EPR Study on the Complex Formed by Charge-Transfer Process between Ground-state Acceptor 2,3-Dicyano-5,6-dichloro-1,4-benzoquinone and Some Donors and on Cation Radical of Perylene (or Pyrene)

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EPR study showed that the semi-quinone radical anion of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) was formed in a charge transfer process between ground-state DDQ as acceptor and each one of following ground state donors, i.e., 4-methyl-4'-tridecyl-2, 2'-bipyridyl; 4-methyl-4'-nonyl-2, 2'-bipyridyl; bis(2, 2'-bipyridyl)(4-methyl-4'-heptadecyl-2, 2'-bipyridyl)ruthenium(2+) perchlorate and perylene. EPR study also showed that there are perylene cation radical and pyrene cation radical in the following experimental conditions; (a) in 98% sulfuric acid. (b) 10^{-3} mol/L perylene (or pyrene) was dissolved in trifluoroacetic acid-nitrobenzene (1:1 V/V).

Keywords   EPR, charge-transfer, oxidation

Introduction

Photoinduced charge-transfer processes as a means of capturing and storing solar energy have been studied extensively. Furthermore, the measurement of the reactive intermediate in photoinduced charge-transfer process has played a very important role for the understanding of this process, and it is well known that EPR can be applied to the study of organic charge-transfer complexes.[1] We have been interested in the hydrophobic acceleration of electron-transfer fluorescence quenching processes,[2-5] and have also studied the complex formed by charge-transfer process between ground-state acceptor chloranil and nine donors with EPR.[1] This paper demonstrates the formation of complexes by charge-transfer processes between ground-state acceptor 2,3-dicyano-5,6-dichloro-

1,4-benzoquinone (DDQ) and some new donors as shown in Scheme 1 with EPR. However, no EPR signal of the perylene cation radical could be observed under similar experimental conditions.

Scheme 1
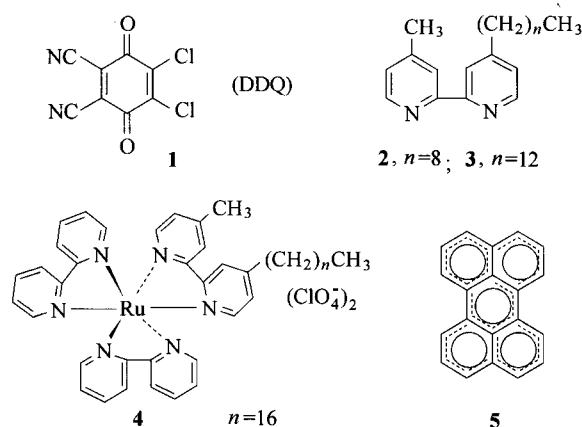
Experimental

Physical measurement

Measurement of EPR spectra   All EPR spectra were measured on the varian E-112 spectrometer with X-band, field moduration frequency 100 kHz. The magnetic field was determined by an H NMR fieldmeter and the microwave frequency was measured by a frequencymeter for super-high frequency. All samples were recorded at

room temperature.

Materials

4-Methyl-4'-tridecyl-2, 2'-bipyridyl; 4-methyl-4'-nonyl-2,2'-bipyridyl and bis(2,2'-bipyridyl)(4-methyl-4'-heptadecyl-2,2'-bipyridyl)ruthenium(2 +) perchlorate were prepared according to literature procedures.[6-10] The samples were identified by elemental analysis, ^{1}H NMR and mass spectrum.

4-Methyl-4'-nonyl-2, 2'-bipyridyl (**2**)　　white plate crystal, mp 52.5—53.5. ^{1}H NMR (CDCl$_3$) δ: 0.95(br. s, Hz, 3H); 1.38(br. s, 12H); 1.60—1.90(m, 2H); 2.53(s, 3H); 2.75(t, J = 6.3, Hz, 2H); 7.15(d, J = 4.8 Hz, 2H); 8.25(s, 2H); 8.55 (d, J = 4.8 Hz, 2H). Mass spectrum [EI, m/z (relative intensity)]: 184 (100.00), 197 (85.36), 295 (4.43, M$^+$ − 1), 296(9.02, M$^+$), 297(7.97, M$^+$ + 1), 298(1.58, M$^+$ + 2). Anal. C$_{20}$H$_{28}$N$_2$. Calcd: C, 81.03; H, 9.52; N, 9.45. Found: C, 80.92; H, 9.85; N, 9.01.

