layers and  $\text{AlLi}$  cathode were prepared by a conventional vacuum-deposition at a base-pressure of  $10^{-5}$  Torr.

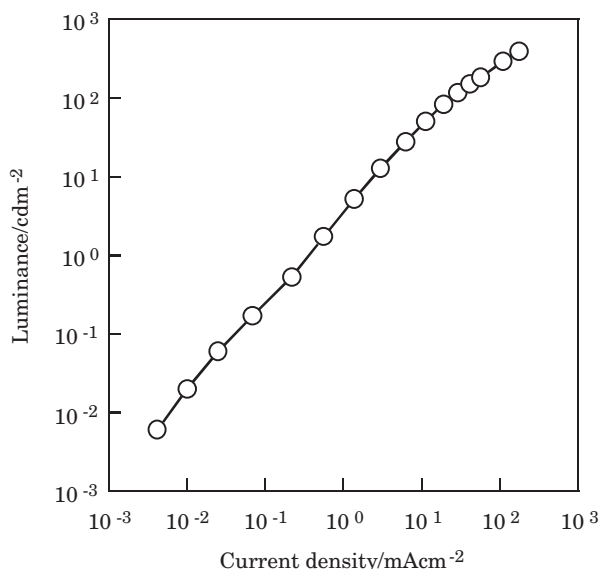
Vacuum-deposited thin films of the tetrameric copper cluster are optically uniform and colorless transparent. Figure 2 shows absorption (broken line) and emission (dotted line) spectra of the copper cluster film. The vacuum-deposited film exhibits sharp absorptions peaking at 246 and 285 nm and green luminescence with a large Stokes shift at 506 nm. The absorption and luminescence bands are in good agreement with those of the copper cluster in  $\text{CH}_2\text{Cl}_2$ .<sup>6</sup> In addition, luminescence life time of the vacuum-deposited film was measured to be  $110 \mu\text{s}$  in vacuum by irradiation of  $\text{N}_2$  laser; the luminescence was proved to be phosphorescence. The observation of absorption and phosphorescence bands demonstrates that the tetrameric copper cluster film with good optical quality was surely formed by a conventional vacuum-deposition.

Solid line in Figure 2 shows electroluminescence spectrum of the heterostructure EL device using the tetrameric copper cluster.



**Figure 2.** Electroluminescent spectrum of heterostructure device consisting of hole-transporting layer of diamine derivative TPD, electron-transporting layer of oxadiazole derivative OXD7 and emissive layer of tetrameric copper cluster  $[\text{CuN}(\text{Si}(\text{CH}_3)_2)_4]$ . Broken and dotted lines shows absorption and photoluminescence spectra of vacuum-deposited film of the tetrameric copper cluster, respectively.

The EL spectrum corresponds well to phosphorescent spectrum of the cluster. It is suggested that recombination of injected carriers, creation of excitons and radiative decay of the excitons occurred within the copper cluster layer owing to the carrier



**Figure 3.** Luminance-current density characteristics of heterostructure device consisting of hole-transporting layer of diamine derivative TPD, electron-transporting layer of oxadiazole derivative OXD7 and emissive layer of tetrameric copper cluster  $[\text{CuN}(\text{Si}(\text{CH}_3)_2)_4]$ .

confinement in the three-layered structure where emissive layer is sandwiched between the organic layers having different carrier-transporting capability.<sup>10</sup>

Figure 3 shows the current density-luminance characteristics of the EL device with the tetrameric copper cluster. The luminance was increased linearly with increasing current density. The luminance reaches  $400 \text{ cdm}^{-2}$  at a current density of  $177 \text{ mA cm}^{-2}$  at a drive voltage of 22 V. The maximum external quantum efficiency was 0.2% at a current density of  $6.2 \text{ mA cm}^{-2}$  at a drive voltage of 15 V. The EL efficiency was a fifth that of a typical organic EL device using tris-(8-hydroxyquinoline) aluminum as an emissive material (about 1%).<sup>11</sup> One reason of the low electrophosphorescence efficiency is probably somewhat low phosphorescence efficiency  $\eta_{\text{phos}}$  of the copper cluster; the  $\eta_{\text{phos}}$  value of the copper cluster in chloroform was estimated to be about 7% by the photoluminescence measurement using quinine sulfate in 0.5 M  $\text{H}_2\text{SO}_4$  as a reference.<sup>12</sup>

In this study, the EL device using the tetrameric copper cluster as an emissive material was demonstrated to exhibit fairly intense electrophosphorescence due to the tetrameric cluster. The result reveals that a family of the tetrameric clusters is one of promising candidates for efficient electrophosphorescent materials. We are now continuing research on the development of efficient electrophosphorescent tetrameric clusters; for example, introducing carrier-transporting chromophore as organic substituent R of the tetrameric clusters, and synthesis of other heavy metal-based clusters ( $\text{M} = \text{Au}, \text{Ag}$ , and so on).

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