QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

Cooperative Binary Ionic Biomorphs and their Metal Nanocomposites

U.S. DEPARTMENT OF ENERGY

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CBI donor-acceptor biomorph

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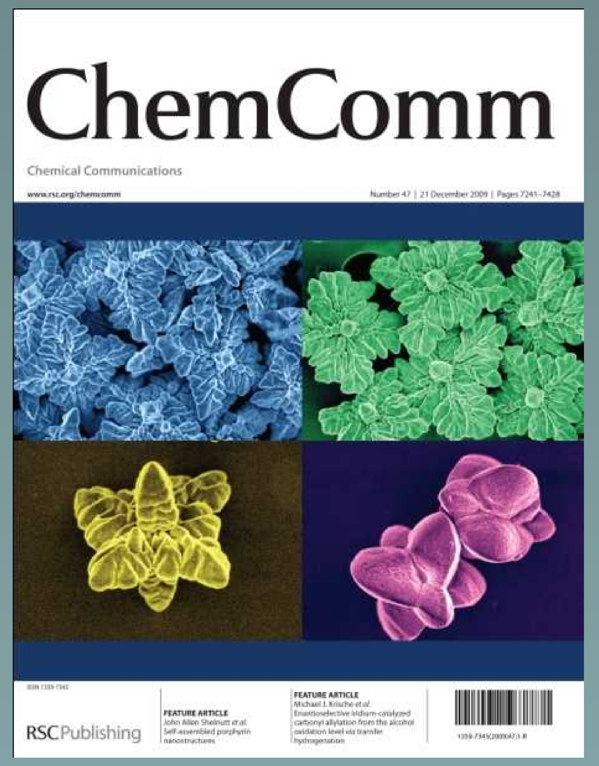
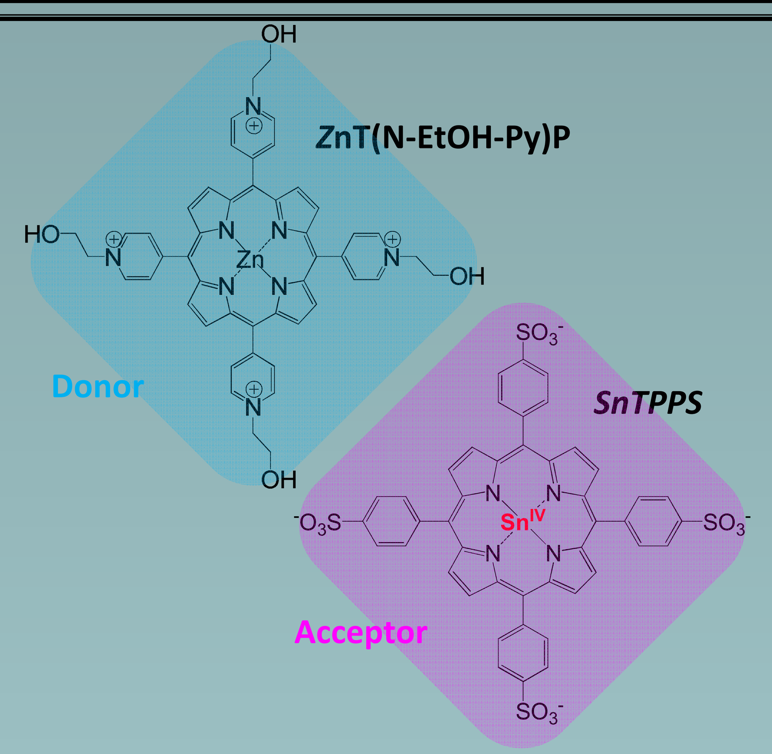
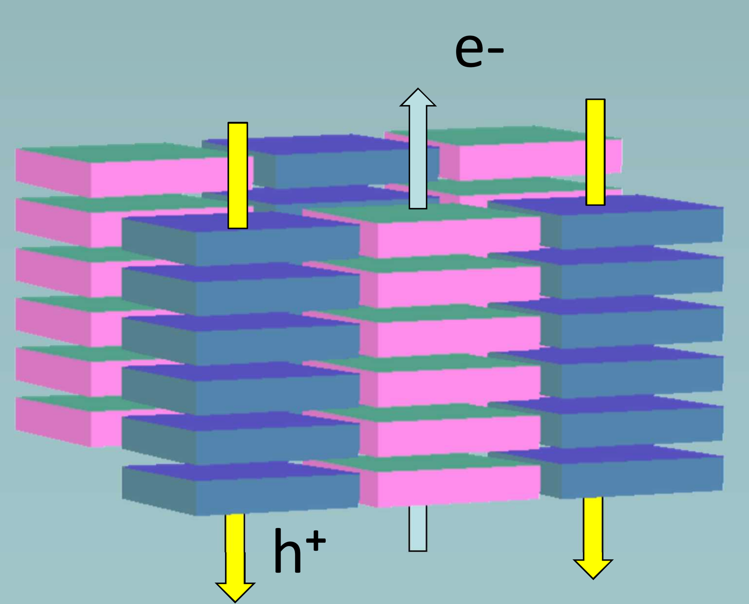
- **Background & Significance**: New composite solids that integrate complementary molecules at the nanometer scale are needed for solar energy technologies, sensors, and optoelectronics.
- **Research goals**: Use ionic self-assembly to produce *cooperative binary ionic (CBI) solids*, a new type of material with tunable collective properties, by combining molecular anions and cations that have aromatic cores with tunable characteristics (*e.g.,* donor or acceptor electronic properties).
- **Major results**: Biomorphs self-assembled from porphyrin electron donors and acceptors are photoconducting ; donor/acceptor –catalyst biomorphs have also been synthesized.
- **Significance**: The synthesis of a new type of nanomaterial with tunable function is demonstrated.



