

# Ultrafast Exciton Dynamics of Phthalocyanine Films with Different Molecular Orientations

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Organic semiconductors (OSCs) have enormous potential in advanced optoelectronic devices, such as organic light-emitting diodes and organic solar cells. To achieve higher performance and functional versatility for these applications, a deeper understanding of the generation and relaxation mechanism of photoexcited excitons in molecular films is essential. In this study, we investigate the ultrafast dynamics of excitons in planar-shape molecules of phthalocyanines (Pc), which can adopt a lying-down or standing-up orientation depending on the substrate used, as shown in Fig. 1.<sup>1</sup> The distinct ionization-energy difference of more than 0.5 eV measured by photoelectron spectroscopy confirms that the Pc thin film on HOPG substrate grows in the lying-down direction and the Pc on ITO grows in the standing-up direction. Exciton energy and population from the molecules with these two different orientations are measured by time-resolved two-photon photoemission (tr-2PPE) with time resolution of 85 fs. In this measurement, we first pump a singlet exciton population in the Pc with a femtosecond pulse and probe its evolution as a function of delay time with an ultraviolet pulse. Singlet excitons have a variety of relaxation pathways, including diffusion between molecules, intersystem crossing to triplet states, and dissociation at the interface with metals. The tr-2PPE experiments show that the exciton relaxation in Pc molecules with the standing-up geometry is dominated by exciton diffusion in the direction perpendicular to the substrate, resulting in relatively slow exciton relaxation. However, for Pc molecules in the lying-down geometry, the excitons undergo faster transfer to the metal interface due to aligned  $\pi$ -orbital overlap with neighboring molecules toward the substrate. These results imply that OSCs exhibit different exciton relaxation dynamics depending on their orientation and suggest that for planar molecules like Pc, the lying-down geometry is more favorable for exciton transfer and dissociation to the metal interface.

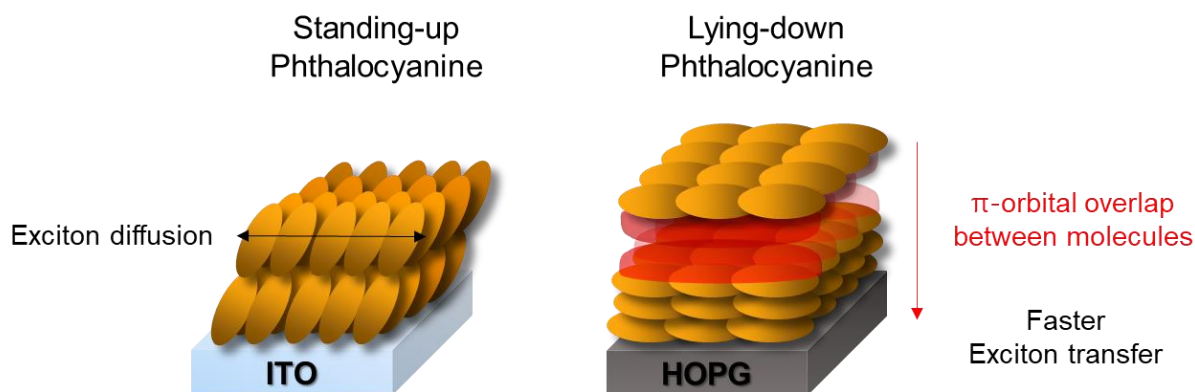


Fig. 1. Orientation of phthalocyanines depending on substrates and exciton transfer

## Acknowledgement

## References

1. H. Lim, S. Yang, S.-H. Lee, J.-Y. Lee, Y. Lee, A. B. Situmorang, Y.-H. Kim, J. W. Kim, *J. Mater. Chem. C* 9, 2156 (2021).