



# Spectroscopic observation of charge transfer complex formation of persistent perfluoroalkyl radical with aromatics, olefin, and ether



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## ABSTRACT

Charge transfer interaction of a persistent perfluoroalkyl radical, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl (PFR-1), with benzene and methyl substituted benzenes (toluene, *m*-xylene, mesitylene), 1-decene, and diethyl ether was investigated by UV–vis spectrophotometric measurement. It was found that the aromatic and olefinic  $\pi$ -electrons and also the unshared electron pair of ether can interact with the low-lying radical orbital of PFR-1 through CT complex formation. The Beer's law was confirmed in the range of 5–20 mM of PFR-1 for the aromatics and 5–40 mM for 1-decene and diethyl ether. The red shift of  $\lambda_{\max}$  occurred with increasing number of methyl substituents on the benzene ring.

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## 1. Introduction

The reactivity of the radical species has been well-studied, especially the fluorinated alkyl radicals by Dolbier et al. in depth, and reviewed [1]. However, unreactivity of the radical species has not been a main subject, and not much concerned, because the most important is the reactivity from the view points of various applications such as the radical polymerization or functionalization based on the radical chain mechanism. Since the discovery of the persistent perfluoroalkyl radicals of perfluoro-2-methyl-3-isopropyl-3-pentyl and perfluoro-2,4-dimethyl-3-isopropyl-3-pentyl (PFR-1 and PFR-2 abbreviations are respectively used hereinafter; Scheme 1), so-called Scherer radicals, they have attracted the scientific community with its uniqueness of semantically wrong nature of no reactivity even against 100% fluorine gas in an extreme case of PFR-2 [2]. The study on these persistent perfluoroalkyl radicals has been hampered with difficult availability due to the need of manipulation of fluorine gas or an electrochemical fluorination cell for the preparation and has accordingly appeared sporadically in the literatures [3–10]. The most recent ones are on the use of PFR-1 as the convenient trifluoromethyl radical source for initiating the polymerization of fluoro monomers [11–13]. Here we unveil some new cryptic nature of the persistent perfluoroalkyl radicals on the unexpected

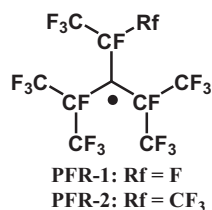
intermolecular interactions with the electrons of some chemicals such as  $\pi$ -electrons of the benzene derivatives or 1-decene and also with the unshared electron pairs of ether through charge-transfer (CT) complexation.

## 2. Results and discussion

For some applicational reason, we added the persistent perfluoroalkyl radical solution containing PFR-1 in ca. 63% concentration into benzene, and then we noticed some faint coloration occurred to give a very pale yellow benzene solution on the fluorous phase of the vessel bottom. The GC analysis of this pale yellow colored benzene solution gives only benzene and PFR-1 peaks, suggesting no chemical reactions between PFR-1 and benzene. So we expect that the color is due to some interaction of PFR-1 with benzene and not by some unexpected reaction products derived from PFR-1 and benzene. Then, we wondered if the coloration and concentration relationship follows the Beer's law or not. The UV–vis absorption spectra in the range between 280 and 780 nm were recorded with various concentrations of PFR-1 (2.50, 5.26, 10.8, 21.4, and 43.3 mM) in benzene (Fig. 1). The Beer's law apparently operates from 2.50 up to 21.4 mM, however, obviously deviates from the linear relationship over 21.4 mM. This is due to the limited solubility of PFR-1 in benzene (Fig. 2). The maximum absorption  $\lambda_{\max}$  was observed at 380 nm with a molar extinction coefficient  $\sigma_{\max}$  of 38.3.

We then investigated the influence of the methyl substituents introduced into the benzene ring. We chose toluene (methylbenzene), *m*-xylene (1,3-dimethylbenzene), and mesitylene

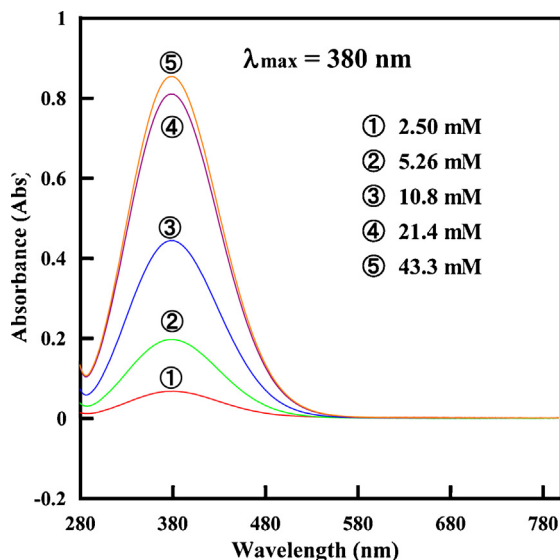
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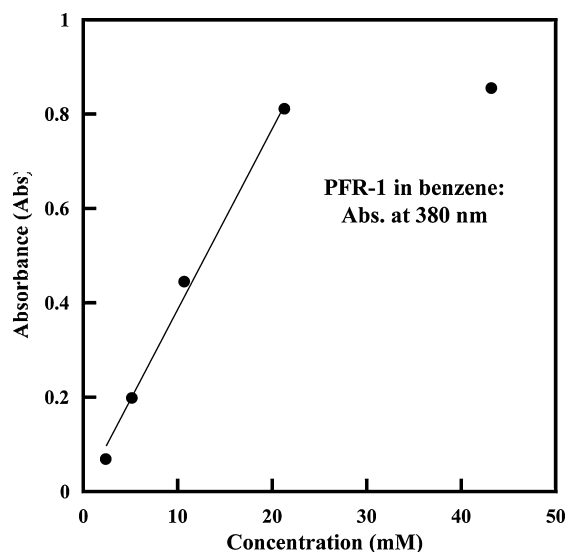
**Scheme 1.** The structures of the persistent perfluoroalkyl radicals.