Research Description

Combine a cationic porphyrin electron donor with an anionic porphyrin electronic acceptor to produce a binary charge-transfer solid.



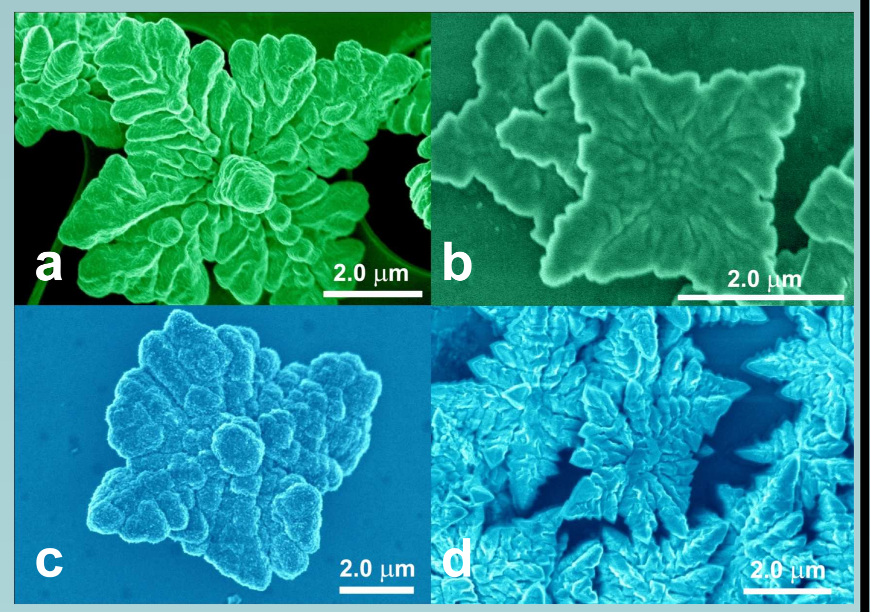


Porphyrins are chlorophyll analogs that strongly absorb light throughout the visible and UV spectrum. Our goal is to produce segregated molecular crystalline packing allowing electron and/or hole transport, especially in photoexcited states.

These cooperative binary ionic (CBI) materials are prepared by simply mixing the two porphyrin aqueous solutions.

The ionic solid that forms has very low solubility in water, so dendritic structures such as the four-leaf clover-like structures (right) form rapidly by diffusion limited aggregation and crystallization.

The clover-like biomorph is formed regardless of whether the metal in the two porphyrin is Zn (donor) or Sn (acceptor).



