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Surface Supported Metal Organic Thin Film Materials Based Heterojunctions for Triplet Triplet Annihilation Upconversion - Shargeel Ahmad – Dalian University of Technology

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Introduction:
It's very important to find the new materials for solar energy conversion technologies which would help us to save energy for future generation. Harnessing the idea of triplet triplet annihilation upconversion (TTA UC) requires a smart hybrid material overcoming required distance for smooth and efficient triplet energy transfer(TEnT). However, the TTA UC process is the one of the best wavelength shift methodology in which the two low energy photons (hu1) having high wavelength are absorbed and transformed into one high energy photons (hu2) with low wavelength via Dexter type energy transfer mechanism. In our previous demonstration we have reported the triplet energy transfer between PtOEP (PtOEP = Pt(II) octaethylporphine) as sensitizer and Zn-perylene SURMOF as acceptor in acetonitrile solution[5] by making solid liquid interface and surface modifications. Here we will put a novel idea of suing solid-solid interface by making SURMOF-SURMOF heterojunction to study TTA UC.
The TTA UC has been studied using variety of materials to enhance the contemporary demands of solar energy. Moreover, notable efforts has been made to utilize the modern surface-anchored metal-organic frameworks (SURMOFs) materials in gas separation,electronics, CO2 reduction, water splitting, photovoltaic, and most recently in TTA-UC system due to its controlled growth orientation, tunable pore size and highest crystallinity.Moreover, previous studies showed that the random orientation of photosensitizer which was dissolved in the solution could also hinder the transfer of triplet energy in the photoelectrochemical cell.

Experimental Strategies:
Preparation of substrates
The quartz glass / FTO glass (SOLARONIX, Switzerland) substrates were cleaned in acetone for approximately ten minutes in an ultrasonic bath then these are treated with plasma under O2 for nearly thirty minutes to generate a surface with -OH (hydroxyl groups).These cleaned substrates were used instantaneously to grow SURMOF.

Preparation of Zn-perylene SURMOF
Liquid phase epitaxy technique is used for the preparation of the Zn-Perylene SURMOFs on top of FTO /Quartz Glass substrates. We prepared a concentration zinc acetate ethanolic solution (1 mM). On top of cleaned FTO we sprayed it for 5s. After 30s wait, 3,9 perylene dicarboxylic acid ethanolic solution was sprayed (concentration:20-40M; spray time: 20 s, waiting time: 30 s). This alternate spray process of Zn-acetate as metal linker and 3,9 perylene dicarboxylic acid as organic linker supported the formation of highly crystalline metal organic framework thin film and more detail can be found somewhere in the literature.

Preparation of Zn-porphyrin SURMOF and Its Heterojunction
SURMOF of Zn (II) metalloporphyrin were fabricated using well established highly throughput automated spray system Briefly, a concentration of 20 mM Zn(II)metalloporphyrins in ethanol (spray time: 25s, waiting time: 35s) and a concentration of 1 mM zinc acetate in ethanol (spray time: 15 s, waiting time: 35 s) were one by one sprayed onto the FTO / Quartz Glass substrates in a layer-by-layer fashion using N2 as a carrier gas (0.2 mbar). In between, pure ethanol was used for rinsing to get rid of the unreacted species from the surface (rinsing time: 5 s). The thickness of the sample was controlled by the number of deposition cycles. Moreover, the SURMOF-SURMOF heterojunction was formed by firstly growing the 20 cycles of Zn-perylene SURMOF and on top of it 20 more cycles of Zn (II) metalloporphyrin SURMOF was added to make heterojunctions. Moreover, the formation of heterojunction which is described in the literature.

Triplet-triplet annihilation upconversion (TTA UC) setup
First of all, 40 mg/ml PMMA (poly methyl (methacrylate) was prepared in the acetonitrile solution. Then as prepared MOF thin film material consisting of FTO/Quartz Glass-Zn-perylene SURMOF+Zn-porphyrin SURMOF were immersed into the well mixed acetonitrile solution of PMMA which was degassed with N2 for half an hour. The heterostructure was characterized for triplet triplet annihilation upconversion using laser light source.

Results and Discussions
Comparative analysis of the ultraviolet-visible (UV-vis) spectrum of Zn-perylene SURMOF, Zn-porphysin SURMOF and Zn-perylene-Zn-porphyrin heterojunction is being shown in Figure 3. The UV¬-vis spectrum of Zn-perylene alone SURMOF range from 358 nm to 470nm (in brown) which is also compared with the solution of free perylene dicarboxylic[11] acids indicating a blue shift in MOF thin film sample. The UV-vis of Zn-porphyrin shows a Sorret Band at

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440nm and two Q bands between 530 nm to 614 nm. The Zn (II) tetraphenylpophyrin molecule shows two Q bands which are different from free base porphyrin generating four Q bands because Zinc+2 ion coordination with porphyrin molecule changes the symmetry of the former molecule The combined UV vis of Zn-perylene SURMOF and Zn-porphyrin SURMOF heterostructure overlaps with all the bands of both MOF thin films shown in figure 3(red).The merging of all the bands in SURMOF heterostructure is very important for efficient absorption of green light and its conversion into blue light.

Conclusion & Significance: The MOF thin film based smart and hybrid materials can be used for enhanced energy conversion triplet triplet annihilation upconversion. The studied hybrid material can be used for the future energy conversion devices. The point of view is that a prototype dye sensitized solar cell device can be fabricated with highly crystalline MOF thin film. Moreover, it has been demonstrated that the photocurrent can be significantly enhanced by overcoming the longer distance which finally may overcome Shockley–Queisserlimit.