Supporting Information for

Chlorinated barium titanate-filled polymer composite with a high dielectric constant and its application to electroluminescent devices

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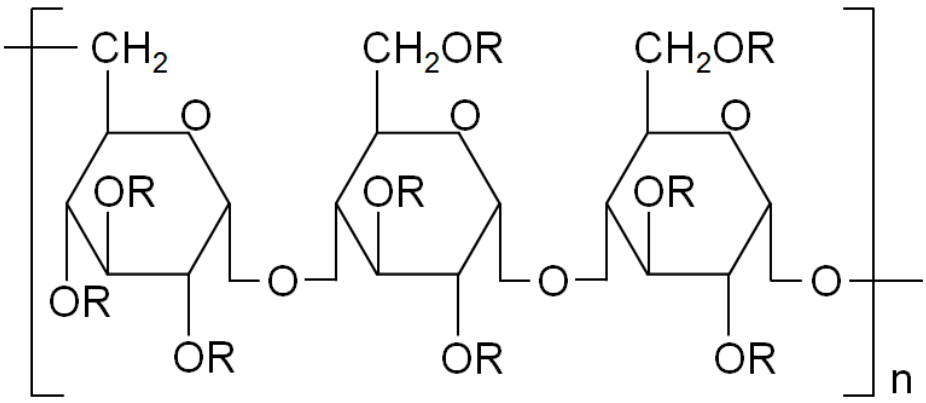
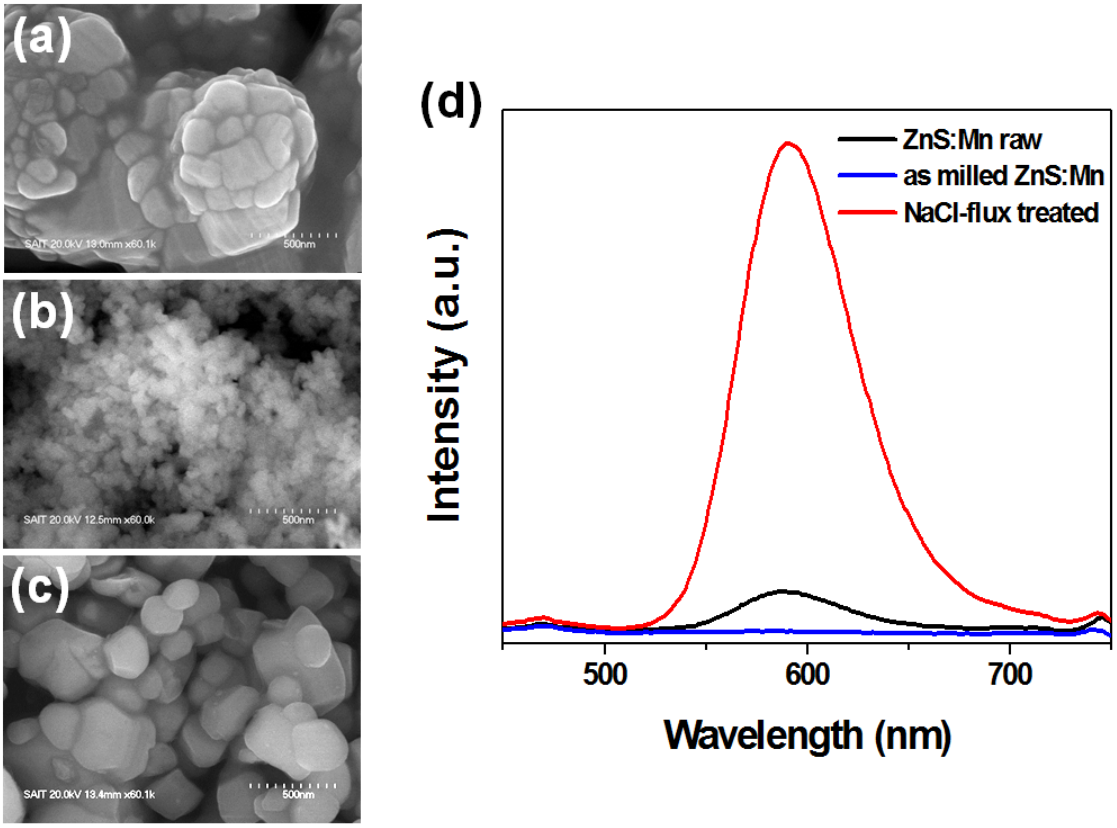
Contents