4-Methyl-4'-tridecyl-2,2'-bipyridyl (**3**)　　white needle crystal, mp 62.5—65.5. ^{1}H NMR (CDCl$_3$) δ: 0.90 (t, J = 4.5 Hz, 3H); 1.32 (br. s, 20H); 1.53—1.90(m, 2H); 2.45(s, 3H); 2.71(t, J = 6.3 Hz, 2H); 7.15(d, J = 4.5 Hz, 2H); 8.25(s, 2H); 8.55(d, J = 4.5 Hz, 2H). Mass spectrum [EI, m/z (relative intensity)]: 184(93.85), 197(100.00), 351 (6.61), 352 (10.65), 353 (7.42), 354 (1.63,). Anal. C$_{24}$H$_{36}$N$_2$. Calcd: C, 81.76; H, 10.29; N, 7.95. Found: C, 81.50; H, 10.05; N, 7.50.

Bis (2, 2'-bipyridyl) (4-methyl-4'-heptadecyl-2, 2'-bipyridyl)ruthenium(2 +) perchlorate (**4**) freshly red solid with metallic luster. ^{1}H NMR (acetone-d_6) δ: 0.85 (t, J = 6.4 Hz, 3H); 1.25 (br. s, 28H); 1.60—1.73(m 2H); 2.55(s, 3H); 2.84(t, J = 7.9 Hz, 2H); 7.35—7.45(m, 2H); 7.50—7.60 (m, 4H); 7.83(d, J = 5.9 Hz, 2H); 7.95—8.05 (m, 4H); 8.15—8.27m, 4H); 8.70—8.76 (m, 2H); 8.81 (d, J = 8.2 Hz, 4H). Anal. C$_{48}$H$_{60}$N$_6$O$_8$Cl$_2$Ru. Calcd: C, 56.47; H, 5.92; N, 8.23; Cl, 6.94. Found: C, 56.37; H, 5.87; N, 8.23; Cl, 7.01.

Perylene was purchased from Aldrich Co. (99$^+$ %) and used without further purification. Pyrene was purified by recrystallization twice from absolute alcohol. CF$_3$COOH and DDQ were purchased from Fluka

Co. and used as received. CH$_3$CN (spectral grade), C$_6$H$_5$NO$_2$ (AR) and H$_2$SO$_4$ (98%, AR) were used without further purification.

Results and discussion

In the experiments of charge-transfer processes, the single-line EPR signal of the samples have been observed (see Figs. 1—4). Our data show that the semiquinone radical anion of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) is formed in a charge-transfer process between ground state DDQ as acceptor and some ground state donors, namely, 4-methyl-4'-tridecyl-2,2'-bipyridyl (**3**); 4-methyl-4'-nonyl-2, 2'-bipyridyl (**2**); bis (2, 2'-bipyridyl) (4-methyl-4'-heptadecyl-2, 2'-bipyridyl) ruthenium(2 +) perchlorate (**4**) and perylene (**5**) (or pyrene). **2** and **3** are well-known ligands in coordination chemistry. In the ground-state charge-transfer process of DDQ with perylene it is possible that there is a ring-current effect because DDQ has a deficient electron ring-current and perylene has a rich electron ring-current.[1] The ligands **2** and **3** have electron-pair donating ability, but **4** is a metallic complex without free ligands. Interestingly, our result indicates that the ruthenium complex could also be used as a donor in a charge-transfer process withDDQ. For pyrene the EPR spectrum is very similar to Fig. 4. However, in the above-mentioned charge-transfer process the cation radical of perylene (or pyrene) could not be found by EPR.

