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

Taizo Ono *, Kazutoku Ohta

National Institute of Advanced Industrial Science and Technology (AIST), Research Institute of Instrumentation Frontier, 2266-98, Anagahora, Moriyama, Nagoya, Aichi 463-8560, Japan

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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 π-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 λ_{max} occurred with increasing number of methyl substituents on the benzene ring.

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 π-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-visual 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 λ_{max} was observed at 380 nm with a molar extinction coefficient σ_{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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* Corresponding author. Tel.: +81 052 736 7491; fax: +81 052 736 7224.
E-mail address: t.ono@aist.go.jp (T. Ono).

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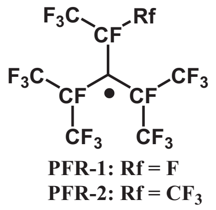

Scheme 1. The structures of the persistent perfluoroalkyl radicals.

(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 λ_{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 σ values for those were 37.9, 26.8, and 23.8, respectively. Both phenomena may be in line with the increasing π-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 π electorons 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 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 λ_{max} and σ_{max} were 344 nm and 12.5 Abs mol^{-1} cm^{-1}, respectively.

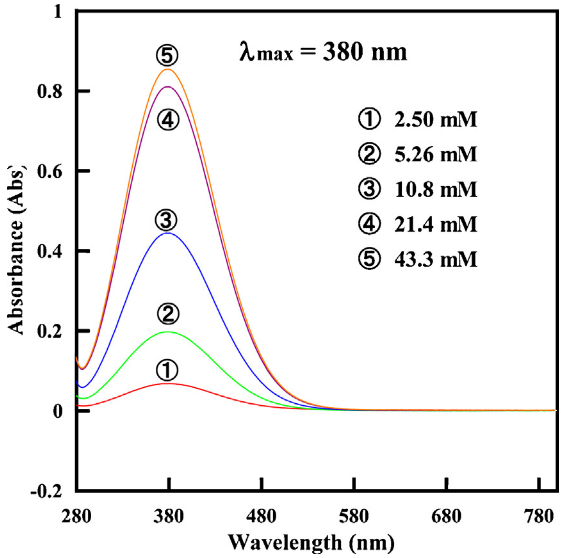

Fig. 1. UV–vis spectra of the PFR-1 solution in benzene under various concentrations.

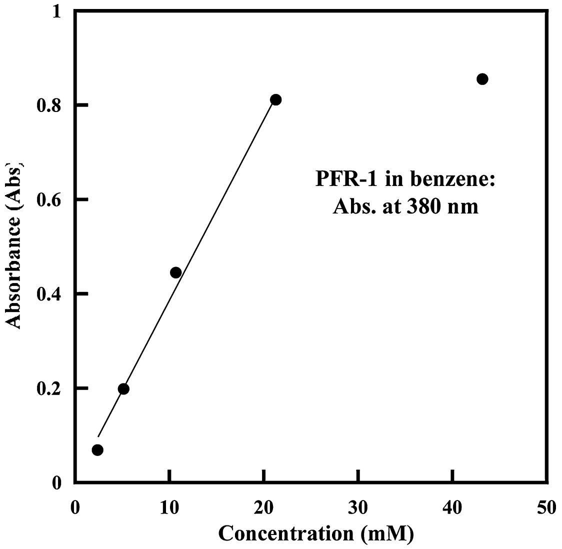

Fig. 2. The plot of the absorbances under various concentrations of PFR-1 (2.50, 5.26, 10.8, 21.4, 43.3 mM) in benzene at the λ_{max} (380 nm). The good linearity between 2.5 and 21.4 mM, follows the Beer' law (correlation coefficient is 0.996). The molar extinction coefficient was 38.3.