(1,3,5-trimethylbenzene) as representatives. As shown in Fig. 3, the coloration becomes red-shifted with more methyl substituents in the benzene ring. The UV–vis absorption spectra were measured in the same manner to see if the Beer's law works or not. All benzene derivatives are subjected to the Beer's law in the same concentration range from ca. 2 mM to ca. 20 mM, and somehow saturation occurred in all cases near ca. 40 mM concentration, again due to the solubility limit of PFR-1 (Fig. 4). The red shift occurred with successive methyl substitutions. Thus, the values of the  $\lambda_{\max}$  changed from 380 nm of benzene to 406, 438 and 477 nm for toluene, m-xylene, and mesitylene, respectively. The corresponding molar extinction coefficients  $\sigma$  values for those were 37.9, 26.8, and 23.8, respectively. Both phenomena may be in line with the increasing  $\pi$ -electron densities of the benzene rings caused by methyl substituents although further theoretical study is needed. The blank UV–vis measurement was carried out for the perfluorohexane solution of PFR-1 at the concentration of 40 mM for the same window of 280–780 nm (Fig. 5). It was confirmed that PFR-1 itself had no absorption at the range of 280–780 nm (only the shoulder was seen outside the range 280–780 nm). Therefore, the UV–vis absorption measured in the above were proved to be all based on the CT mechanisms between PFR-1 and the benzene derivatives.

We then investigated on the  $\pi$  electrons of the olefins which are less dative than the above benzene derivatives for the CT interaction with PFR-1. We chose 1-decene as a representative for this purpose. The coloration was invisible in this case as is seen in the picture (Fig. 6). However, the UV–vis absorption spectra of the 1-decene solution of PFR-1 measured under various concentrations supported the existence of the same kind of intermolecular



**Fig. 1.** UV–vis spectra of the PFR-1 solution in benzene under various concentrations.

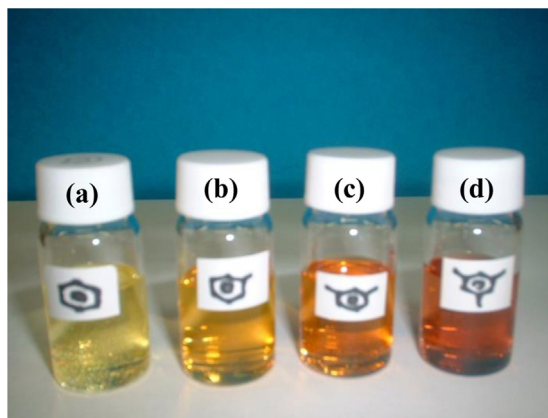


**Fig. 2.** The plot of the absorbances under various concentrations of PFR-1 (2.50, 5.26, 10.8, 21.4, 43.3 mM) in benzene at the  $\lambda_{\max}$  (380 nm). The good linearity between 2.5 and 21.4 mM, follows the Beer's law (correlation coefficient is 0.996). The molar extinction coefficient was 38.3.

interactions which was subjected to Beer's law in the same concentration range from ca. 2 mM to ca. 20 mM, and further to ca. 40 mM concentration in contrast with the benzene derivatives, suggesting higher solubility of PFR-1 in 1-decene (Fig. 7). The values of  $\lambda_{\max}$  and  $\sigma_{\max}$  were 344 nm and 12.5 Abs mol<sup>-1</sup> cm<sup>-1</sup>, respectively.

We next concerned the possibility of CT interaction with the unshared electron pair of the ether. A very pale yellow color developed when PFR-1 was dissolved into diethyl ether. The Beer's law was satisfied in the whole range of concentrations 2.58, 5.67, 11.8, 22.1 and 43.5 mM like the 1-decene case due to the high solubility of PFR-1 in diethyl ether (Fig. 8). The values of  $\lambda_{\max}$  and  $\sigma_{\max}$  were 332 nm and 15.4, respectively.

It is not unusual to see such coloration by the combination of electron donors and acceptors through the CT complex formation. The well known in fluorine chemistry is the CT complex formation between hexafluorobenzene and benzene or *N,N*-dialkyl anilines [14,15]. However, there is no precedent, in the best of our



**Fig. 3.** Coloration of the methylated benzene solutions of PFR-1 by charge-transfer interactions. Red shift occurred with increasing number of methyl substituents in benzene ring.

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