Notably, EPR spectrum of radical cation of perylene produced by the oxidation using an oxidizing agent, i.e., 98% H$_2$SO$_4$, has been reported[11] by Malachesky et al., while Reymond and Fraenkel[12] have reported a new method for the synthesis of cation radicals of aromat-
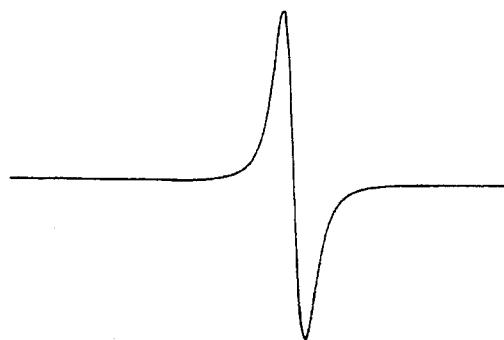

Fig. 1　EPR spectrum of DDQ (1.1 × 10^{-2} mol/L) in CH$_3$CN in the presence of **2** (4.8 × 10^{-2} mol/L).
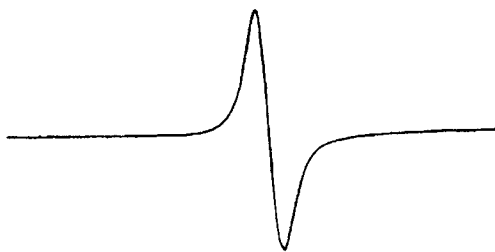
Fig. 2   EPR spectrum of DDQ $(1.1 \times 10^{-2}$ mol/L) in CH$_3$CN in the presence of **3** $(5.3 \times 10^{-2}$ mol/L).
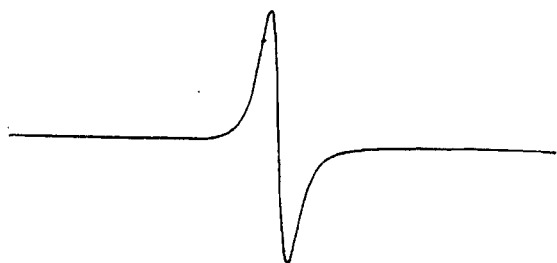

Fig. 3   EPR spectrum of DDQ $(1.0 \times 10^{-2}$ mol/L) in CH$_3$CN in the presence of **4** $(3.0 \times 10^{-3}$ mol/L).
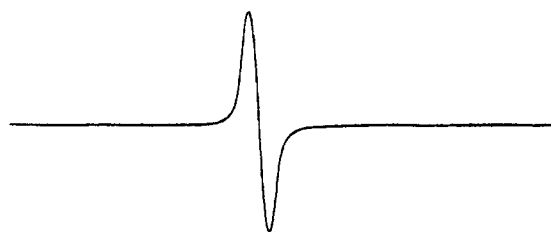
Fig. 4   EPR spectrum of DDQ $(1.0 \times 10^{-2}$ mol/L) in CH$_3$CN in the presence of perylene $[(1\text{—}2) \times 10^{-3}$ mol/L].

ic hydrocarbons. In this method, 1 mL of CF$_3$COOH is added to 1 mL of 10^{-3} mol/L solution of the parent hydrocarbon in CH$_3$NO$_2$. Therefore, the study of cation radicals of both perylene and pyrene has attracted our attention.

Aromatic hydrocarbons whose $E_{1/2}^{OX}$ (oxidation half-wave potential) corresponds to less than 1.2 V (vs. Ag/AgClO$_4$ reference electrode) are oxidized by Reymond and Fraenkel's method to form the cation radical. The $E_{1/2}^{OX}$ related to SCE can be obtained by adding 0.34 V to the oxidation potential versus Ag/AgClO$_4$, namely, 1.2 V + 0.34 V = 1.54 V (SCE), as reported in Ref. 13. The oxidation half-wave potentials for perylene and

pyrene are 0.85 V and 1.16 V (vs. SCE)[14] respectively. According to the above-mentioned assessment, perylene and pyrene could be oxidized to form the corresponding cation radical. However, we found that the solubility of large aromatic hydrocarbons in nitromethane is very limited, and nitrobenzene appears to be an excellent solvent for perylene and pyrene. As a consequence, the nitrobenzene was used as a solvent in our experiments.

