A Photocrosslinkable Dendrimer Consisting of a Nucleobase

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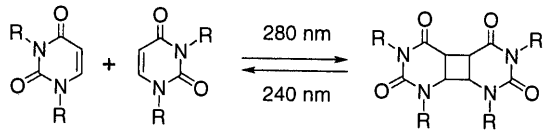
Upon irradiation at 280 nm in CH_3CN, dendritic polyuracils L*n*U-OBn (*n* = 3, 4) were crosslinked by a [2+2] photodimerization of the uracil units to give intramolecularly "locked" dendrimers, which were unlocked by irradiation at 240 nm.

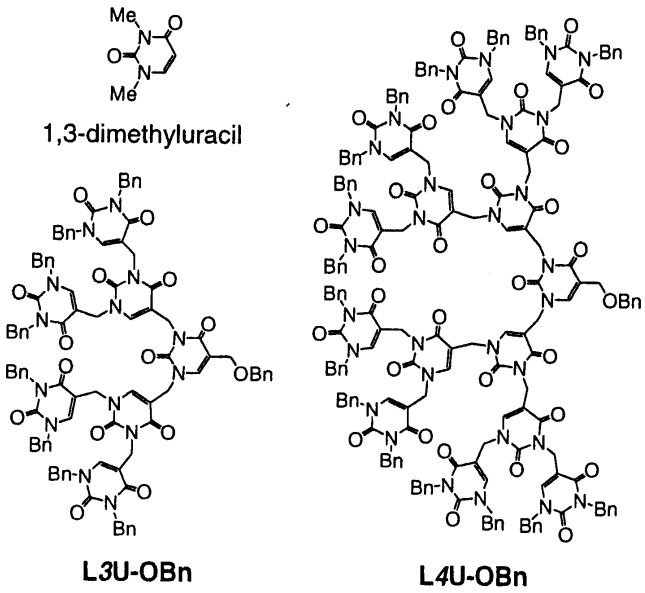
Nucleobases play important roles in biological systems due to their capability of forming multiple hydrogen bonds, and have been utilized as key motives for host-guest chemistry and supramolecular chemistry.[1] On the other hand, one of the attractive features of pyrimidine nucleobases is their activity for reversible [2+2] photodimerization.[2] For example, thymine and uracil derivatives dimerize by ultraviolet irradiation (280 nm) to form a cyclobutane ring, which is cleaved into the monomeric forms upon irradiation with a shorter-wavelength light (240 nm) (Scheme 1). Thus, a variety of photofunctional materials and supramolecular systems consisting of pyrimidine nucleobases have been developed.[3]



Scheme 1.

Dendrimers are hyper-branched three-dimensional macromolecules,[4] and have a potential as a host molecule for trapping of guest molecules within their pseudo-network structures.[5] Recently, we have reported a new class of dendritic macromolecules consisting of uracil units L*n*U-OBn (*n* = 3, 4).[6] In the present paper, we report that the polyuracil dendrimers can be intramolecularly locked via photoinduced dimerization of the uracil units.[7]

When an CH_3CN solution of L*4*U-OBn (7.5 μM, [uracil unit]$_0$ = 112.5 μM) in a quartz cell under Ar was exposed at 20 °C to a monochromatized light at 280 ± 1 nm (150-W xenon arc lamp coupled with a diffraction grating), the absorbance at 275.6 nm due to the uracil units was gradually decreased (Figure 1a) while exhibiting two isosbestic points at 249.2 and 298.0 nm. The reaction mixture after irradiation for 14 h showed new ^{1}H NMR signals assignable to cyclobutane rings (δ 3.70-3.83). The MALDI-TOF-MS spectrum showed a single peak with a mass value identical to the molecular weight of the starting dendrimer ([M+Na]$^+$), while no other peaks due to intermolecularly crosslinked products were detected in the higher molecular weight region. Furthermore, the SEC profile showed no substantial change in the chromatogram before and after the irradiation. Therefore, the photodimerization of the uracil units took place exclusively in an *intramolecular* fashion.



