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Trinuclear Group 11 Pyrazolate Complexes with Supramolecular Assembly for Phosphorescent Chemosensors of Benzene Vapors

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ABSTRACT

Group 11 metal pyrazolate complexes have generally reported as phosphorescent inorganic compounds with characteristics of emission, color and quantum yield from a weak metal-metal interaction in their supramolecular assemblies. These pyrazolate complexes have been used for the chemical sensors (chemosensors) of organic volatile compounds (VOCs) such as alcohol and benzene derivatives due to their hazardous and carcinogenic effects on human health and environment. Although, trinuclear copper(I) pyrazolate complex **2**(**Cu**) from 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand (**1**) was reported as a phosphorescent chemosensor for the detection of ethanol, there are only limited reports on chemosensors of benzene with low sensing capability even with the same complex or complicated molecular design and expensive precursor. Therefore, by using the same ligand, we highlight sensing capability of pyrazolate complexes using group 11 metal ions for phosphorescent chemosensors of benzene. Upon excitation at 284, the resulting complexes showed emission bands with a peak centered at 616, 473 and 612 nm with characteristics of phosphorescent lifetime in 8.2, 7.8 and 8.9 microseconds and large Stokes shift in 332, 189 and 328 nm for **2**(**Cu**), **2**(**Ag**) and **2**(**Au**), respectively. These emission spectra were in good agreement with their colors from dark green to red-orange upon exposure to a UV lamp with an excitation at 254 nm in dark room. Upon exposure to benzene vapors for 5 minutes, chemosensor **2**(**Cu**) showed the same blue shifting of its emission band from 616 to 572 nm with Stokes shift of 44 nm and emitted bright orange to green as reported previously. However, the shifting of original intensity cannot be easily recovered even with external stimuli. By using the same exposure time, chemosensor **2**(**Ag**) showed quenching phenomenon up to 37% of its original emission intensity with color change from dark green to almost less emissive. Interestingly, original emission intensity of chemosensor **2**(**Au**) was drastically quenched up to 81% with color changes from red-orange to less emissive. Such quenching for chemosensor **2**(**Au**) can recover its original intensity up to 82% without external stimuli. Hence, it is suggested that the benzene vapors will tend to diffuse directly to the shorter Au(I)-Au(I) interaction in chemosensor **2**(**Au**) between two complex molecules so that light-emitting capability from the metallophilic interaction can be significantly decreased. This result indicates that suitable molecular design of ligand and metal ion in pyrazolate complex is important strategy for phosphorescent chemosensors of benzene vapors.

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