Chemical structure of the cyanoethyl pullulan polymer (CEP)



R = H or CH_2CH_2CN

Characteristics of the nano-sized ZnS:Mn particles



Nano-sized ZnS:Mn phosphor powders were prepared as following: First, the bulk ZnS:Mn phosphors (Mitsubishi Chemical Corp., MLP-035, Fig. (a)) were treated by beads mill (Ultra apex mill, Kotobuki). After the treatment, ZnS:Mn phosphor powders were pulverized (see Fig. (b)). The pulverized ZnS:Mn particles were treated by NaCl-flux at 700 ^{o}C for 30 min and then it was washed three times with D.I. water (see Fig. (c)). Figure (d) shows PL spectra of raw ZnS:Mn, milled ZnS:Mn, and NaCl-flux treated ZnS:Mn phosphor particles. PL intensity at 590 nm of the nano-sized ZnS:Mn after the NaCl-flux treatment was greatly increased compared to the raw ZnS:Mn.

Characteristics of the inorganic powder electroluminescence

Inorganic powder electroluminescence (EL), which was operated at the frequency ranged in 400 Hz-1 kHz, produces light emission under a high electric field without a thermal generation.[1, 2] Inorganic EL devices consist of the top electrode, dielectric layer, emitting layer, and bottom electrode. In an emitting layer, phosphor powders should be suspended in a dielectric (e.g., polymer), which acts as a binder as well since phosphor powders cannot form a film by themselves.[2] In addition, the polymer can protect the phosphor powder from the humidity and oxygen. The dielectric layer composed of barium titanate powders and polymer is used in an inorganic powder EL device to avoid catastrophic dielectric breakdown. The higher dielectric constant has, the higher EL intensity exhibits.[3-5] In general, the powder EL device can be fabricated on a flexible substrate because all component layers are flexible.[6] The powder EL device can be affected by the polarity of applied voltage since a high luminance is occurred at the inverted polarity due to its mechanism.[1, 2] For this reason, the luminance increases with increasing a frequency.

1. S. Shinoya *et al.*, *Phosphor Handbook* (CRC Press, Boca Raton, 1999).

2 .Y. A. Ono, *Electroluminescent Displays* (World Scientific, Singapore, 1995).

3. J.-Y. Kim *et al.*, *Org. Electron.*, 2011, **12**, 529.

4. J.-Y. Kim *et al.*, *J. Mater. Chem.*, 2012, **22**, 20158.

5. J.-Y. Kim *et al.*, *Org. Electron.*, 2012, **13**, 2959.

6. J.-Y. Kim *et al.*, *IEEE T. Electron Dev.*, 2010, **57**, 1470.

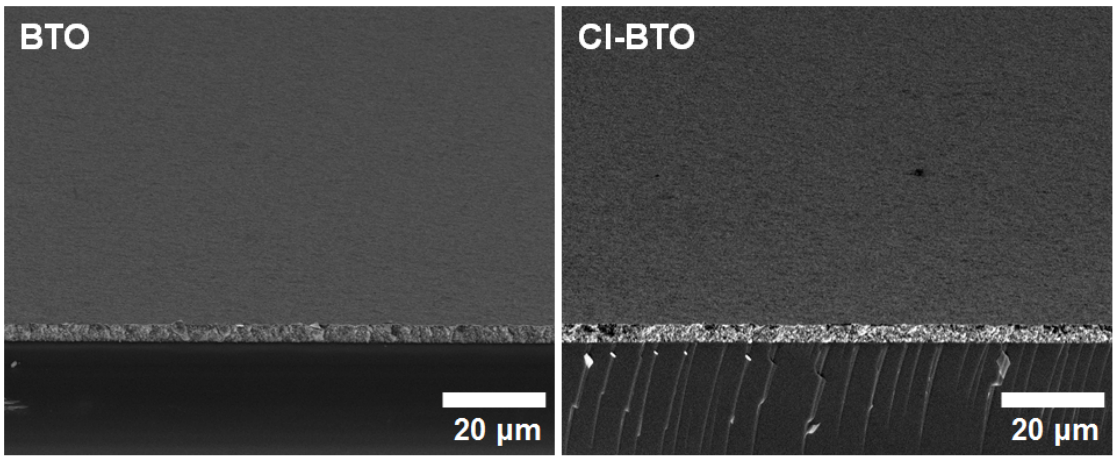


Figure S1. SEM images of the surfaces for composite films with BTO and Cl-BTO.

