

## **<sup>19</sup>F NMR Study on the Charge-Transfer Process between Ground-State Acceptor Fluoranil (or Pentafluorophenyl Carboxylate) and Some N-Alkylphenothiazine Donors**

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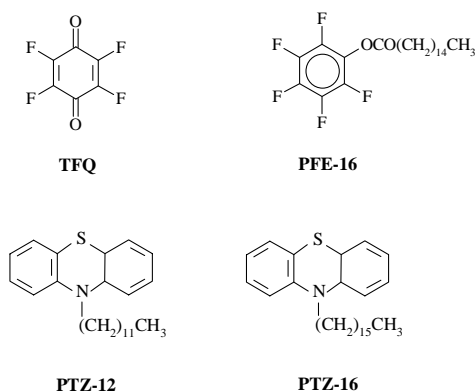
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**Abstract:** The line positions of <sup>19</sup>F NMR absorption of fluoranil (**TFQ**) or pentafluorophenyl carboxylate (**PFE-16**) in the presence of N-alkylphenothiazine donors have been measured. By comparing the <sup>19</sup>F chemical shift in C<sub>6</sub>D<sub>6</sub> of **TFQ** or **PFE-16** in the absence of the donor with those in the presence of the donor, the difference of these chemical shifts was found to be large. In the presence of the donor, <sup>19</sup>F upfield shifts of **TFQ** or **PFE-16** have been observed. The experimental results showed that there is a charge-transfer process between **TFQ** or **PFE-16** and the donor. When **TFQ** or **PFE-16** accepts the charge from the donor, its <sup>19</sup>F resonance moves upfield.

**Keywords:** NMR, charge-transfer, chemical shift.

Photoinitiated electron-transfer processes are of fundamental interest in chemistry. Generally there are two kinds of study. 1) Studies involving intermolecular electron transfers of the excited chromophore of an acceptor (or donor) with the ground state of a donor (or acceptor). 2) Studies of intramolecular electron transfers between linked acceptors and donors. In pursuing our study on aggregation and self-coiling of organic molecules brought about by hydrophobic-lipophilic interactions (HLI), we are naturally interested in studying whether HLI can also facilitate the above-mentioned electron-transfer processes. Intramolecular electron transfer is of basic interest in supramolecular photochemistry<sup>5</sup> and of practical importance in the molecular mimicry of photosynthetic processes. Several research systems have been reported<sup>6-9</sup>. One system consists of covalently linked carotenoid-porphyrin-quinone derivatives and others consist of linked donor-chromophore-acceptors, *e.g.*, a substituted tris (bipyridyl) ruthenium (II) [Ru(bpy)<sub>3</sub><sup>2+</sup>] chromophore covalently attached through flexible polymethylene chains to a N, N'-diquaternary-2, 2'-bipyridinium salt (diquat, DQ<sup>2+</sup>) electron acceptor and to a phenothiazine donor linked through a bipyridine and another polymethylene chain. It has been reported that NMR methodology can be applied to the study of charge-transfer process between a donor and an acceptor<sup>10-12</sup>. Upfield <sup>19</sup>F chemical shift in NMR

measurement of **TFQ** with a donor such as **PTZ-12** indicates that the charge density of **TFQ** is increased by the process of charge-transfer. The above-mentioned facts indicate that fluoranil is a good acceptor, and we thus expect that **PFE-16** would behave similarly. The present work shows that the aforesaid expectation is correct. The acceptors and the donors used in the present work are showed in **scheme 1**.

**Scheme 1**

## Experimental

Fluoranil (**TFQ**) was purchased and used without further purification. Pentafluorophenyl palmitate (**PFE-16**) and N-hexadecyl phenothiazine (**PTZ-16**) are new compounds<sup>13a</sup>, **PTZ-12** has been reported<sup>13b</sup> without data on UV and elemental analysis. The prepared samples were identified by <sup>1</sup>H NMR, <sup>19</sup>F NMR, UV-Vis spectra and elemental analysis.

## Physical measurements

The <sup>19</sup>F NMR spectra were recorded on a Bruker Am 300 NMR spectrometer at 282.386 MHz.

### Pentafluorophenyl palmitate (**PFE-16**)

White solid, mp 50.5–51.8 °C. UV-Vis: λ<sub>max</sub> = 198nm (ε = 1.1 × 10<sup>4</sup> M<sup>-1</sup>·cm<sup>-1</sup> cyclohexane). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ0.9–1.8 (29H, m), δ2.7 (2H, t), <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>) δ-75.89 (2F, d), δ-81.32 (1F, t), δ-85.55(2F, t). Anal. Calcd for C<sub>22</sub>H<sub>31</sub>O<sub>2</sub>F<sub>5</sub>: C, 62.56; H, 7.35; F, 22.51. Found: C, 62.60; H, 7.50; F, 22.46.

