Design of macrocycles as versatile visible-light photoinitiators for bulk free-radical and cationic polymerizations

Louise Breloy,[1] Davy-Louis Versace[1]

[1] *Institut de Chimie et des Matériaux Paris-Est (UMR-CNRS 7182-UPEC), Thiais*
Email: breloy@icmpe.cnrs.fr, versace@icmpe.cnrs.fr

Macrocyclic molecules such as porphyrins (Pps) and phthalocyanines (Pcs) constitute an unlimited library of structures with versatile and fascinating chemistry. Certain features, such as unique electrochemical, photochemical and photophysical properties have opened a multitude of applications, ranging from photodynamic therapy in cancer treatment, chemical sensors, solar cells, nonlinear optics, and recently to photoinitiating systems for controlled radical, free-radical and cationic polymerizations.[1,2] Thanks to their exceptional absorption spectra, some macrocycle-based systems could initiate polymerization up to red-light and NIR irradiation.

Many studies reported the use of macrocycles as highly performing photoinitiators (PIs) for bulk polymerization. Widely studied as photosensitizers for iodonium salts,[3] it appeared recently that they could also induce inter- or intra-molecular H-abstraction in presence of amine groups.[4] Besides, incredible versatility of macrocycles allows them to be more than simple PIs. For instance, they can play a double role of photosensitizers for photo-dynamic therapy, leading to inactivation of bacterial cells on polymer surfaces.[5] Silver-complexed Pcs were also proposed for one-pot photo-induced synthesis of nanocomposites.[6] Despite a growing interest, initiation mechanisms by macrocycles remain poorly understood: Their structural variety seems to lead to an equal variety of mechanisms, offering huge opportunities of investigations.

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