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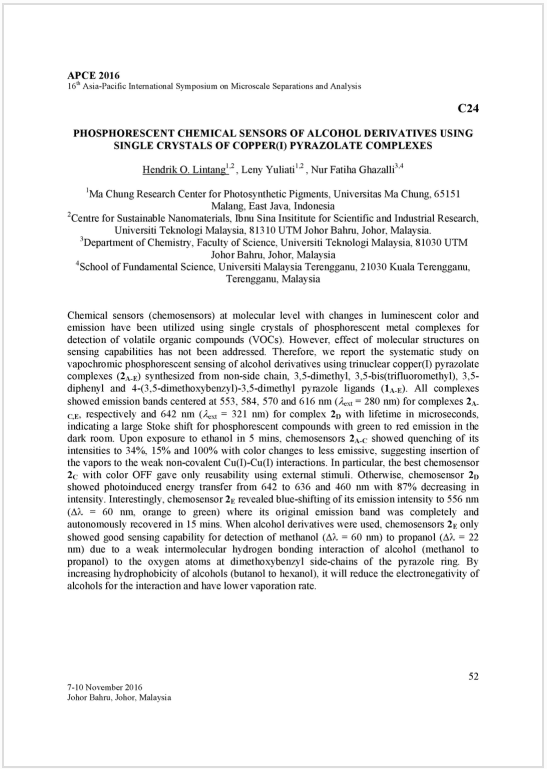

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C24

PHOSPHORESCENT CHEMICAL SENSORS OF ALCOHOL DERIVATIVES USING SINGLE CRYSTALS OF COPPER(I) PYRAZOLATE COMPLEXES

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Chemical sensors (chemosensors) at molecular level with changes in luminescent color and emission have been utilized using single crystals of phosphorescent metal complexes for detection of volatile organic compounds (VOCs). However, effect of molecular structures on sensing capabilities has not been addressed. Therefore, we report the systematic study on vapochromic phosphorescent sensing of alcohol derivatives using trinuclear copper(I) pyrazolate complexes ($\mathbf{2}_{A-E}$) synthesized from non-side chain, 3,5-dimethyl, 3,5-bis(trifluoromethyl), 3,5-diphenyl and 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligands ($\mathbf{1}_{A-E}$). All complexes showed emission bands centered at 553, 584, 570 and 616 nm (λ_{ex} = 280 nm) for complexes $\mathbf{2}_{A-C,E}$, respectively and 642 nm (λ_{ex} = 321 nm) for complex $\mathbf{2}_{D}$ with lifetime in microseconds, indicating a large Stoke shift for phosphorescent compounds with green to red emission in the dark room. Upon exposure to ethanol in 5 mins, chemosensors $\mathbf{2}_{A-C}$ showed quenching of its intensities to 34%, 15% and 100% with color changes to less emissive, suggesting insertion of the vapors to the weak non-covalent Cu(I)-Cu(I) interactions. In particular, the best chemosensor $\mathbf{2}_{C}$ with color OFF gave only reusability using external stimuli. Otherwise, chemosensor $\mathbf{2}_{D}$ showed photoinduced energy transfer from 642 to 636 and 460 nm with 87% decreasing in intensity. Interestingly, chemosensor $\mathbf{2}_{E}$ revealed blue-shifting of its emission intensity to 556 nm ($\Delta\lambda$ = 60 nm, orange to green) where its original emission band was completely and autonomously recovered in 15 mins. When alcohol derivatives were used, chemosensors $\mathbf{2}_{E}$ only showed good sensing capability for detection of methanol ($\Delta\lambda$ = 60 nm) to propanol ($\Delta\lambda$ = 22 nm) due to a weak intermolecular hydrogen bonding interaction of alcohol (methanol to propanol) to the oxygen atoms at dimethoxybenzyl side-chains of the pyrazole ring. By increasing hydrophobicity of alcohols (butanol to hexanol), it will reduce the electronegativity of alcohols for the interaction and have lower vaporation rate.

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