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 λ_{max} and σ_{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

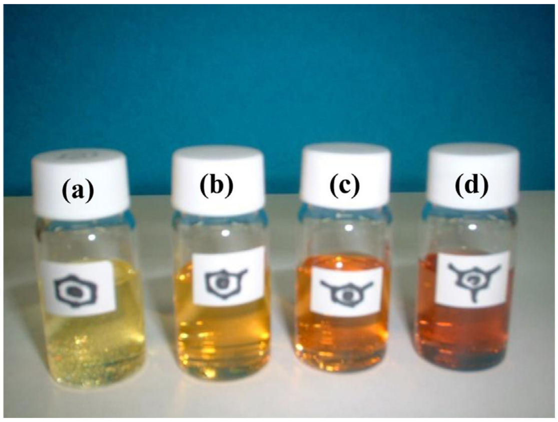

Fig. 3. Coloration of the methylated benzene solutions of PFR-1 by charge-transfer interactions. Red shift occurred with increasing number of methyl substituents in benzene ring.

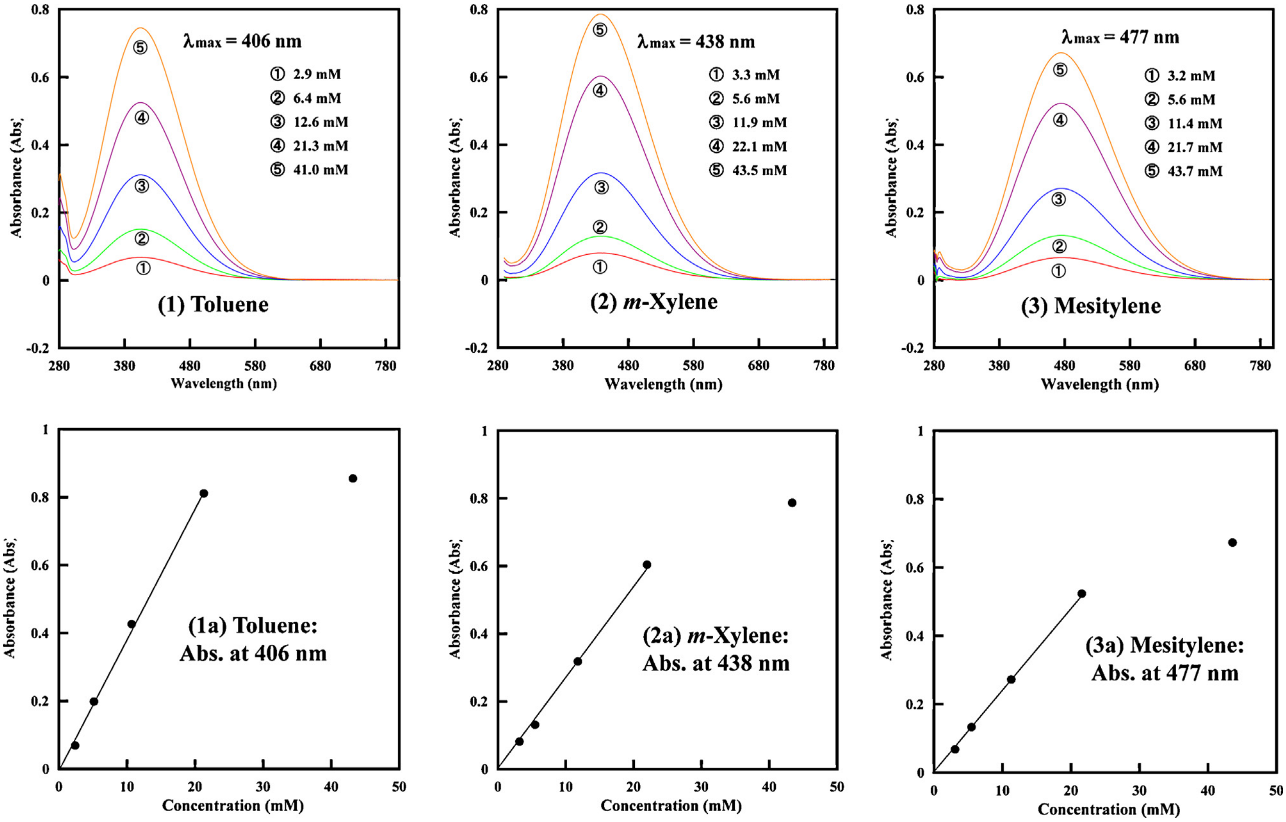

Fig. 4. UV–vis absorption specta of PFR-1 solutions in various methylated benzene derivatives, (1) toluene, (2) *m*-xylene, and (3) mesitylene under various concentrations. The absorbance vs concentration plot was made at each λ_{max} (1a) 406 nm for toluene, (2a) 438 nm for *m*-xylene, (3a) 477 nm for mesitylene. The Beer's law operates at 3–20 mM, but not at ca. 45 mM due to the solubility limit of PFR-1 in each benzene derivative (correlation coefficients are 0.9977, 0.9993, and 0.9998, respectively. The corresponding molar extinction coefficients are 37.9, 26.8, 23.8, respectively.

knowledge, for the CT complex formation between alkyl radical and benzene, olefin and ether.

Undoubtedly, a main reason for the persistency of PFR-1 comes from the steric hindrance caused by 5 trifluoromethyl groups surrounding the radical center, by extruding ups and downs from the nodal plane passing through three carbons next to the radical center. As is well known, the size of a trifluoromethyl group is between the sizes of *iso*-propyl and *tert*-butyl groups in the hydrocarbon system [16]. These trifluoromethyl armor prevent any reagents from attacking the radical center. For example, a biradical oxygen molecule has no access to