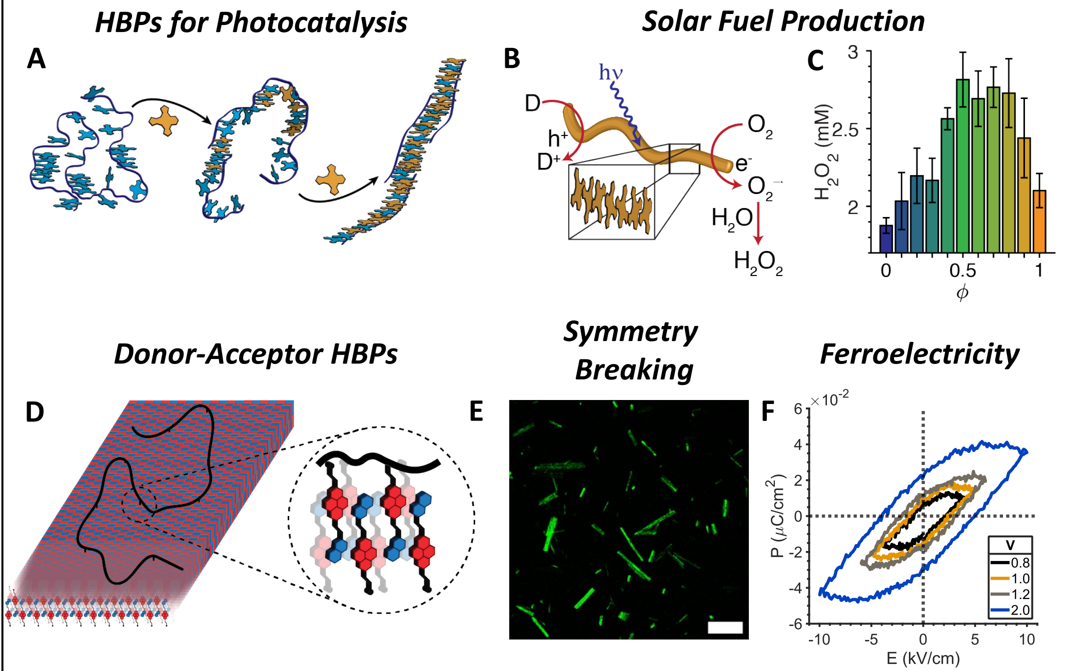
DMR-1508731

Self-Assembly and Properties of Hybrid Bonding Polymers

Samuel I. Stupp, Northwestern University at Chicago

This program has allowed us to continue our development of crystalline hybrid bonding polymers (HBPs). HBPs are nanomaterials in which covalent and supramolecular polymers are chemically integrated through specific noncovalent interactions. Recent efforts have focused on understanding how HBPs composed of chromophore-functionalized covalent polymers and chromophore amphiphile small molecules self-assemble in water across a range of different co-assembly ratios (ϕ). Detailed electron microscopy, X-ray scattering, and spectroscopic analyses along with computational modeling studies have revealed that HBPs self-assemble into nanostructures where covalent polymer backbones wrap around crystalline chromophore cores. This unique structure gives rise to interesting properties, including enhanced rates of photocatalytic hydrogen peroxide production. We have also found that HBP formation can induce symmetry breaking, which leads to ferroelectricity in HBPs based on electron donor–acceptor chromophores. These ferroelectric HBPs could be used to create devices like computer memories that are more energy efficient and lightweight than their traditional counterparts. These properties open new possibilities for the development of advanced electronics and the metal-free production of solar fuels.



*(**A**) Schematic representation of ullazine HBP self-assembly. (**B**) Photocatalytic hydrogen peroxide production cycle in ullazine HBPs. (**C**) Hydrogen peroxide production by ullazine HBPs after 2 h of blue light illumination. (**D**) Schematic representation of donor-acceptor HBPs. (**E**) Second harmonic generation (SHG) confocal microscopy image of donor-acceptor HBPs (ϕ = 0.5) showing strong SHG signal, which indicates symmetry breaking (scale bar = 25 μm). (**F**) Polarization plot of a donor–acceptor HBP (ϕ = 0.3) showing a parallelogram shape indicative of ferroelectricity.*

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Our NSF program supports graduate students and postdoctoral fellows conducting fundamental research in synthetic organic chemistry, polymer chemistry, and materials characterization. The program also allows us to create novel nanomaterials with great potential function as biological and energy materials. For example, the work highlighted here could enable efficient solar fuel production and the development of advanced electronic devices, all without the use of heavy metals.

This project benefited tremendously from the contribution of an undergraduate student and provided a valuable learning environment for this student and all others involved. The undergraduate student plans to continue working on this project for his remaining years at Northwestern before going on to graduate school and a career in scientific research.

A B

*(**A**) Members of the Stupp lab. (**B**) An undergraduate student at work in the lab learning to synthesize materials for our donor–acceptor hybrid bonding polymers.*