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ABSTRACT

The objective of this research was to synthesise and characterize stable low-temperature ionic copper(II) mixed carboxylates as hybrid heat-light solar-cell materials. Their general formula is $K_n[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})_n(\text{RCOO})_{4-n}]$, where $n = 1-3$, and R = saturated or unsaturated alkyl group.

Two methods were used to prepare these complexes: one-pot and ligand-exchange reactions. The complexes were analysed by CHN elemental analyses, FTIR spectroscopy, UV-vis spectroscopy (solid and solution), TGA, DSC, room-temperature magnetic susceptibility, cyclic voltammetry (CV), and for suitable complexes, by photoluminescence spectroscopy (PL). Crystalline complexes were analysed by single-crystal X-ray crystallography.

The one-pot reaction was successfully used to prepare five ionic dinuclear copper(II) mixed-carboxylates. All complexes were square pyramidal at Cu(II) centre(s). The binding mode of the carboxylate ligand was either *syn-syn* or *syn-anti* bridging and/or chelating. Their optical band gap energy and thermal stabilities range from 2.89 eV to 3.11 eV, and from 175 to 817°C, respectively. All dinuclear complexes were antiferromagnetic and showed quasireversible redox properties.

The ligand-exchange reaction was successfully used to prepare six ionic precursor complexes of general formula $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})(\text{RCOO})_3]$, where R is $\text{CH}_3\text{CH}=\text{CH}$, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$, $(\text{CH}_3)_3\text{C}$, $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)$ and $\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_2)$. These complexes were either tetrahedral or square pyramidal at Cu(II) centre(s). The binding mode of the carboxylate ligand was either *syn-syn* bridging or monodentate and chelating. Their optical band gap energy and thermal stability range from 2.18 eV to 2.63 eV and from 170 to 225°C, respectively. The square

pyramidal complexes were antiferromagnetic, while the tetrahedral complex was ferromagnetic. All complexes showed quasireversible redox properties.

$[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_3]$ was not successfully converted to $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_3]$, using KOH.

Eight of the above complexes showed photoluminescence properties when excited at 267 nm (intraligand $n \rightarrow \pi^*$ electronic transition) or 325 nm (LMCT electronic transition). The chemical formulas of these complexes are:

- $\text{K}[\text{Cu}(\text{CH}_3\text{CH}=\text{CHCOO})(\text{OH})_2(\text{H}_2\text{O})].\text{H}_2\text{O}$
- $\text{K}_2[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})_2(\text{CH}_3\text{CH}=\text{CHCOO})_2(\text{H}_2\text{O})_2]$
- $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_3\text{CH}=\text{CHCOO})_3(\text{CH}_3\text{CH}_2\text{OH})_2]$
- $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_3\text{CH}=\text{CHCOO})_3].2\text{H}_2\text{O}$
- $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_3(\text{CH}_3\text{CH}_2\text{OH})(\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH})]$
- $\text{K}_3[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})_3(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})(\text{CH}_3\text{CH}_2\text{OH})_2].\text{H}_2\text{O}$
- $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})_3(\text{CH}_3\text{CH}=\text{CHCOO})(\text{C}_5\text{H}_5\text{N})].\text{C}_5\text{H}_5\text{N}$
- $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})(\text{CH}_3(\text{CH}_2)_7\text{CH}((\text{CH}_2)_5\text{CH}_3)\text{COO})_3(\text{H}_2\text{O})_2]$

All complexes have an emission peak at about 550 nm, and therefore are potential solar materials as they were able to capture and trap the photonic energy corresponding to MLCT transition.

ABSTRAK

Objektif utama penyelidikan adalah untuk mensintesis dan mencirikan kuprum(II) karboksilat tercampur ionik yang stabil dan bersuhu rendah sebagai bahan sel suria hibrid haba-cahaya. Formula umum kompleks adalah $K_n[Cu_2(p-OC_6H_4COO)_n(RCOO)_{4-n}]$, dengan $n = 1-3$, dan R = kumpulan alkil tepu atau tak tepu.