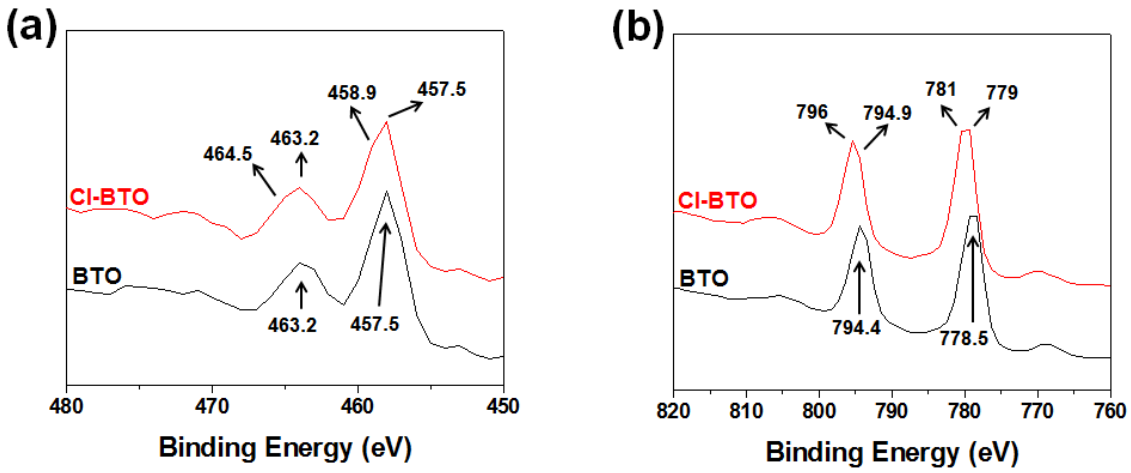


Figure S2. XPS spectra of the BTO particles with and without CF treatment for (a) the Ti-O region ranging from 450 to 480 eV and (b) the Ba-O region ranging from 760 to 820 eV.

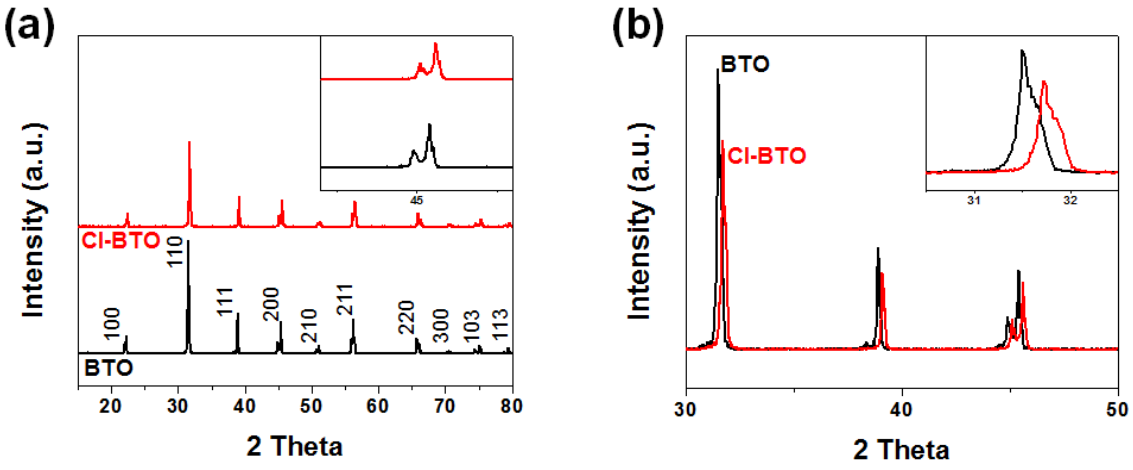


Figure S3. (a) XRD patterns of the BTO particles with and without CF treatment. The inset is the enlarged patterns around 2 theta of 45°. (b) XRD patterns of the BTO and Cl-BTO particles ranging from 30 to 50°. The inset is the enlarged patterns around 2 theta of 31.5 °.

