Hybrid Polymer-Inorganic Solar Cells and Light-Emitting Diodes with Polyoxometalates as Dual-Function Optical Spacer and Electron Injection Layers

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Introduction
Air stable polymer electronic devices such as photovoltaics (PVs) and light-emitting diodes (PLEDs) usually require the use of high workfunction metal cathodes. However, high workfunction metals such as Al limit electron injection in PLEDs resulting in lower electroluminescence (EL) quantum efficiency. In PVs, optical interference effects at the highly reflective Al cathode may also limit charge photogeneration due to the reduced optical-electric field near the electrode. Here, we report that polyoxometalates (POMs) that represent a family of water soluble inorganic molecular oxides can be deposited as thin overlayers between the active layer and the Al cathode to fabricate air-stable hybrid polymer-inorganic PLEDs and PVs resulting in a significantly improved device performance.

Experimental Details Multilayer PLEDs and bulk-heterojunction PVs were fabricated on indium-tin-oxide (ITO) coated glass substrates with a PEDOT-PSS hole injecting layer. The active emissive or photoactive layer was either a polyfluorene based light-emitting polymer or a donor/acceptor regioregular poly(3-hexylthiophene):PCBM blend (1:1 wt.%) heterostructure where PCBM is a fullerene derivative, namely (6,6)-phenyl-C_{70}-butyric acid methyl ester. Next, a thin tungstate polyoxometalate layer such as $H_3PW_{12}O_{40}$ or $(NH_4)_6P_2W_{18}O_{62}$ was deposited from an orthogonal solvent between the active layer and the Al cathode in order to avoid dissolution of the active underlayer. Devices were characterized in air with a combination of absorption, PV quantum efficiency, electroluminescence (EL) spectra and (photo)current density-voltage-luminance (J-V-L) characteristics.

Results and Discussion
Insertion of the solution-processed polyoxometalate layer between the active layer and the Al cathode resulted in lower operating voltage and higher EL quantum efficiencies in polyfluorene PLEDs. It also increased the generated photocurrent and the corresponding PV power conversion efficiency by a factor of up to 1.5. The enhanced PLED performance is attributed to the improved electron injection and transport at the Al/POM interface (as a result of the more favorable energetic level alignment) that results in improved charge balance and more efficient charge recombination. In PVs, the enhanced photoactive layer absorption and spatial light redistribution in the bulk, supported by an increased photogenerated current and verified by detailed optical simulations of the field strength inside the device, leads to an improved PV efficiency. Moreover, the exciton blocking ability of POMs as a result of their large bandgap is also thought to contribute to reduced exciton losses at the Al/POM interface and improve the PV photocurrent.

Conclusions We demonstrate improved performance hybrid polymer-inorganic LEDs and PVs based on a multilayer device structure employing an active polymer layer as the emitting or the photoactive layer and a solution-processed polyoxometalate compound overlayer. The lower operating voltage and higher EL quantum efficiency in PLEDs is attributed to the improved electron injection from the Al cathode. The increased PV efficiency is shown to occur as a result of the spatial redistribution of light in the PV and the POM layer acting as an efficient optical spacer/exciton blocking layer.