### N-Dodecylphenothiazine (**PTZ-12**)

Light yellowish liquid, UV-Vis: λ<sub>max</sub> = 256 nm (cyclohexane). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ0.4–1.4 (23H, m), δ3.0 (2H, t), δ6.1–6.5 (8H, m), Anal. Calcd for C<sub>24</sub>H<sub>33</sub>NS: C, 78.47; H, 8.99; N, 3.81; S, 8.72, Found: C, 78.46; H, 9.10; N, 3.42; S, 9.09.

### N-Dexadecylphenothiazine (PTZ-16)

White solid, mp 50~51 °C, UV-Vis:  $\lambda_{\text{max}} = 256\text{nm}$  ( $\epsilon = 7.5 \times 10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$  cyclohexane). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ 0.4~1.4 (31H, m),  $\delta$ 3.0 (2H, t),  $\delta$ 6.1~6.7 (8H, m), Anal. Calcd for C<sub>28</sub>H<sub>41</sub>NS: C, 79.43; H, 9.69; N, 3.30; S, 7.56, Found: C, 79.48; H, 10.22; N, 2.78; S, 8.03.

### Results and Discussion

The chemical shift of <sup>19</sup>F atoms of **TFQ** is -18266.5 Hz in the absence of the donor in C<sub>6</sub>D<sub>6</sub> solutions; in the presence of **PTZ-12** as a donor, the <sup>19</sup>F chemical shift of **TFQ** is -18953.3 Hz. The difference of these two <sup>19</sup>F chemical shifts is 686.8 Hz. In <sup>19</sup>F NMR spectrum, a more negative <sup>19</sup>F chemical shift corresponds to a shift upfield. The appearance of the upfield <sup>19</sup>F chemical shift of **TFQ** in the presence of **PTZ-12** indicates that there is a charge transfer from **PTZ-12** to **TFQ** in C<sub>6</sub>D<sub>6</sub> solution. The other interesting example is that with **PFE-16** as an acceptor and with **PTZ-16** as a donor in C<sub>6</sub>D<sub>6</sub> solution. In the <sup>19</sup>F NMR spectrum of **PFE-16** alone, the line position of *o*-fluorine atom in phenyl ring is -75.89 ppm, the chemical shift of *p*-fluorine atom in phenyl ring is -81.32 ppm and that of *m*-fluorine atom is -85.55. In the presence of **PTZ-16**, the chemical shifts of *o*, *p*, *m*-fluorine atoms in phenyl ring are -77.25, -81.55 and -85.96 ppm respectively. Thus these results indicate that there is a charge transfer from **PTZ-16** to **PFE-16**. The result also shows that **PFE-16** can be used as an acceptor.

On the basis of the above-mentioned results, it will be possible to study the electron-transfer process facilitated by HLI between excited N-hexadecyl carbazole (**CBZ-16**) and **PFE-16**. In consequence of an electron-transfer process the fluorescence of (**CBZ-16**)<sup>\*</sup> can be quenched by adding **PFE-16** in the  $\Phi = 0.40$  DX-H<sub>2</sub>O system, where  $\Phi$  is the volume fraction of the organic component (dioxane) of an aquiorano mixture. The fluorescence quenching of excited **CBZ-16** by adding **PFE-16** has been observed and preliminary results of this study can be summarized by **Table 1**<sup>13a</sup>, which shows that the  $I_{353\text{ nm}}$  value decreases with increasing [**PFE-16**] and thus suggests that HLI may have facilitated this process. In conclusion, both the ground-state charge-transfer process between **PTZ-16** and **PFE-16** in C<sub>6</sub>D<sub>6</sub> and electron transfer fluorescence quenching process between excited **CBZ-16** and **PFE-16** have been demonstrated. Furthermore, **PFE-16** as an acceptor in charge-transfer process has been demonstrated for the first time.

**Table 1** The dependence of  $I_{353\text{ nm}}$  of excited **CBZ-16** ( $1 \times 10^{-7}$  M) on the amount of **PFE-16** added in the  $\Phi = 0.40$  DX-H<sub>2</sub>O system.

<b>PFE-16</b> ( $10^{-7}$ M)	0	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
$I_{353\text{ nm}}$	222.6	216.9	208.3	199.8	192.7	188.1	179.3	172.7	166.9

\* The experimental uncertainty is  $\pm 5\%$ .

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