Photoactive molecular building blocks can be spatially integrated into the crystalline lattice of covalent organic frameworks (COFs), allowing us to create models for organic bulk heterojunctions and porous electrodes for photoelectrochemical systems. In this presentation, we will address means of controlling the morphology and packing order of COFs in thin films [1] and with spatially locked-in building blocks.[2] We will discuss different strategies aimed at creating electroactive networks capable of light-induced charge transfer. For example, we have developed a COF containing stacked thienothiophene-based building blocks acting as electron donors with a 3 nm open pore system, which showed light-induced charge transfer to an intercalated fullerene acceptor phase.[3] Contrasting this approach, we have designed a COF integrated heterojunction consisting of alternating columns of stacked donor and acceptor molecules, promoting the photo-induced generation of mobile charge carriers inside the COF network.[4] Additional synthetic efforts have led to several COFs integrating extended chromophores capable of efficient harvesting of visible and near infrared light, for example [5]. Extending newly developed thin film growth methodology to a solvent-stable oriented 2D COF photoabsorber structure, we have recently established the capability of COF films to serve in photoelectrochemical water splitting systems.[6] Related COF films can also act as ultrafast solvatochromic chemical sensors.[7] The great structural diversity and morphological precision that can be achieved with COFs make these materials intriguing model systems for organic optoelectronic materials.

References