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FROM DYNAMIC STRUCTURES TO FUNCTIONAL MATERIALS

Aryl Azo Pyrazole-Driven Photoswitching of Supramolecular Peptide Self-Assembly

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Peptides are versatile molecules which modulate numerous biological phenomena. Chemists utilise the self-assembling behaviour of the peptides to design functional materials, finding various applications in smart drug delivery, bioelectronics, self-healing hydrogels and catalysis. Imparting responsiveness into the peptide assembly to external stimuli, allows smart control of functions in peptide materials.[1] In particular, light can be an extremely non-invasive and inexpensive trigger to control the structure of the peptide and thus control its supramolecular aggregation and function. Till date, azobenzene has been the most widely used moiety which can provide photocontrol over the peptide folding or assembly. When attached to peptides, it often suffers from either low E to Z conversion efficiency or short half-life of the Z isomer.[2] Herein, we have utilized the aryl azo pyrazole photowitch to design a photo switchable peptide which shows superior conversion to the Z isomer at the photo stationary state upon irradiation with 365nm light. Also, the half life time of this peptide is higher compared to the azobenzene analogues.

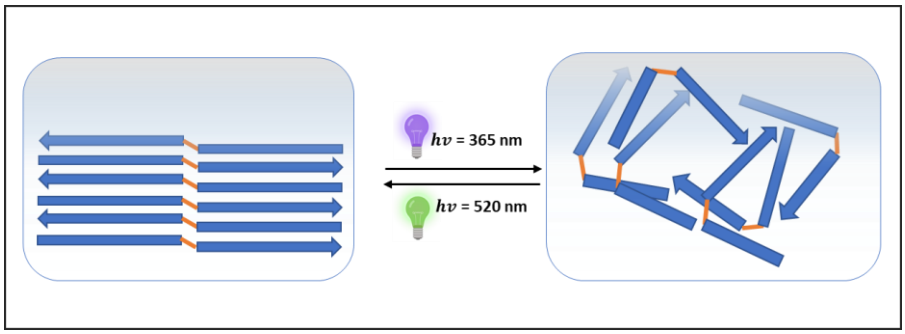

Figure 1. The reversible photo switching from ordered to disordered assembly of the peptides using UV and green light.

Circular dichroism spectral data indicates that the pristine peptide self-assembles into β-sheet in phosphate buffer of pH 7.5 and this ordered arrangement is destroyed when the peptide assumes the folded Z conformation. This supramolecular assembly can be obtained back by turning the conformation of the peptide to the E isomer using green light and reversible switching can be achieved at least in five cycles without hysteresis. This reversible self-assembly has potential to act as a photo-activable catalyst.

[1] L. Chen, *et al*., *Aggregate*, **7**, e70346 (**2026**)
[2] R. Parlato, *et al*., *Journal of the American Chemical Society,* **146**, 2062 (2024)