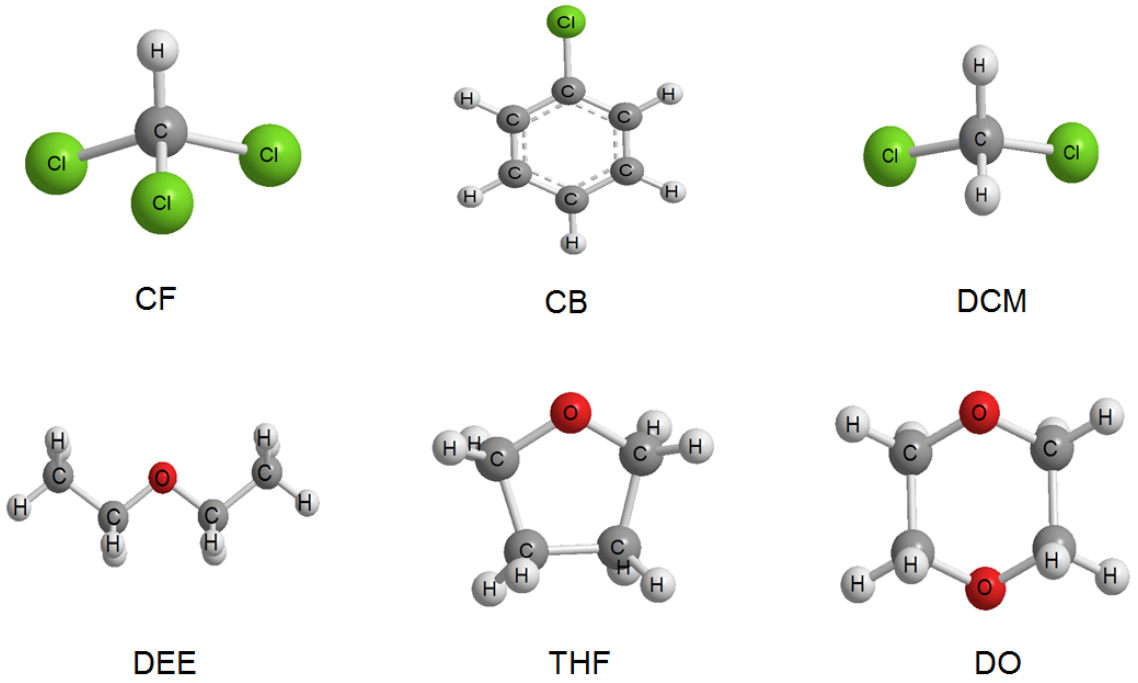


Figure S4. Molecular structures of the chlorinated solvents, i.e., chloroform (CF), chlorobenzene (CB), and dichloromethane (DCM), and non-chlorinated solvents, i.e., diethyl ether (DEE), tetrahydrofuran (THF), and 1,4-dioxane (DO). These structures were taken by digital tool (Cambridge Software, Chemoffice 8.0).

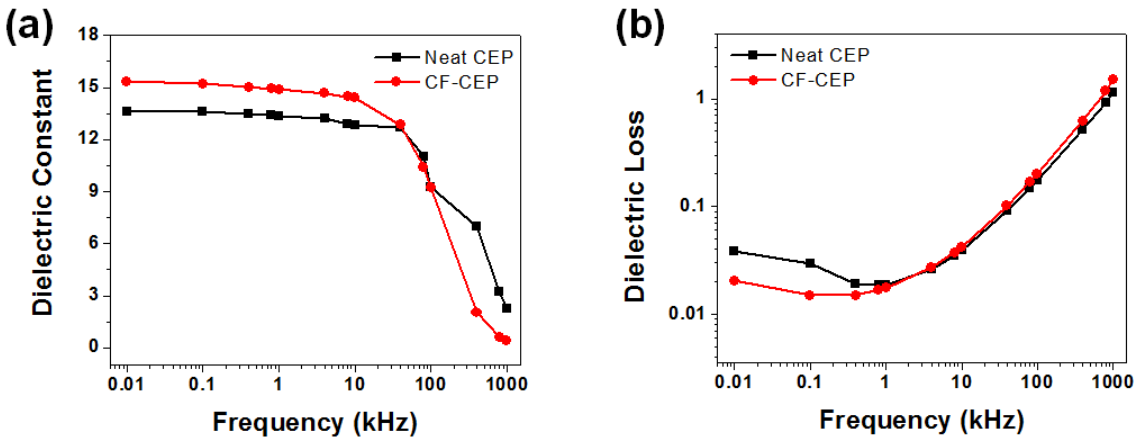


Figure S5. (a) The dielectric constant and (b) dielectric loss of the polymer films with and without CF additive at 0.1 V and various frequencies ranging from 10 Hz to 1 MHz.