Photochromic nanopolymersomes as smart encapsulating platform

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Abstract

Nature has inspired the development of artificial nanosystems in which different stimuli promote the switching between equilibrium and out-of-equilibrium states. Those based on the photochromic effect have been widely studied because they allow the spatiotemporal switch of state. To mimic photochromic nanosystems, the scope of this study includes the synthesis of photochromic amphiphilic copolymers and their self-assembly in well-defined polymersomes suitable for encapsulation of hydrophobic and hydrophilic cargoes. First, photochromic amphiphilic copolymers were synthesized by the one-step nucleophilic addition of amine-containing 4-aminoazobenzene (AZO) and amine-PEG3-Biotin (biotin) moieties onto a poly(ethylene-alt-maleic anhydride) (PEMA) backbone, i.e., AZO-PEMA and biotin-AZO-PEMA. The synthesized copolymers contained residual carboxylic acids as hydrophilic groups, AZO moieties as photoswitchable chemical hydrophobic groups, and biotin moieties as a protein-binding ligand and hydrophilic groups. Then, both amphiphilic copolymers were self-assembled in nanopolymersomes with the in-situ encapsulation of cargoes of different molecular nature: (i) molecules as methylene blue (MB) and ferrocene (Fc), (ii) the enzyme horseradish peroxidase (HRP); and (iii) inorganic platinum nanoparticles (PtNPs). These polymersomes were highly stable with a high cargo-retention efficiency even for weeks. The ability of AZO-based polymersomes to isomerize upon ultraviolet (UV) irradiation at 365 nm was employed to change the permeability of polymersome bilayer by switching polarity from a nonpolar *trans*- to a *cis*-azobenzene with increased polarity. This conformational transition in the bilayer promoted selective permeability. Small hydrophilic molecules such as MB can be released while nanometer-sized cargos such as HRP and PtNPs remain in the polymersomes' hydrophilic core. However, small substrates can penetrate the polymersomes bilayer, yielding photochromic nanoreactors. The AZO-based polymersomes demonstrated the potential to switch permeability and could find applications to cargo release and off-on reactions.

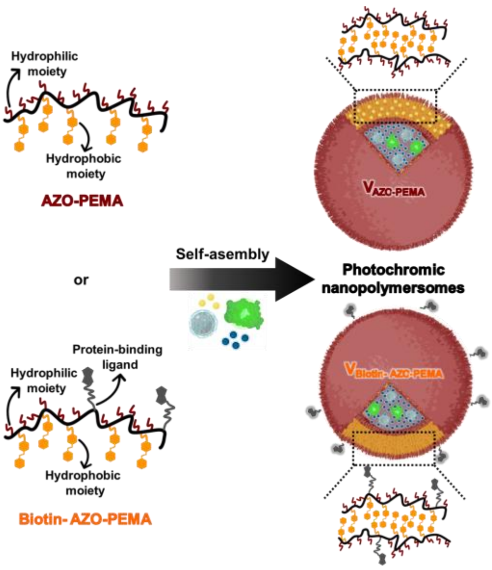

Figure 1. Schematic representation of photochromic nanopolymersomes.

References

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