Base or No Base? Evaluating DSCs' Performance with Asymmetric Copper Redox Mediators and the Essential Role of a Lewis Base Additive

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Dye-sensitized solar cells (DSCs) utilizing copper-based redox mediators have demonstrated superior performance compared to traditional iodine and cobalt systems, especially under low light conditions. This is primarily due to their low reorganization energy yielding efficient dye regeneration with a small driving force and thus assisting in gaining a high open-circuit voltage. However, until now, most of the high-performing copper-based electrolytes have required the presence of a Lewis base additive to achieve efficient DSCs. In this study, we report for the first time a functioning Lewis-base-free DSC with an asymmetric copper-based electrolyte system. This approach provided us with a lone electrolyte system needed to assess the necessity and influence of the Lewis base N-methylbenzimidazole (NMBI) in DSCs. This was accomplished by the design of the ligand L1 that features an NMBI moiety directly connected to 2,2′-dipyridyl. The ligand L1 was used to prepare two Cu(II) complexes, CuII(dmby)(L1)+2 and CuII(L1)2+2, that were used with CuI(dmby)2+1 for the formulation of asymmetric redox mediators. The electrolyte containing CuII(L1)2+2 and CuI(dmby)2+1 demonstrated a power conversion efficiency (PCE%) of 0.27% in the absence of any Lewis base additive, marking the first instance of measurable photocurrent generation in a DSC with panchromatic organic dyes and copper-based electrolyte system. This enabled us to study the exact effect of NMBI's presence on dye regeneration, electron recombination, and electrochemical performance by various spectroscopic means. In the presence of NMBI, performance was significantly enhanced, with the best-performing device incorporating CuII(dmby)(L1)+2 and CuI(dmby)2+1, achieving a PCE% of 21.6% under 1000 lx light power. Stability tests over 35 days under ambient light conditions showed that the latter DSC retained 92% of its initial efficiency. Our findings offer crucial insights into the fundamental role of NMBI in passivating the TiO2 surface and mitigating electron recombination processes in copper-based DSCs, in addition to ligand design strategies for optimizing asymmetric copper-based redox mediators.