the radical center and even the smallest reagent gas, a hydrogen molecule, is also unable to access to the radical center due to the presence of this armor, thus there is no reactivity to PFR-1 [17]. With this sterically rigid armor in mind, the molecular orbital interactions between the radical's SOMO and benzene's HOMO seem to be difficult. We wonder if some CT interaction may occur through the rim of the PFR-1 molecule, but at first we investigated that CT interaction may occur between π-electrons of the benzenes and the PFR-1 precursor olefin, hexafluoropropene trimers (perfluoro-4-methyl-3-isopropyl-2-pentene and perfluoro-2,4-dimethyl-3-ethyl-2-pentene), because these perfluoroolefins has a low-lying C=C double bond orbital embedded inside the trifluoromethyl armor with almost the same molecular frameworks. Thus, we examined the UV–vis spectrum of the toluene solution of a hexafluoropropene trimer mixture (ca. 40 mM). The shoulder absorbance near 280 nm due to the π–π^* transition of the C=C double bond appeared, but there was no CT-based UV–vis absorption (Fig. 9). Therefore, it is very unlikely that the CT interaction of PFR-1 with the solvents studied above may occur through the direct HOMO-SOMO interactions. At present moment, all the discussion given here is qualitative and not rigid, so that the in-depth theoretical treatment for what mechanism operates for the present CT-complex system is necessary for the future study.

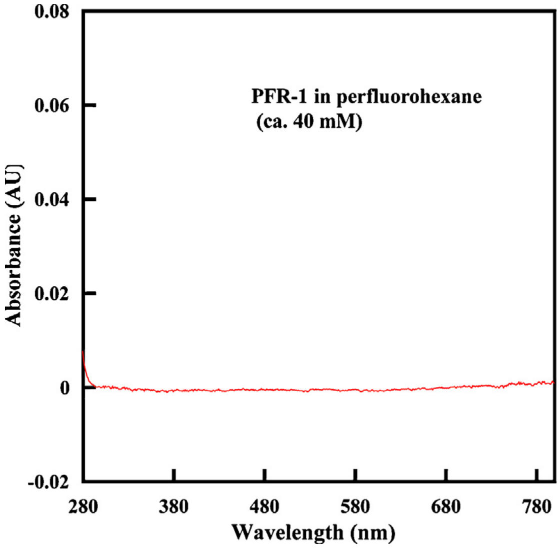

Fig. 5. A UV–vis spectrum of the PFR-1 solution (ca. 40 mM) in perfluorohexane showed no absorption at the range of 280–780 nm.

