Cooperative Network Formation via Two-Colour Light-Activated λ-Orthogonal Chromophores

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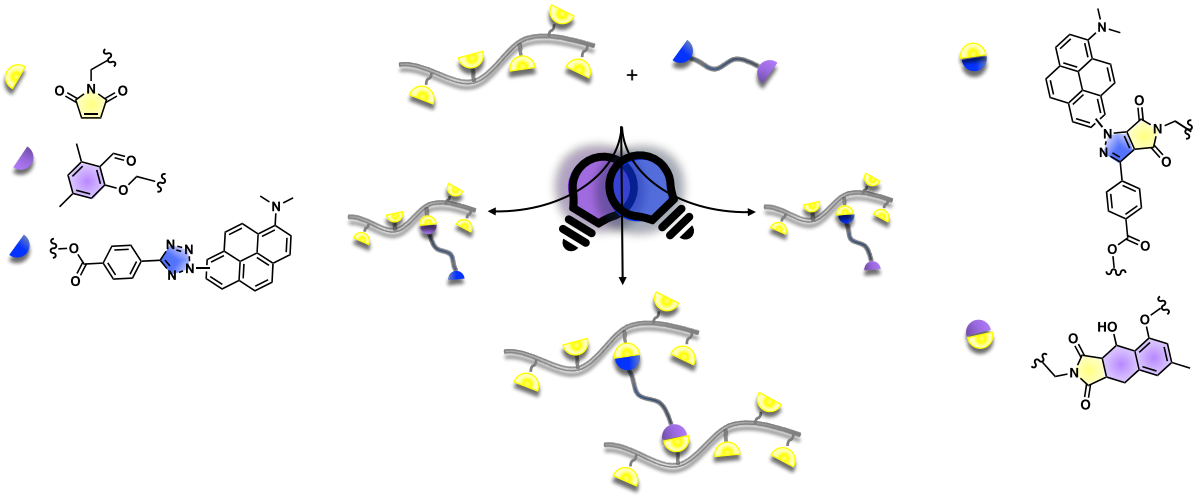
Propelling a specific reaction independently by activating only one of the photoreactive sites within a single molecule is a formidable challenge. Here, a heterotelechelic dilinker molecule is synthesized by combining two fully sequence-independent λ-orthogonal chromophores to exploit their disparate reactivity with the same reaction partner, a maleimide-containing polymer. It is shown that the network formation only occurs when the system is exposed to irradiation with two colours of light either in a sequence-independent stepwise or in a simultaneous fashion. One-colour irradiation activates solely one of the photoreactive sites, resulting in a linker-decorated post-functionalized polymer. The functionalized polymers formed after each separate irradiation with one color of light was characterized using ^{1}H-NMR spectroscopy. The changes in the topology of the maleimide decorated polymer after each irradiation step and onset of crosslinking upon two-colour irradiation were monitored by size exclusion chromatography. Finally, physical gelation was observed solely upon exposure of the resin to two colours of light, but not upon exposure to one colour. The newly introduced photoreactive system reveals the potential of wavelength orthogonal chemistry in precision macromolecular synthesis.



Scheme 1. Illustration depicting the photochemical polymer post-functionalization with one colour of light irradiation and cooperative network formation with two colours of light irradiation of the photoreactive system comprising a maleimide-containing polymer and a heterotelechelic dilinker with UV (325 nm) and/or blue (450 nm) LEDs.