

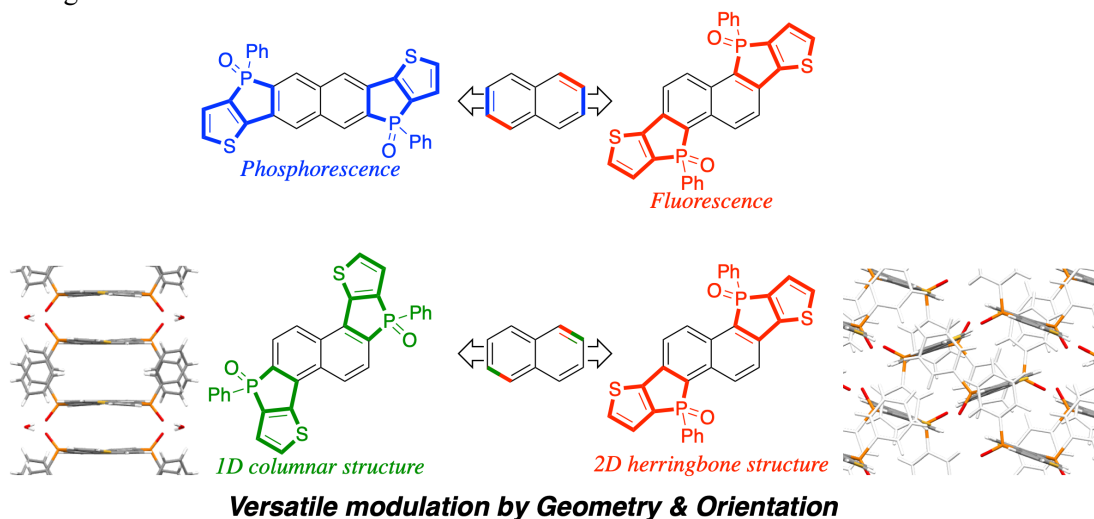
Modulation of Physicochemical Properties of Thiophene-fused Naphthodiphospholes by Precise Fusion of Heterole Rings

(¹Graduate School of Engineering, Kyoto University, ²WPI-iCeMS, Kyoto University) ○ Keiichi Ishida,¹ Tomohiro Higashino,¹ Hiroshi Imahori^{1,2}

Keywords: *Phosphole, Thiophene, Fluorescence, Phosphorescence*

Fused polycyclic aromatics have been vigorously pursued over the years because of their attracting structural, electronic, and photophysical features associated with the rigid and planar π -conjugated frameworks. For polycyclic aromatics with heterole-fused structures, the orientation of fused heterole rings as well as the geometry of their fused structures has a large impact on the physicochemical properties. In this regard, we expected that introducing two phosphorus atoms into polycyclic aromatics would provide an assortment of isomers originated from not only the position and orientation of the phosphole rings, but also the orientation of substituents on the phosphorus atoms (i.e., *trans/cis* configurations).

Herein, we designed and synthesized a series of six isomers of thiophene-fused naphthodiphospholes based on our envision. The isomers with fused structures on 2,3/6,7-positions showed phosphorescence due to enhanced spin-orbit coupling, whereas the isomers with fused structures on 1,2/5,6-positions displayed intense fluorescence. In addition, the *cis* isomers with 1,2/5,6-fused structure exhibited different packing structure in the solid states (i.e., 1D columnar structure and 2D herringbone structure) according to the orientation of fused heterole rings. Therefore, we demonstrated that the positions of heterole rings are of utmost importance to tune their electronic properties, and the orientations of heterole rings and substituents on the phosphorus atoms play critical roles in the molecular arrangements in the solid states.¹



1) Ishida, K.; Higashino, T.; Wada, Y.; Kaji, H.; Saeki, A.; Imahori, H. *ChemPlusChem*, in press.