Redox active chromophore in oriented metal-organic thin films: Effect of structural modulation on host-guest charge transfer interactions

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Metal-organic structures with periodic arrangement of chromophoric linkers provide a useful platform to study the photophysics of organic chromophores. Particularly, strong π-stacking arrangement, charge transfer (CT), energy transfer, photon upconversion, photovoltaic effect etc have been evidenced in crystalline metal-organic structures.[1-3] Through space CT interactions are very interesting in the context of electrical conductivity.[4] Metal-organic frameworks, known to be an insulator or poor conductor can become an efficient conductor by imposing CT characteristics.[5] Charge transfer crystals are already well-known as conducting material. Although this approach is effective, not much study has been devoted to such systems.

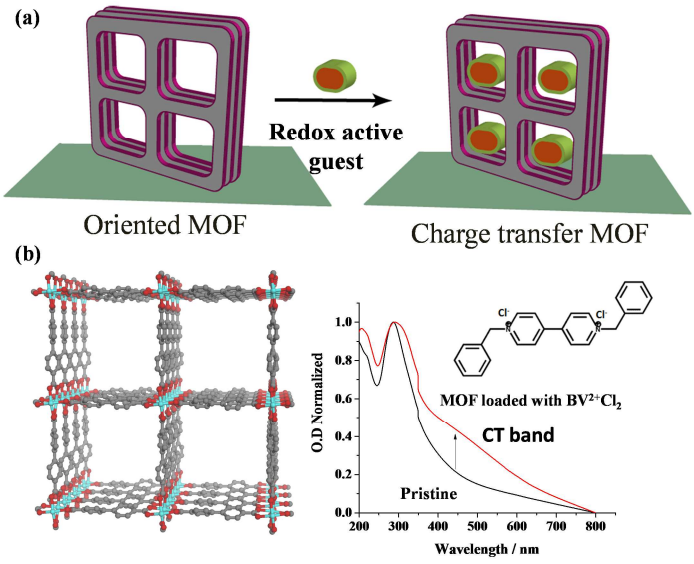

Figure 1. (a) Schematic of the redox active guest inclusion in oriented crystalline SURMOF. (b) Pristine $Cu_2(bpdc)_2(bpy)$ SURMOF grown along (001) direction (left); Appearance of CT band ~ 450-500 nm after inclusion of guest in $Cu_2(bpdc)_2(bpy)$.

Here, we have taken a strategic approach to study host-guest CT interactions in metal-organic structures and their impact in electrical conductivity. As a host system, we have fabricated three surface mounted metal-organic frameworks (SURMOFs) as thin films with a specific orientation with biphenyl dicarboxylate (bpdc) linker; $Cu_2(bpdc)_2$ (**1**),

$Cu_2(bpdc)_2(dabco)$ (**2**) and $Cu_2(bpdc)_2(bpy)$ (**3**). The 2D square-grid like layers formed by Cu-paddlewheel and bpdc remain similar in all three structures, however the distance between the layers increases from **1** to **3**. All three structures are nanoporous and hence easily encapsulate benzyl viologen dichloride ($BV^{2+}Cl_2$), a well-known redox active acceptor molecule as guest. Inclusion of $BV^{2+}Cl_2$ in the host frameworks induces strong CT interaction between BPDC and guest molecule, revealed by strong absorption in the visible range of absorbance spectra. To further investigate the effect of host structure on the CT formation transient absorption studies are carried out. Such CT characteristics are also correlated with electrical conductivity measurements.

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