

Two-Dimensional Polymers and Covalent Organic Frameworks

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Two-dimensional polymers and their layered frameworks (covalent organic frameworks: COFs) are a class of crystalline porous materials that allow an atomically precise integration of components into a 2D or 3D periodicity. The recent synthetic progress has shown that 2D COFs are useful platform for designing conducting, where 2D polymer sheets are organized in a superimposed way to generate a layered architecture that provides periodic π pathways for charge-carrier transport.¹⁻⁷⁾

We pioneered the design and synthesis of COFs by integrating π -electronic units into the 2D polygon skeletons. In this year, we focus on our challenge for the molecular design of donor–acceptor COFs with periodically ordered electron donor–acceptor π -columnar structure and maximized bicontinuously segregated p-n interface, which provide a new molecular configuration and mechanism for optoelectronics and photovoltaics.

1. Charge Dynamics in 2D Polymers and COFs

The donor–acceptor heterojunction is a key structure in current technologies, including transistors, light-emitting diodes, and photovoltaics, because it controls the charge dynamics in the devices. Covalent organic frameworks (COFs) are crystalline molecular skeletons that allow atomically precise integration of building blocks into periodic array structures. In this regard, we have demonstrated arene, porphyrin, and phthalocyanine COFs that provide periodically ordered columnar arrays of π -components and show outstanding semiconducting and photoconductive properties. We

recently synthesized a donor–acceptor COF that gives rise to a periodically ordered bicontinuous heterojunction structure. This heterojunction structure provides ambipolar pathways for charge collection, and would be ideal for the current semiconducting devices that involve photoenergy transformations; however, the charge dynamics, which is a key mechanism that controls the energy transformation, remains unclear.

We determined the charge dynamics of a donor–acceptor COF using time-resolved spectroscopy. In the COF, the heterojunctions allow an ultrafast electron transfer from the donor to the acceptor columns. The light absorption is directly coupled with charge dissociation to generate free charges in the donor and acceptor π -columns within 2 ps. The stacked π -columns delocalize the charges, suppress charge recombination, and retain the charges for a prolonged period of time. The COFs enable rapid charge separation and exceptional long-term charge retention, thereby providing a key mechanistic basis to envisage the high potential of donor–acceptor COFs for photoelectric applications.

To clarify the charge dynamics in the solid-state COFs, we performed time-resolved electron-spin resonance (TR-ESR) spectroscopy. Before the 700-nm laser flash, the TR-ESR was silent over the entire magnetic field range. After the laser flash, the TR-ESR signal rapidly increased in intensity as a result of a very rapid charge separation. The TR-ESR signal exhibited an increase up to $t = 1.5 \mu\text{s}$ and then decayed slowly. Therefore, we monitored the TR-ESR spectra at $t = 1.5 \mu\text{s}$ as a function of the magnetic field and obtained a time-slice profile, which can be reproduced with a single emission-type Lorentzian with a g value of 2.0059 and a narrow spectral width of 0.75 mT. The g value of 2.0059 confirms the forma-

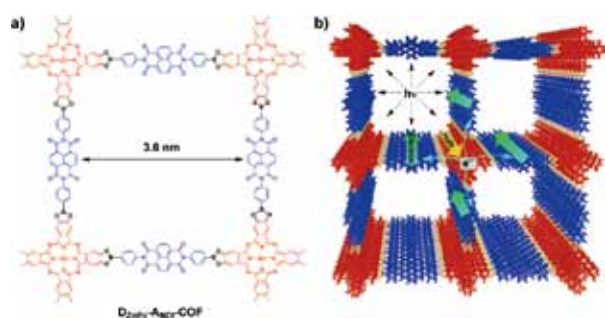


Figure 1. a) Structural representation of a donor–acceptor COF ($D_{ZnPc}-A_{NDI}$ -COF). Donor and acceptor units are shown in red and blue, respectively. The dotted black lines suggest the extension of periodic structures. b) Illustration of a 2×2 cell of the 0.8-Å slipped AA-stacking COF and photochemical events.

tion of $ZnPc^{*+}$ and NDI^{*-} species. The narrow spectral width of the COF is consistent with a weak magnetic dipolar interaction between two spins because they are spatially separated and delocalize in the donor and acceptor columns. The TR-ESR measurements at 80 K also confirmed the charge-separated state, as evidenced by a single emission-type Lorentzian profile with the same g value of 2.0059. Through curve-fitting of the time profiles to an exponential function given by $\Phi = \alpha \exp[-t/\tau_{CS}]$, where α , t , and τ_{CS} are the proportional factor, time, and lifetime, respectively, the τ_{CS} values of the solid-state COFs at 280 K was determined to be 1.8 μ s.

These dynamics provide mechanistic insights into the key photochemical processes involved in optoelectronics and photoenergy conversion systems and suggest that the donor–acceptor COFs are promising high-performance semi-conducting materials for use in applications.

2. Control Crystallinity and Porosity of Covalent Organic Frameworks through Managing Interlayer Interactions Based on Self-Complementary π -Electronic Force

COFs provide a useful skeleton for designing a new sort of organic semiconductors that feature columnar π -arrays periodically aligned at a nanometer-scale precision.^{3,6)} In this sense, the 2D COFs serve as a new platform for designing organic 2D materials with structural periodicity that is difficult to be achieved with other molecular architectures. However, controls over the crystallinity and porosity, which are key parameters in the applications, have been elusive.

We demonstrated the strategy using imine-linked porphyrin COFs, in which fluoro-substituted and non-substituted arenes at different molar ratios were integrated into the edge

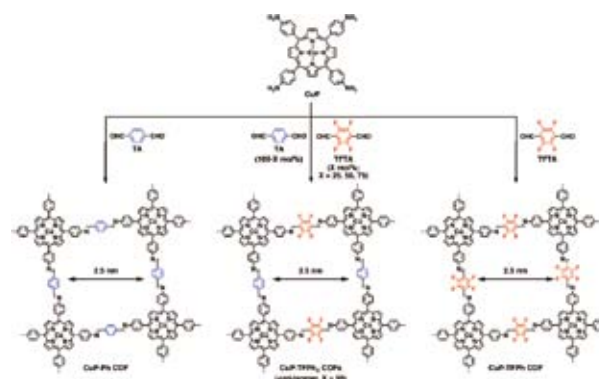


Figure 2. Schematic representation of the synthesis of COFs integrated with self-complementary π -electronic interactions (CuP-TPhX COFs, $X = 25, 50,$ and 75) and the CuP-Ph COF and CuP-TPh COF controls.

units (Figure 2). The porphyrins occupy the vertices and the arene units locate the edges of mesoporous two-dimensional COFs.

We demonstrated the control of COFs using self-complementary π -electronic interactions. Computational studies in conjunction with structural resolutions reveal that the self-complementary π -electronic force maximizes the total crystal stacking energy and minimizes the unit cell size. As a result, the COFs show an improved crystallinity and enhanced porosity, with the greatest effects observed when the interactions are strongest. Together with a prominent effect on changing the π -cloud distribution in the framework and lowering the HOMO-LUMO gap, the present work suggests a new means to designing COFs through managing the interlayer interactions.

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Award

JIN, Shangbin; CSJ presentation Award.