



# Development of organic semiconductor materials with small exciton binding energies toward photoelectric conversion applications

Department of Soft Nanomaterials, SANKEN (The Institute of Scientific and Industrial Research)

Assistant Professor Seihou Jinnai

<https://researchmap.jp/jinnai.seihou?lang=en>

Professor Yutaka Ie

<https://researchmap.jp/read0105668?lang=en>



## Abstract

Photoelectric and photocatalytic energy conversion systems based on organic semiconducting materials are emerging as promising next-generation, environmentally friendly technologies. The performance of these devices and catalysts largely depends on the dissociation of photoexcited excitons into free charge carriers. However, in organic semiconductors, the exciton binding energy is typically much higher than that in inorganic semiconductors such as silicon, which fundamentally limits the charge separation efficiency.

To address this challenge, our group has focused on reducing the exciton binding energy ( $E_b$ ) through precise molecular design. We have developed unique saddle-structured or spiro-structured organic semiconductors that enabled tuning molecular aggregation behavior and frontier orbital arrangements. These strategies have successfully lowered the  $E_b$  compared to conventional materials. When incorporated into device architectures, these organic semiconductors have led to enhanced performance in single-component organic solar cells (OSCs), bulk-heterojunction OSCs, and homogeneous organic photocatalysts.

## Background & Results

The performance of OSCs and organic photocatalysts critically depends on the efficiency of exciton dissociation into free charge carriers. A key parameter governing this efficiency is the  $E_b$ , which represents the Coulomb attraction between the electron-hole pair. Organic semiconductors typically exhibit large  $E_b$  values of 0.3–1 eV, over an order of magnitude higher than those of inorganic semiconductors such as silicon (~0.015 eV). Consequently, efficient operation of OSCs and photocatalysts has traditionally relied on donor-acceptor heterojunctions or structural designs that maximize interfacial contact areas. However, such architectures often result in energy conversion losses, reduced operational stability, and increase material and fabrication costs, thereby underscoring the need for new approaches in organic semiconductors and device architectures.

Our group has been developing organic semiconductors aimed at reducing the  $E_b$ . According to Coulomb's law,  $E_b$  can be decreased by increasing the relative dielectric constant ( $\epsilon_r$ ) or extending the charge separation distance ( $R$ ) in the excited state. Based on this concept, we have designed and synthesized unique saddle-structured or spiro-structured organic semiconductors. By precisely tailoring their aggregation and the spatial distribution of frontier molecular orbitals, these materials exhibit enhanced  $\epsilon_r$  or  $R$ , respectively. As a result, these organic semiconductors were found to exhibit smaller  $E_b$  values compared to conventional systems. When employed as active layers, these materials not only improved the efficiency of bulk-heterojunction OSCs but also enabled single-component OSCs and homogeneous organic photocatalysts.

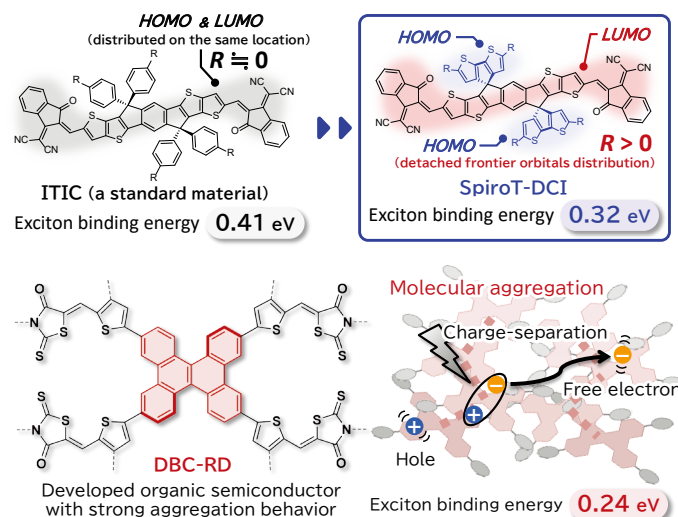
## Significance of the research and Future perspective

This study provides pioneering insights into the influence of molecular aggregation and frontier orbital arrangement on the exciton binding energy in organic semiconductors. It also experimentally demonstrates strategies towards bulk-heterojunction organic solar cells, single-component organic solar cells, and organic photocatalysts.

$$\text{Exciton binding energy} \approx \frac{e^2}{4\pi\epsilon_0 \times \epsilon_r \times R}$$

$e$ : Elementary charge  
 $\epsilon_0$ : Vacuum dielectric constant  
 $\epsilon_r$ : Relative dielectric constant  
 $R$ : Charge distance

Fig. 1: Exciton binding energy and Coulomb's equation.



## Functioned as organic solar cell and organic photocatalyst materials

Fig. 2: Development of organic semiconductor materials with small exciton binding energy.

### Patent

### Treatise

### URL

### Keyword

Mori, Hiroki; Jinnai, Seihou; Ie, Yutaka et al. A dibenzo[g,p]chrysene-based organic semiconductor with small exciton binding energy via molecular aggregation. *Angew. Chem. Int. Ed.* 2024, 63(41), e202409964. doi: 10.1002/anie.202409964

Wang, Kai; Jinnai, Seihou; Ie, Yutaka et al. Nonfullerene acceptors bearing spiro-substituted bithiophene units in organic solar cells: tuning the frontier molecular orbital distribution to reduce exciton binding energy. *Angew. Chem. Int. Ed.* 2024, 63(47), e202412691. doi: 10.1002/anie.202412691

<https://www.sanken.osaka-u.ac.jp/labs/omm/>

organic solar cell, organic semiconductor, organic photocatalyst, organic functional material, exciton binding energy