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Assembling model tris(bipyridine)ruthenium(II) photosensitizers into ordered monolayers in the presence of the polyoxometallate anion [Co4(H2O)2(α-PW9O34)2]10−

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The complexes cis-[Ru(1)2Cl2] and [Ru(1)2(bpy)][PF6]2 in which 1 is dioctadecyl (2,2′′-bipyridine)-4,4′′-dicarboxylate have been synthesized and fully characterized; the single crystal structures of the syn,syn- and anti,anti-conformers of 1 have been determined. Pressure–area isotherms for monolayers of cis-[Ru(1)2Cl2] on water, aqueous Co4POM (Co4POM = K10[Co4(H2O)2(α-PW9O34)2]) or aqueous KCl subphases exhibit collapse pressures of 25–27 mN m−1 and mean molecular areas of 220 ś 10 Å2. The similarities between these isotherms confirm that there are no significant interactions between neutral cis-[Ru(1)2Cl2] and the anionic Co4POM cluster as the monolayer is formed. In contrast, use of the cationic [Ru(1)2(bpy)]2+ complex results in higher collapse pressures on pure water (54 mN m−1) or aqueous KPF6 (48 mN m−1) subphases, but a collapse pressure of only 17 mN m−1 on an aqueous Co4POM subphase. The data are consistent with the monolayer forming at the air–Co4POM interface being significantly less stable than that at the air–water interface, and point to substantial electrostatic interactions between [Ru(1)2(bpy)]2+ and the anionic Co4POM which can lead to a reduction in the integrity of the film. The introduction of DODA (DODA = dimethyldioctyldecylammonium bromide) stabilizes the monolayers on aqueous Co4POM; mole ratios of [Ru(1)2(bpy)][PF6]2–DODA of 1 : 5 and 1 : 20 lead to collapse pressures of 41 and 53 nM m−1, respectively. Brewster angle microscopy has been used to image the monolayers and to monitor the effects of the presence of DODA. Langmuir–Blodgett (LB) films of cis-[Ru(1)2Cl2] and [Ru(1)2(bpy)][PF6]2 with and without Co4POM have been produced on mica substrates. Atomic force microscopy reveals that LB films formed in a single dipping cycle of cis-[Ru(1)2Cl2] from a water subphase are distinct from those formed on aqueous Co4POM. The former consists of islands of height ≈3, 6 or 9 nm; these values compare with a modelled molecular diameter of cis-[Ru(1)2Cl2] of ≈3 nm and are consistent with the formation of mono-, bi-, or trilayers of cis-[Ru(1)2Cl2]. In contrast, LB films formed from cis-[Ru(1)2Cl2] on aqueous Co4POM consist of small aggregates of variable height. LB films formed from [Ru(1)2(bpy)][PF6]2 on aqueous subphase exhibit small aggregates but there is a very low surface coverage of the complex on mica (2 domains per μm2); the coverage increases (18 domains per μm2) when the films are formed in the presence of Co4POM but is significantly lower than for cis-[Ru(1)2Cl2] (75 domains per μm2). No significant difference in the morphology of the LB films containing [Ru(1)2(bpy)][PF6]2 is observed in the presence of DODA.

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