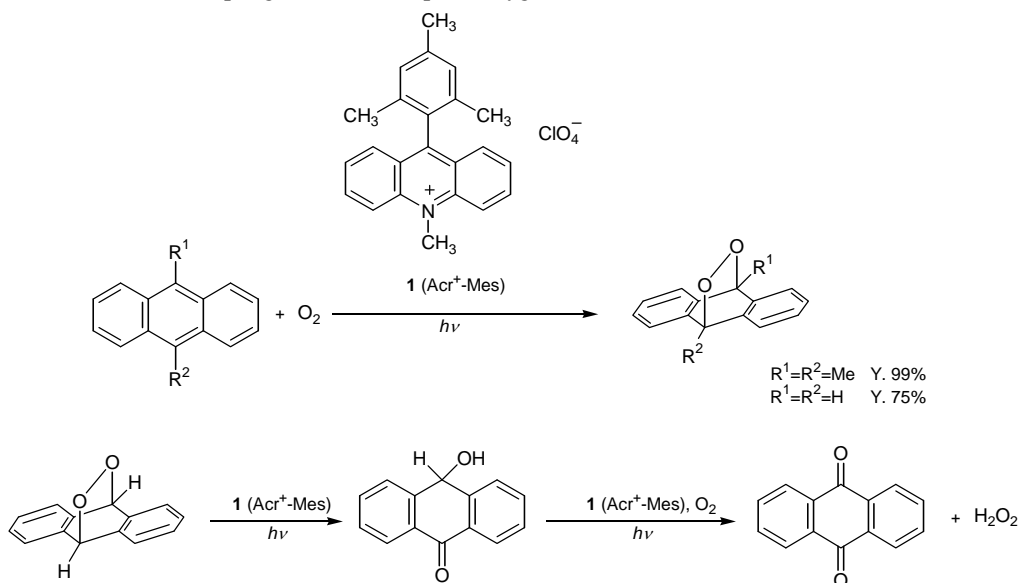


Selective Oxygenation using Effective Electron-Transfer Photocatalysts

The depletion of hydrocarbon energy reserves and the problems of global warming associated with the consumption of massive amounts of fossil fuels have made solar energy an attractive energy source. The sun already provides an enormous amount of energy on the earth and most animal and plant life is dependant upon this solar energy for their existence. The utilization of solar energy has already been developed in a number of fields such as photovoltaics and solar heating in order to maintain the quality of human life as well as the environment. One area that is still undeveloped is the potential for chemical reactions based on solar energy. Photosynthesis and respiratory chain, which are the crucial processes for both plant and animal life are based on electron-transfer reactions. If the photosynthetic process can be controlled by using artificial synthetic compounds, this process can lead to the development of useful solar energy system.

Fukuzumi and co-workers have developed the multi-step electron-transfer systems that are constructed by linking together the light-harvesting molecules, electron acceptors and electron donors through covalent bonds to mimic the photosynthetic reaction center. Moreover, they have successfully developed simple donor-acceptor dyads, 9-substituted-10-methylacridinium and coumarin derivatives, which appear to be superior to those of natural photosynthetic reaction center. These derivatives form high-energy and long-lived charge-separated state by a one step photoinduced electron transfer. They have also reported that these are very useful as catalysts of various photoreactions, i.e., radical coupling reactions and photooxygenations.

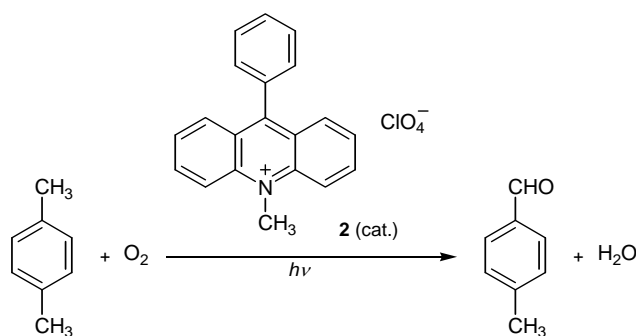


One example is the oxygenation reaction of anthracenes. Irradiation of visible light to oxygen-saturated acetonitrile solution containing 9-mesityl-10-methylacridinium perchlorate **1** (Acr⁺-Mes) first initiates formation of an electron-transfer state of Acr⁺-Mes. Then further electron transfer from anthracenes and the Acr⁺ moiety of Acr⁺-Mes to the Mes⁺ moiety and oxygen occur, respectively. This results in simultaneous production of anthracene radical cations and superoxide ion. Then, radical coupling of these two entities leads to the formation of 9,10-epidioxyanthracenes. When R¹ and R² are hydrogen, further photoirradiation facilitates the reaction to produce 10-hydroxyanthrone as an intermediate, and finally yields anthraquinone and hydrogen peroxide H₂O₂ as the final products. When olefins are used in place of anthracenes, dioxetane is selectively produced. Further photoirradiation cleaves an O-O bond of dioxetane, leading to formation of ketones.¹⁾