Continuous irradiation for, e.g., 80 h resulted in a 35% decrease in the absorbance at 275.6 nm, which corresponds to the dimerization of approximately six uracil units, on average, per dendritic molecule.[8]

In order to investigate the effect of dendritic architecture on the photodimerization, one-generation smaller L*3*U-OBn and non-dendritic 1,3-dimethyluracil were irradiated at a concentration of the uracil units being equal to the case of L*4*U-OBn: Lower-generation L*3*U-OBn, upon irradiation at 280 nm, displayed an absorption spectral change similar to L*4*U-OBn, but the dimerization rate was estimated to be almost a half of that of L*4*U-OBn (Figure 1b). Furthermore, non-dendritic 1,3-dimethyuracil showed a negligibly small spectral change (4%) even after 14-h irradiation. The larger photodimerization rate observed for L*4*U-OBn can be ascribed to a higher local concentration of the uracil units in the dendritic architecture.

Acetone is known to sensitize the photodimerization of uracil to promote the cyclobutane ring formation.[2] In fact, compared with the above case in CH_3CN, the photodimerization of 1,3-dimethyluracil in acetone proceeded much faster, where the absorbance at 266.0 nm was decreased to 15% of the initial value within only 2 h. In sharp contrast, the photodimerization in L*4*U-OBn was not accelerated in acetone, suggesting a possibility that the uracil units in L*4*U-OBn are rather isolated from the solvent cage.

Irradiation of photo-crosslinked L*4*U-OBn with a shorter-wavelength light (240 nm) resulted in an increase in absorbance at 275.6 nm, indicating a photocleavage of the cyclobutane ring to regenerate uracil functionalities. MALDI-TOF-MS spec-

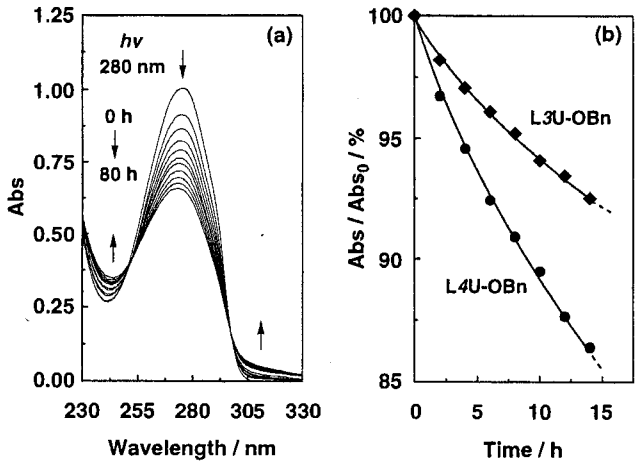


Figure 1. Irradiation of L*n*U-OBn (n = 3, 4) with UV light (280 nm) in CH_3CN at 20 °C. (a) Absorption spectral change of L*4*U-OBn. (b) Plots of the absorbance at 275.6 nm versus time.

trometry of the reaction mixture again showed a single molecular ion peak identical to that of unirradiated L*4*U-OBn. However, the reaction was not fully reversible, as it showed a saturation signature in the absorption spectral change profile. For example, when an CH_3CN solution of L*4*U-OBn, after irradiation at 280 nm for 80 h ($abs_{275.6}$ = 1.00 → 0.65, Figure 1a), was exposed to a 240-nm light, the absorbance of the reaction mixture was increased to reach a plateau at 0.76 in 10 h. This observation suggests that the uracil units on different layers exhibit different reactivities toward photodimerization and cyclobutane ring cleavage, considering a possible effect of the packing density of the uracil units on the reactivity.

In conclusion, we have shown that the polyuracil dendritic macromolecule serves as a new photoresponsive material which can be "locked" and "unlocked" by selective excitations. Studies on applications to host-guest chemistry and materials and biomedical sciences would be worthy of further investigation.[9]

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