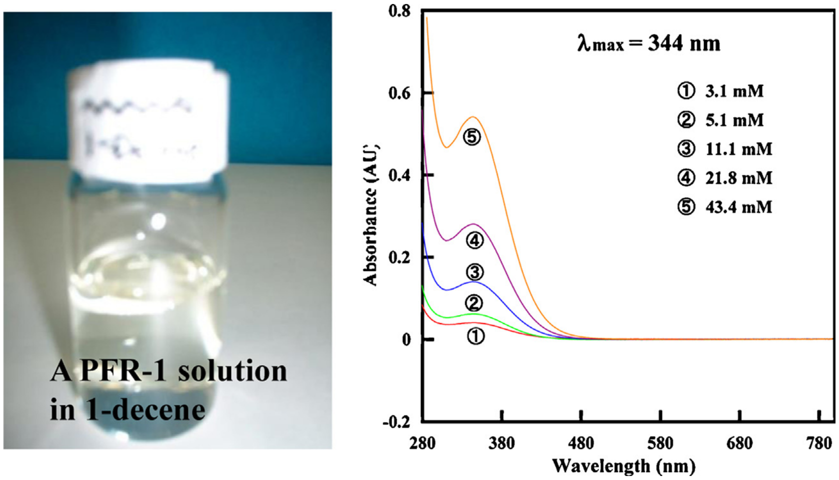

Fig. 6. The photo of the PFR-1 solution (43.4 mM) in 1-decene and the UV–vis spectra measured under various concentrations (3.1, 5.1, 11.1, 21.8, and 43.4 mM).

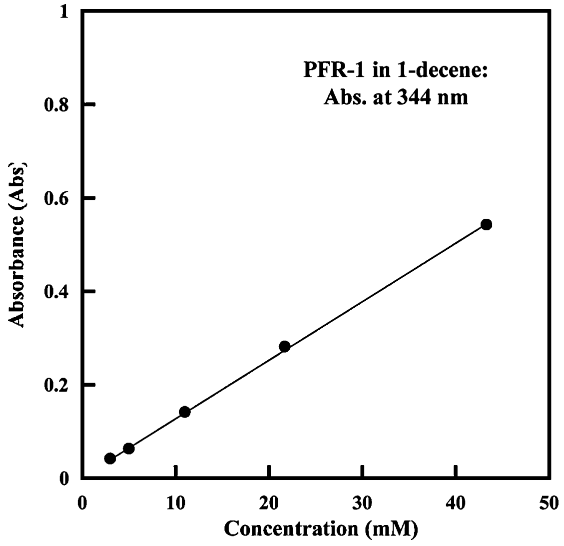

Fig. 7. The plot of the absorbances under various concentrations of PFR-1 (3.1, 5.1, 11.1, 21.8, and 43.4 mM) in 1-decende at the λ_{max} (344 nm). The good linearity in the whole range shows the Beer' law is satisfied (correlation coefficient is 0.9996). The molar extinction coefficient was 12.5.

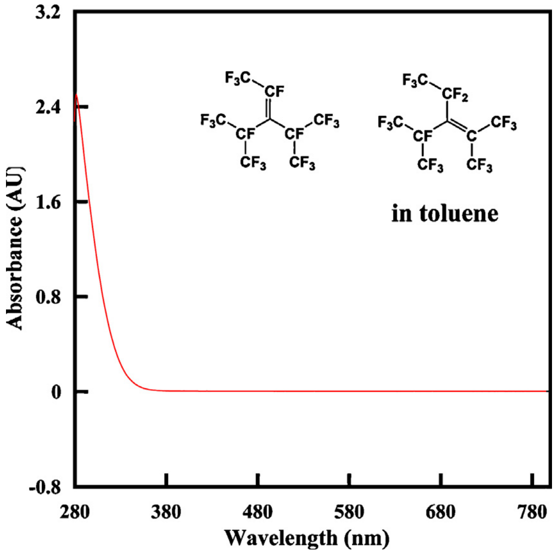

Fig. 9. UV–vis spectrum of the perfluorohexane solution of hexafluoropropene trimers containing perfluoro-4-methyl-3-isopropyl-2-pentene and perfluoro-2,4-dimethyl-3-ethyl-2-pentene with 1:2 ratio in 40 mM concentration.

