Stereodefined Poly(p-phenylene vinylene) Copolymers with Wavelength-Selective Light Responsivity

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While poly(*p*-phenylene vinylene) (PPV) and its derivatives have been studied for many years, structural diversification while retaining polymerization control remains a synthetic challenge, thereby impeding the modulation of physical properties of PPVs. Ring-opening metathesis polymerization (ROMP) of [2.2] paracyclophane-1,9-dienes (PCDs) provides a unique avenue to access highly precise and diverse PPVs, but the multi-step route required to prepare PCDs creates a synthetic bottleneck and limits the adoption of this manufacturing approach. In addition, the unique one-way *cis*-to-*trans* photoisomerization leveraged to yield the more optoelectronically desirable all-*trans* PPVs is not only limited by the high-energy UV light necessary to achieve this configurational change but is also an underutilized tool for accessing complex stereodefined architectures. To address these issues, we developed a divergent synthesis of arylated PCDs from a common precursor accessible on gram-scale, markedly broadening the scope of functionalized PPVs and enabling the synthesis of wavelength-specific photoisomerizable PPVs. This talk will first discuss the divergent synthetic route designed to obtain a broad scope of chromophore-incorporated PPVs. The second part of this talk will explore the structure-dependent photoisomerization behavior of the arylated PPVs, including photoisomerization kinetics at various wavelengths. Finally, we will discuss how this unprecedented reactivity was harnessed to access a set of well-defined stereoblock copolymers. This efficient divergent synthetic strategy combined with a greater control of the photoisomerization of *cis*-linkages in PPVs opens the door to previously inaccessible optoelectronic materials.