Dua kaedah digunakan untuk menyediakan kompleks-kompleks tersebut: tindak balas satu pot dan penukaran ligan. Kompleks dianalisis menggunakan analisis unsur CHN, spektroskopi FTIR, spektroskopi UV-vis (pepejal dan larutan), TGA, DSC, kerentanan magnet suhu bilik, voltametri siklik (CV), dan bagi kompleks yang sesuai, spektroskopi berfotopendaflour (PL). Kompleks berhablur dianalisis menggunakan kristalografi sinar-X hablur tunggal.

Tindak balas satu pot berjaya digunakan untuk menyediakan lima kuprum(II) karboksilat tercampur dinuklear ionik. Kesemua kompleks adalah piramid segi empat sama pada pusat Cu(II). Mod pengikatan ligan karboksilat adalah sama ada titian *syn-syn* atau *syn-anti* dan/atau kelat. Tenaga sawar optik dan kestabilan terma adalah dalam julat 2.89 eV hingga 3.11 eV, dan 175 hingga 817°C, masing-masing. Kesemua kompleks dinuklear adalah antiferomagnet dan menunjukkan sifat redoks kuasiberbalik.

Tindak balas penukaran ligan berjaya digunakan untuk menyediakan enam prekursor kompleks ionik berformula umum $[Cu_2(p-HOC_6H_4COO)(RCOO)_3]$, dengan R ialah $CH_3CH=CH$, $CH_3(CH_2)_7CH=CH(CH_2)_7$, $(CH_3)_3C$, $CH_3(CH_2)_3CH(CH_2CH_3)$ dan $CH_3(CH_2)_7CH(CH_2)$. Kompleks-kompleks tersebut adalah sama ada tetrahedron atau piramid segi empat sama pada pusat Cu(II). Mod pengikatan ligan karboksilat adalah sama ada titian *syn-syn* atau monodentat dan kelat. Tenaga sawar optik dan kestabilan terma adalah dalam julat 2.18 eV hingga 2.63 eV, dan 170 hingga 225°C, masing-

masing. Kompleks piramid segi empat sama adalah antiferomagnet, manakala kompleks tetrahedron adalah feromagnet. Semua kompleks menunjukkan sifat redoks kuasiberbalik.

$[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_3]$ tidak berjaya ditukarkan kepada $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO})_3]$, dengan menggunakan KOH.

Lapan daripada kompleks-kompleks di atas menunjukkan sifat berfotopendarflour apabila diuja pada 267 nm (peralihan elektron intraligan $\pi\text{-}\pi^*$) atau pada 325 nm (peralihan elektron LMCT). Formula kimia kompleks-kompleks tersebut adalah:

- $\text{K}[\text{Cu}(\text{CH}_3\text{CH}=\text{CHCOO})(\text{OH})_2(\text{H}_2\text{O})].\text{H}_2\text{O}$
- $\text{K}_2[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})_2(\text{CH}_3\text{CH}=\text{CHCOO})_2(\text{H}_2\text{O})_2]$
- $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_3\text{CH}=\text{CHCOO})_3(\text{CH}_3\text{CH}_2\text{OH})_2]$
- $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_3\text{CH}=\text{CHCOO})_3].2\text{H}_2\text{O}$
- $\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_3(\text{CH}_3\text{CH}_2\text{OH})(\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH})]$
- $\text{K}_3[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})_3(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})(\text{CH}_3\text{CH}_2\text{OH})_2].\text{H}_2\text{O}$
- $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})_3(\text{CH}_3\text{CH}=\text{CHCOO})(\text{C}_5\text{H}_5\text{N})].\text{C}_5\text{H}_5\text{N}$
- $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})(\text{CH}_3(\text{CH}_2)_7\text{CH}((\text{CH}_2)_5\text{CH}_3)\text{COO})_3(\text{H}_2\text{O})_2]$

Kesemua kompleks mempunyai satu puncak pemancaran pada sekitar 550 nm, dan dengan itu adalah berpotensi sebagai bahan suria kerana boleh menyerap dan menyimpan tenaga foton yang sepadan dengan peralihan MLCT.