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Heterogeneous Photochemical Reaction of 1-Methyl-2-arylcyclopropanes with Surface Hydroxy Groups

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Pyrene or phenanthrene chromophores were introduced onto the surface of a poly(2-hydroxyethyl methacrylate) film by heterogeneous photochemical reaction of 1-methyl-2-arylcyclopropanes with the film in acetonitrile.

Chemical modification of the surface of materials by photofunctional molecules is quite important in developing a new class of photocatalysts, photochromic devices, optical materials and so forth. Graft polymerization, corona–plasma discharge and chemical etching methods have been widely applied to surface modification of various materials.[1] In most cases, however, the regioselectivity of a key reaction is poor so that the chemical structure of the modified surface is not well defined. Cation radicals of arylcyclopropanes produced by photoinduced one-electron transfer with an electron acceptor are known to undergo regioselective polar addition with alcohols,[2] so that this particular photochemical reaction is expected to functionalize hydroxy groups on the surface of materials with chemically well-defined structures. Furthermore, photochemical methods are certainly superior to thermal reactions in respect to simultaneous spatial patterning and functionalization of the surface of materials.

An example of such a heterogeneous photochemical reaction is of 1-methyl-2-arylcyclopropane, where the aryl group is 1-pyrenyl **1** or 9-phenanthryl **2**, with the hydroxy groups of a poly(2-hydroxyethyl methacrylate) (PHEMA) film (see Scheme 1). Irradiation of a PHEMA film (*ca.* 20 nm thickness) prepared on a quartz plate was carried out under N_2 atmosphere with the film in contact with an acetonitrile solution of **1** or **2** (both *E*/*Z* mixture) and dimethyl terephthalate (DMTP). The film was irradiated at 313 nm for 1–2 h from the opposite side of the solution phase and then immersed in acetonitrile for 2 h to remove the reactants and air-dried prior to measurements.

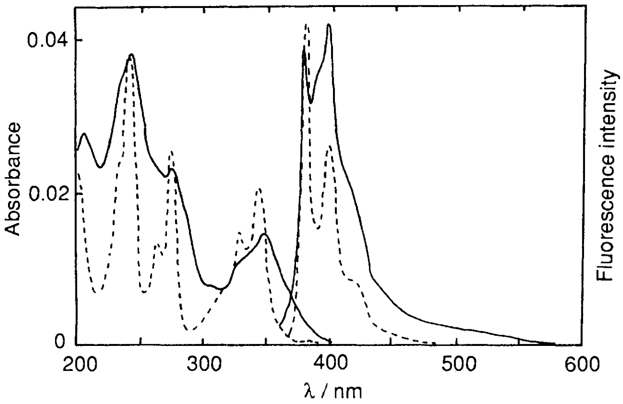
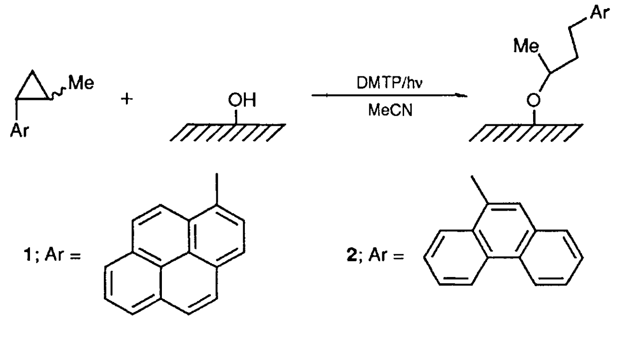


Fig. 1 Absorption and fluorescence spectra (excited at 340 nm) of the PHEMA film modified with **1** (solid line) and **1** in acetonitrile (dotted line). Absorbance and fluorescence intensity were normalized to the absorbance at 230 nm and the maximum intensity, respectively. Irradiation (313 nm) of a PHEMA film was performed with [Py] = 5.2 × 10^{-2} and [DMTP] = 2.5 × 10^{-2} mol dm^{-3} in acetonitrile for 2 h (Py = pyrene).

The absorption and fluorescence spectra of the pyrene-modified film are shown in Fig. 1 together with those of **1** in acetonitrile. Although the absorption spectrum of the film is broader and slightly red-shifted compared with that of **1**, a characteristic absorption can be assigned to the pyrenyl chromophore introduced into the film. The modified film shows fluorescence analogous to **1**. The vibrational structure of the fluorescence in 370–410 nm is largely different from that of **1** and the broad excimer-like band around 510 nm is observed. The results suggest that **1** is chemically introduced into the PHEMA film. The photochemical reaction of **2** and the PHEMA film also gave a characteristic absorption and fluorescence of the phenanthrene chromophore. It is noteworthy that the photochemical reaction failed in the absence of DMTP as the electron acceptor. The cation radical of the cyclopropane produced by one-electron transfer between the excited state of **1** or **2** and DMTP is responsible for the present surface functionalization reaction.[2]

In order to characterise the chemical structure of the film, we performed static secondary ion mass spectroscopy (SIMS) on the phenanthrene modified film. The presence of the



cationic fragments originating from the phenanthrene chromophore ($m/z = 190 \sim 232$) was confirmed while the DMTP fragments were not detected at all. Simple adsorption of the reactants onto the film cannot explain the present results. The pyrenyl or phenanthryl chromophore is thus concluded to be covalently attached to the hydroxy group of the film. Analogous results were obtained when the arylcyclopropanes were replaced by arylpropenes as reported previously.[3] As a model reaction, the photochemical reaction of **2** and methanol in the presence of DMTP selectively afforded 3-methoxy-1-(9-phenanthryl)butane and the regioselectivity of the reaction was in good accordance with that of 1-methyl-2-phenylcyclopropane.[2] This strongly suggests that the reaction of **1** or **2** with the hydroxy group of a PHEMA film proceeds in a regioselective manner, with 2-(4-arylbutyl) ether formation, as shown in Scheme 1. Recently, Dinnocenzo *et al.* reported that the nucleophilic addition of the arylcyclopropane radical cation proceeded with complete inversion of the carbon centre.[4] The present method is very useful to prepare the surface of asymmetic materials by the use of asymmetric arylcyclopropanes as a starting material. The arylcyclopropanes are therefore more advantageous than the arylpropenes in respect to the functionality added to the modified surface.[3] Besides a PHEMA film, the present reaction can be applied to the glass surface covered with 3-hydroxypropylsilane or 3-mercaptopropylsilane as well as to a polyvinylalcohol film. Spatial patterning of a PHEMA film by pyrene **1** was also shown to be possible with ~50 μm resolution. Simultaneous photochemical spatial patterning and functionalization of materials surface with the asymmetric arylcyclopropanes will provide new materials possessing the surface functionality of non-linear optical or ferroelectric properties.

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