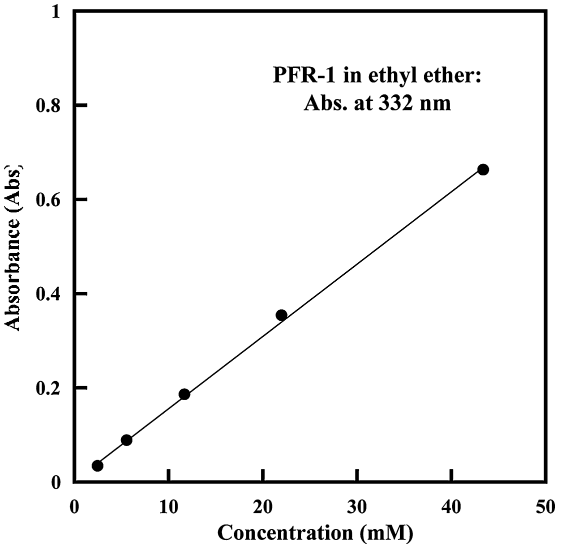

Fig. 8. The plot of the absorbances under various concentrations of PFR-1 (2.58, 5.67, 11.8, 22.1, and 43.5 mM) in diethyl ether at the λ_{max} (332 nm). The good linearity in the whole range shows the Beer' law is satisfied (regression coefficient is 0.9993). The molar extinction coefficient was 15.4.

3. Conclusions

The charge transfer (CT) interactions between the persistent perfluoroalkyl radical, perfluoro-2-methyl-3-isopropyl-3-pentyl (PFR-1), and π-electrons of aromatics were confirmed by the coloration in the visible light region. The UV–vis absorption spectra showed the Beer's law operated in the range of ca. 3–20 mM for benzene, toluene, *m*-xylene, and mesitylene, and the red shift of λ_{max} occurred with increasing numbers of the methyl substituents, thus, 380, 406, 438 and 477 nm in this order. The spectroscopic saturation of CT-band absorption seen in ca. 40 mM of PFR-1 in these benzene derivatives is very likely to the solubility limit of the PFR-1 in these aromatic solvents. The same kind of CT interactions of PFR-1 with π-electrons of 1-decene and also with the unshared electron pair of diethyl ether was observed. Due to the higher solubility of PFR-1 in 1-decene and diethyl ether, the Beer's law worked at higher concentration (up to ca. 40 mM of PFR-1).

4. Experimental

Hexafluoropropene trimers are obtained as a mixture of perfluoro-4-methyl-3-isopropyl-2-pentene and perfluoro-2,4-dimethyl-3-ethyl-2-pentene with almost 1–2 molar ratio from

Daikin Industries Co. Ltd. 1-Decene and diethyl ether were distilled prior to use. PFR-1 was prepared by direct fluorination of the hexafluoropropene trimers mixture at room temperature by introducing undiluted fluorine gas into the bottom of the long column of the mixture placed in a long glass reaction tube under vigorous stirring. The rate of the gas introduction was regulated so as to be totally absorbed and F_2 bubbles does not reach the surface of the reaction mixture. Under this reaction conditions, all fluorine gas was utilized to the full for the formation of PFR-1 without any loss. The fluorination was sustained until all the starting trimers are consumed. The resultant solution was analyzed by GC to be 63% of PFR-1 and 37% of perfuoro-2,4-dimethyl-3-ethylpentane (area % by GC). The UV–vis measurement was carried out on the sample solutions obtained by vigorously shaking the above 63% PFR-1 solution with each solvent at the concentration from ca. 3 to 40 mM based on the assumption that the added PFR-1 is all dissolved into the solvent. However, in the benzene and benzene derivatives cases, fluorous phases remained at the bottom of the solutions to some extent in the ca. 40 mM concentrations and thus, the real concentration is less than the expected values for these cases. The UV–vis measurement was carried out over the range from 280 to 780 nm by using Shimadzu UV–VIS–NIR Spectrometer UV-3600 with a quartz tube having a 1-cm light path.

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