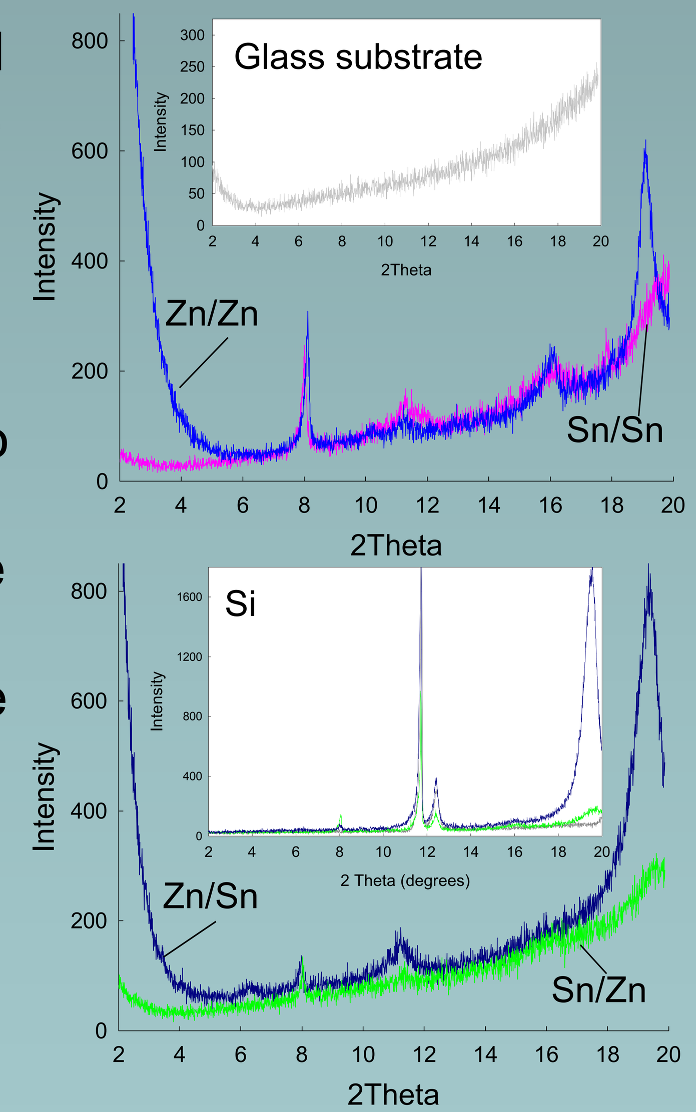
SEM images of clover-like structures obtained mixing solutions of:

(a)SnTPPS^{4-} and ZnT(N-EtOH-4-Py)P^{4+}
(b)ZnTPPS^{4-} and SnT(N-EtOH-4-Py)P^{4+}
(c)SnTPPS^{4-} and SnT(N-EtOH-4-Py)P^{4+}
(d)ZnTPPS^{4-} and ZnT(N-EtOH-4-Py)P^{4+}.