In the experiments, we found that when 1 mL of CF$_3$COOH was added to 1 mL of 10^{-3} mol/L perylene or pyrene in nitrobenzene solution at room temperature in air, then their cation radical signals were obtained immediately after putting the sample tubes containing the above samples into the sample holder. Furthermore, we found that the perylene cation radical was stable for more than one week. By comparing the result of utilizing CF$_3$COOH/nitrobenzene as an oxidizing medium (see Fig. 5) with the result of utilizing 98% H$_2$SO$_4$ as an oxidizing medium (see Fig. 6), the latter is a better method of preparation of perylene cation radical than that of the former method if the hyperfine splitting EPR data are desired. In 98% H$_2$SO$_4$ the hyperfine splitting of EPR spectrum of perylene cation radical are presented clearly in Fig. 6.
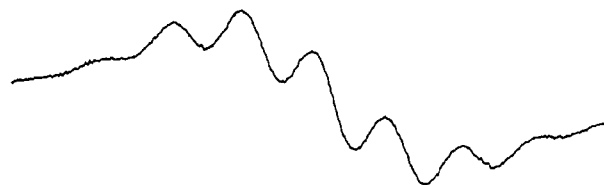

Fig. 5   EPR spectrum of perylene $[(1\text{—}2) \times 10^{-3}$ mol/L] dissolved in CF$_3$COOH-C$_6$H$_5$NO$_2$ $(1:1, V/V)$ solution.

In the experiment of charge-transfer process between DDQ and perylene, although DDQ is an oxidizing agent of high electron affinity, the result indicates that there is no EPR singal of perylene cation radical (see Fig 4). Therefore, it is not a suitable system to produce perylene cation radical. The above-mentioned results indicate that the CF$_3$COOH-nitrobenzene system $(1:1, V/V)$ is better than the DDQ system for EPR studies of perylene (or pyrene) cation radical. In EPR studies of aromatic cation radicals, other oxidizing agents have been used.[15] None of these oxidants has yet been found

to be superior to H_2SO_4 for studies of EPR hyperfine structure of cation radicals, in accordance with our above-mentioned result.

When $(1—2) \times 10^{-3}$ mol/L pyrene was dissolved in 98% H_2SO_4, the EPR spectrum showed the signal of pyrene cation radical (see Fig. 7). Furthermore, in $(1—2) \times 10^{-3}$ mol/L pyrene dissolved in CF_3COOH-$C_6H_5NO_2$ (1 : 1, V/V) solution, the EPR signal of pyrene cation radical also appeared, but the signal is weaker than that in 98% H_2SO_4.
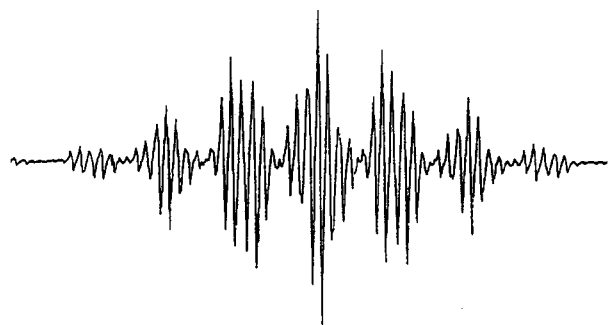

Fig. 6   EPR spectrum of perylene $[(1—2) \times 10^{-3}$ mol/L] dissolved in 98% H_2SO_4.
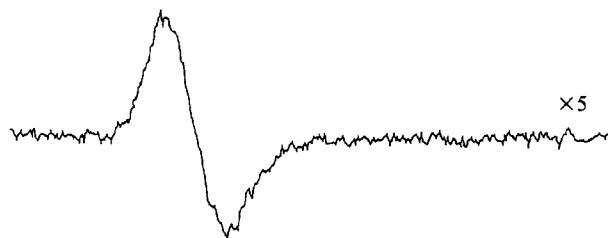

Fig. 7   EPR spectrum of perylene $[(1—2) \times 10^{-3}$ mol/L] dissolved in 98% H_2SO_4.

In conclusion, the present findings are consistent with our previous observations in which the donor cation radicals of the aromatic hydrocarbons, $i. e.$, pyrene and perylene, were not detected from the ground state charge-transfer process of DDQ with perylene (or pyrene), although the $DDQ^{\overline{\cdot}}$ was observed.

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