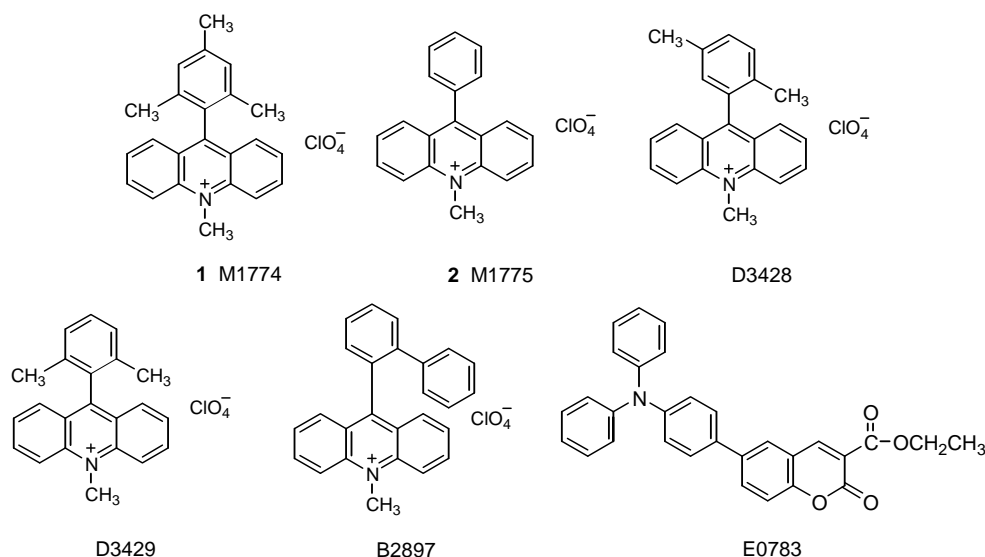
Keywords : environmentally-friendly oxidation, aerobic photo-oxidation, 9-substituted-10-methylacridinium

2008. Oct., R-5073E

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In addition, it has been reported that *p*-xylene can be selectively oxygenated using 9-phenyl-10-methylacridinium perchlorate **2** as a photocatalyst.²⁾ According to the study, it was demonstrated that visible light irradiation of an oxygen-saturated chloroform solution induced electron transfer from *p*-xylene to the singlet excited state of **2**, and yielded exclusively *p*-tolualdehyde as a final product with 100% selectivity. In this reaction, no di-aldehyde form has been produced by further photoirradiation, because *p*-tolualdehyde has a higher redox potential compared to *p*-xylene and hence *p*-tolualdehyde cannot undergo the photoinduced electron transfer as *p*-xylene does. Usually, powerful oxidizing agents are required to oxygenate *p*-xylene which frequently leads to over oxidation, making it difficult to obtain selectively mono-oxygenated *p*-xylene. Therefore, selective oxygenation of *p*-xylene using **2** has received much attention for future applications.



The 9-substituted-10-methylacridinium and coumarin derivatives that Fukuzumi and co-workers developed enable the efficient transformation of photoenergy into a chemical energy and to facilitate a useful reactions such as oxygenation. All the reactions occur using only photoenergy at ambient temperature, and additional energy from heating is not required. Moreover, air can be used as the oxygen source. Thus, the oxygenation reaction using these derivatives as a photocatalyst is an extremely clean and economical system, since reactions occur using photoenergy and oxygen which comprises 20% in the atmosphere.

Efficient use of our limited resources on the earth and environmentally-benign production of materials has attracted increasing attention. In this context, these derivatives provide promising applications.

M1774	9-Mesityl-10-methylacridinium Perchlorate	(1)	1g	5g
M1775	10-Methyl-9-phenylacridinium Perchlorate	(2)	1g	5g
D3428	9-(2,5-Dimethylphenyl)-10-methylacridinium Perchlorate		1g	5g
D3429	9-(2,6-Dimethylphenyl)-10-methylacridinium Perchlorate		1g	5g
B2897	9-(2-Biphenyl)-10-methylacridinium Perchlorate		1g	5g
E0783	Ethyl 6-[4-(Diphenylamino)phenyl]coumarin-3-carboxylate		200mg	1g

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