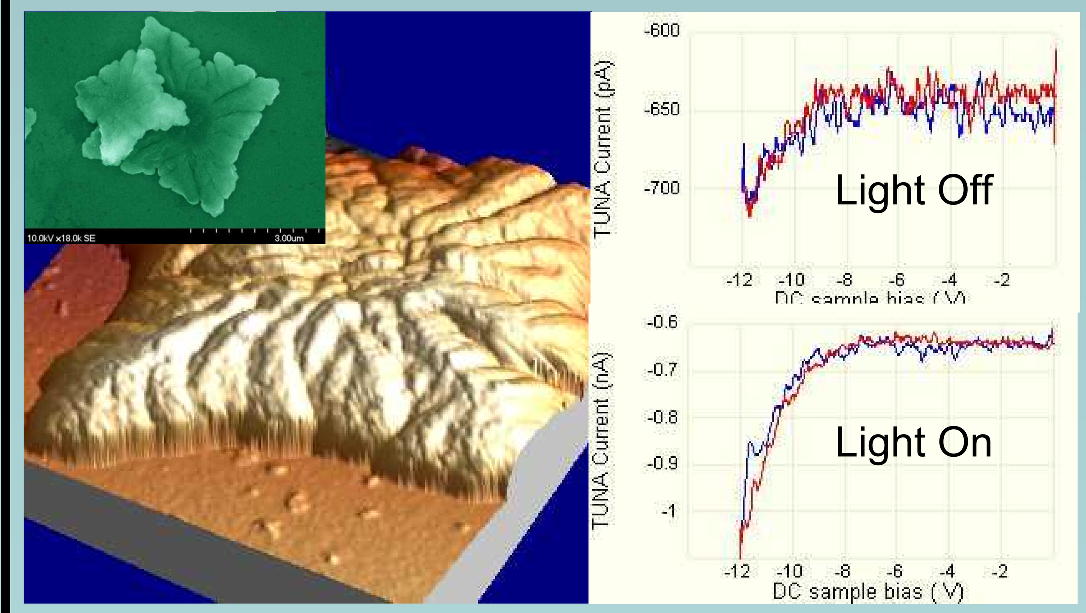
Major Results & Impact

The clover-like CBI structures obtained with these Zn(II) and Sn(IV) porphyrins share a common crystalline molecular arrangement as has been verified by XRD measurements (at right).

This is significant because the ability to change the metals in the porphyrin anions and cations allow us to tune the electronic and optical properties of these CBI biomorphs. For example, we might want an electron to transfer from the anionic porphyrin to the cation porphyrin rather than vice versa. This might stabilize the electron transfer between segregated stacks and possibly promote free charge carrier formation.

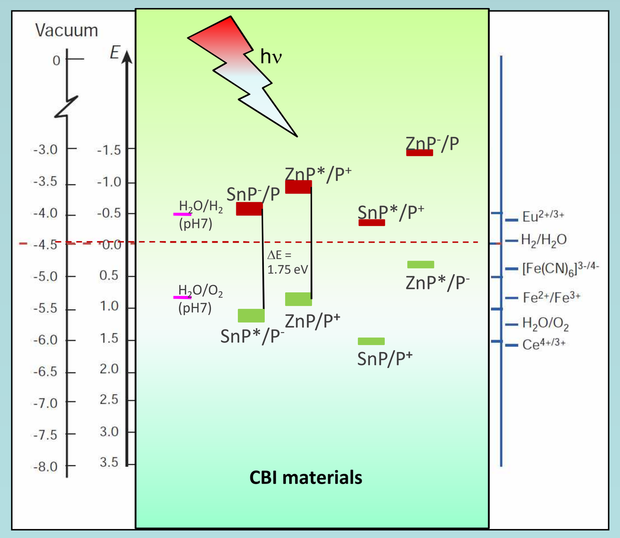


XRD patterns for the Zn/Zn, Sn/Sn, Sn/Zn, and Zn/Sn clovers.



AFM tapping mode image of the Zn/Sn clovers (far left), an SEM image (Inset), and tunneling current traces (light on & light off) for conduction between the p-type Si substrate and a point on the top surface of the clover.

Indeed, the Zn/Sn clovers (above) are photoconductors. The figure at right depicts the energy levels of the valence and conduction bands of the porphyrin donors and acceptors. In contrast, the Sn/Zn clovers are insulators possibly because electron transfer is to the anionic porphyrin.

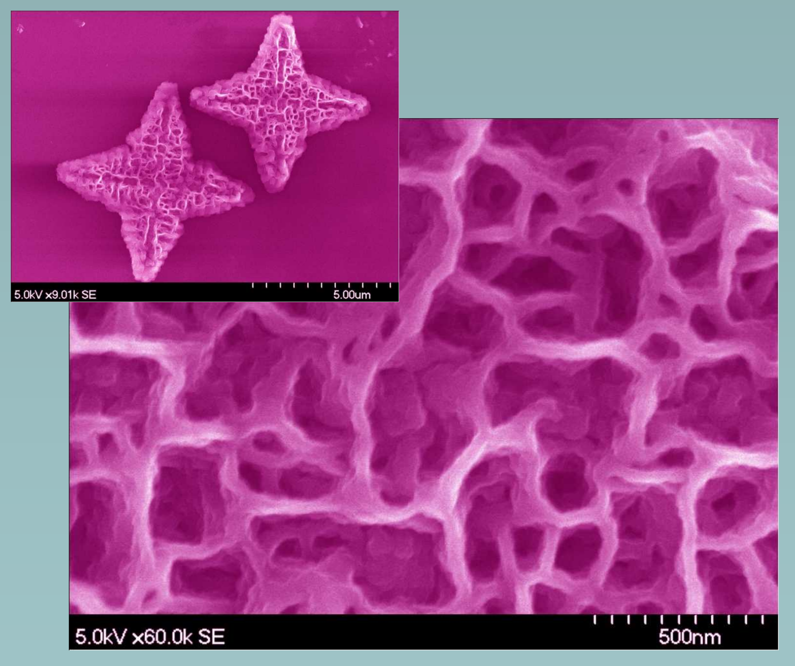


The Future

Much needs to be done to understand the synthesis, crystalline structure, and collective properties of these new CBI materials. Future studies should include:

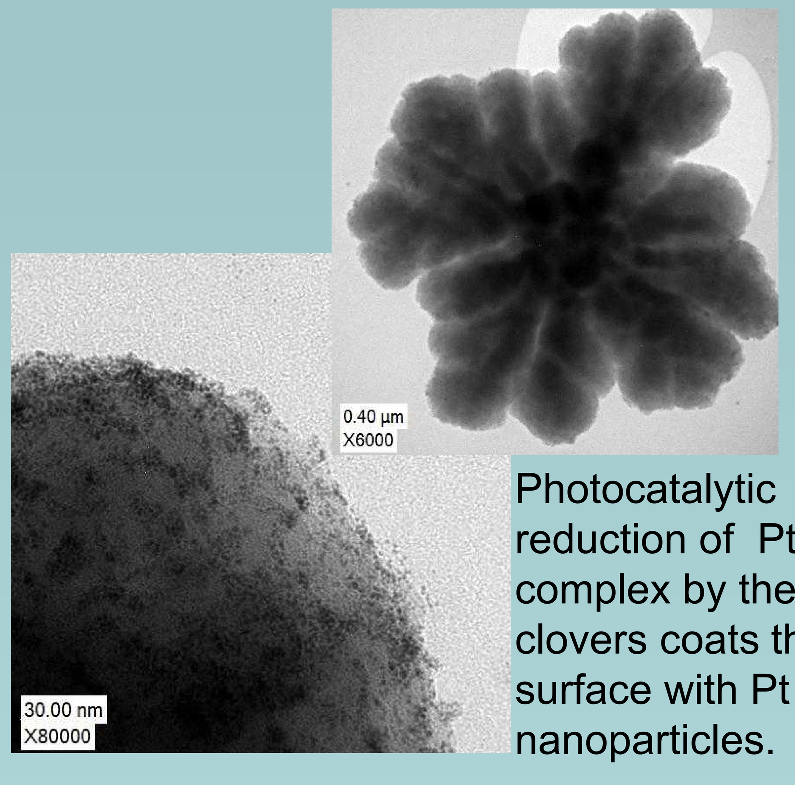
Other functional combinations of porphyrins are possible such as electron donors or acceptors with catalytic porphyrins.

The biomorph at right combines an electron donor (Zn porphyrin) with a CO_2 reduction catalyst (Co porphyrin).



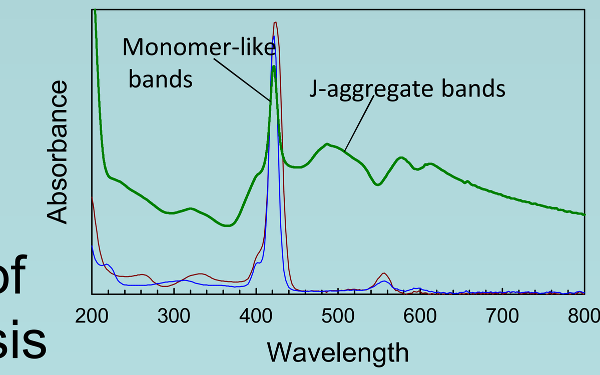
Composites of the CBI structures with metals will also be investigated for applications in light harvesting and electron transfer for solar technologies.

Photocatalysis by the clovers has been demonstrated by their ability to reduce metal complexes, but many questions remain concerning the mechanism and the ability to catalyze solar fuel production.



Photocatalytic reduction of Pt complex by the clovers coats the surface with Pt nanoparticles.

Basic electronic, optical, and structural studies of this new class of solid are needed to fully realize their potential. Deeper understanding of the electron-transfer processes might enable the use of the CBI materials in artificial photosynthesis systems and organic solar cells, which is the ultimate goal of this project.



UV-visible light absorption by the Zn/Sn clovers.

NNSA National Nuclear Security Administration

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