Publication

A counterion study of a series of [Cu(PˆP)(NˆN)][A] compounds with bis(phosphane) and 6-methyl and 6,6'-dimethyl-substituted 2,2'-bipyridine ligands for light-emitting electrochemical cells

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The syntheses and characterisations of a series of heteroleptic copper(i) compounds [Cu(POP)(Mebpy)][A], [Cu(POP)(Me(2)bpy)][A], [Cu(xantphos)(Mebpy)][A] and [Cu(xantphos)(Me(2)bpy)][A] in which [A](-) is [BF4](-), [PF6](-), [BPh4](-) and [BAr4F](-) (Mebpy = 6-methyl-2,2 '-bipyridine, Me(2)bpy = 6,6 '-dimethyl-2,2 '-bipyridine, POP = oxydi(2,1-phenylene)bis(diphenylphosphane), xantphos = (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphane), [BAr4F](-) = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) are reported. Nine of the compounds have been characterised by single crystal X-ray crystallography, and the consequences of the different anions on the packing interactions in the solid state are discussed. The effects of the counterion on the photophysical properties of [Cu(POP)(N<ˆ>N)][A] and [Cu(xantphos)(N<ˆ>N)][A] (N<ˆ>N = Mebpy and Me(2)bpy) have been investigated. In the solid-state emission spectra, the highest energy emission maxima are for [Cu(xantphos)(Mebpy)][BPh4] and [Cu(xantphos)(Me(2)bpy)][BPh4] (lambda emmax = 520 nm) whereas the lowest energy lambda emmax values occur for [Cu(POP)(Mebpy)][PF6] and [Cu(POP)(Mebpy)][BPh4] (565 nm and 563 nm, respectively). Photoluminescence quantum yields (PLQYs) are noticeably affected by the counterion; in the [Cu(xantphos)(Me(2)bpy)][A] series, solid-state PLQY values decrease from 62% for [PF6](-), to 44%, 35% and 27% for [BF4](-), [BPh4](-) and [BAr4F](-), respectively. This latter series of compounds was used as active electroluminescent materials on light-emitting electrochemical cells (LECs). The luminophores were mixed with ionic liquids (ILs) [EMIM][A] ([EMIM](+) = [1-ethyl-3-methylimidazolium](+)) containing the same or different counterions than the copper(i) complex. LECs containing [Cu(xantphos)(Me(2)bpy)][BPh4] and [Cu(xantphos)(Me(2)bpy)][BAr4F] failed to turn on under the LEC operating conditions, whereas those with the smaller [PF6](-) or [BF4](-) counterions had rapid turn-on times and exhibited maximum luminances of 173 and 137 cd m(-2) and current efficiencies of 3.5 and 2.6 cd A(-1), respectively, when the IL contained the same counterion as the luminophore. Mixing the counterions ([PF6](-) and [BF4](-)) of the active complex and the IL led to a reduction in all the figures of merit of the LECs.
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