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A new organophosphorus scaffolds for functional materials

For the advancement of the field of organic electronics, the development of new p-conjugated organic materials is indispensable. One of the effective strategies for creating unique organic functional materials is the incorporation of heteroatoms into the backbone or peripherals of hydrocarbon-based π-conjugated systems, because such operation often endows the parent molecules with significant structural and/or electronical perturbations. Therefore, scientists have been seeking for novel heteroatom-incorporated π-conjugated scaffolds, building blocks, and synthetic methods thereof. In this context, very recently, much attention has been paid to the incorporation of phosphorus atoms into π-electon systems, and some promising scaffolds have been extensively developled (Fig. 1A).

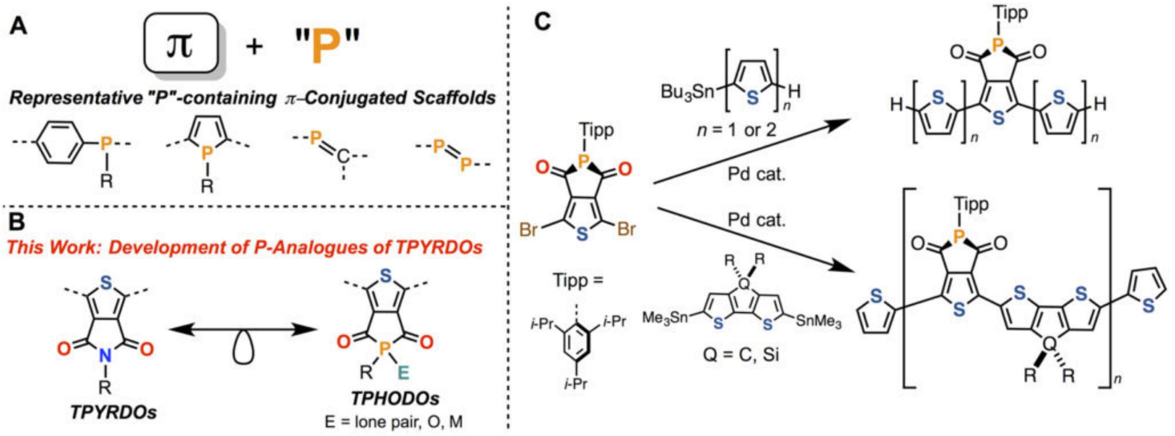

Fig. 1.

The scientists from Osaka University (Japan) led by Professors Takeda and Minakata have devised a new entry of phosphorus-containing p-conjugated scaffolds, thieno[3,4-*c*]phosphole-4,6-diones (TPHODOs, Fig. 1B). Intriguingly, TPHODOs are regarded as isoelectonic phosphorus-analogues of thieno[3,4-*c*]pyrrole-4,6-diones (TPYRDOs, Fig. 1B), which have been emerging as a promising electron-acceptor unit for constructing donor(D)-acceptor(A) narrow bandgap conjugated polymeric materials.

Firstly, the research team developed a novel and fundamental building block, 2,5-dibrominated TPHODO, and the utility of the building block has been successfully demonstrated by preparing phosphorus-containing D-A-D florescent small molecules and D-A conjugated narrow bandgap polymers through Pd-catalyzed Stille cross-coupling reactions (Fig. 1C). Importantly, when compared to their N-analogues (TPYRDOs), the newly developed phosphorus compounds were found to show higher electron affinities (EAs) and more red-shifted emissions. More importantly, these TPHODOs are post-functionalizable through the complexation with a gold complex and P-oxidation, allowing for lowering the LUMO levels and emission energies significantly.

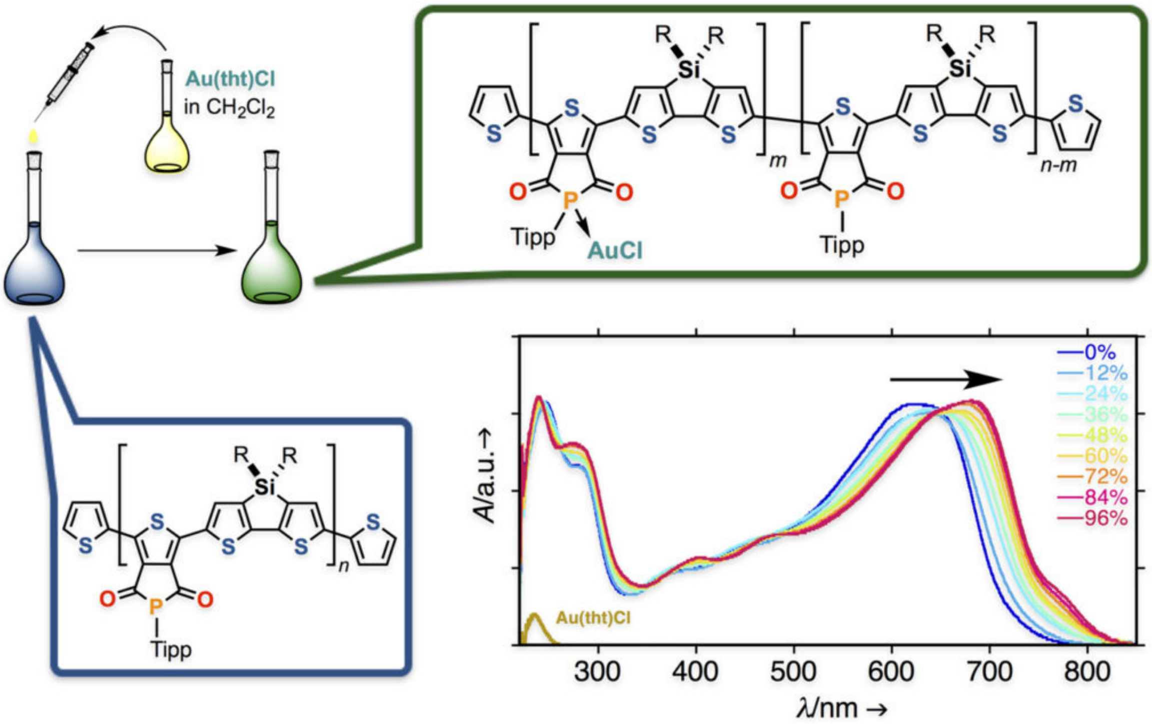

Fig. 2.

By making the use of the post-functionalizability of the TPHODOs, the scientific team has succeeded in tuning the optical bandgap of a D-A conjugated polymer just by adding an aliquot containing gold complex into the solution of the polymer (Fig. 2). The more gold complex is added, the narrower the bandgap of the polymeric material becomes. From an application perspective, the adjustment of the bandgap of polymeric materials in the solid forms after the device fabrication could be tuned by a similar way in the future.

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Publication

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