Preparation and Characterization of a π-Conjugated Donor–Accepter-type Ligand Molecule with Redox Abilities

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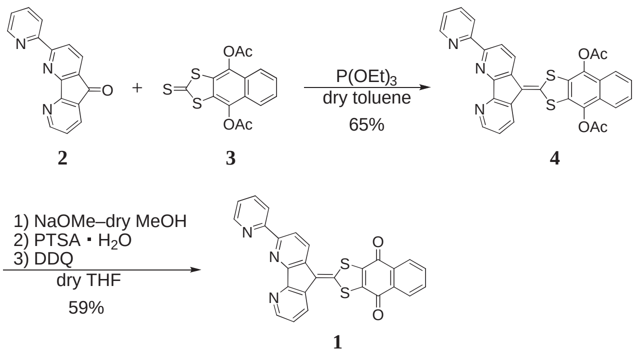
We have synthesized a zwitterion-like molecule **1** having an *N*,*N*,*N*-tridentate ligand site for metal complexation. Compound **1** exhibited negative solvatochromism of the intramolecular charge-transfer (ICT) band in its UV–visible absorption spectrum for different polarity of solvents. Its anion radical ($\mathbf{1}^{-\bullet}$) was generated from both electrical and chemical reduction of the *p*-naphthoquinone moiety.

The interaction between localized d spins through coupling with delocalized π electrons has attracted much attention in the field of molecular magnetism and conduction.[1] Recently, tetrathiafulvalene (TTF)-based molecules with coordination function have been synthesized for the study of π–d systems which have metal-ion binding groups at the molecular periphery.[2] We reported a π-donor ligand and examined magnetic properties of its transition-metal complexes.[3] The Fe^{II} complex shows typical paramagnetic behavior corresponding to a high-spin state ($S = 2$) due to iron(II) ion in distorted octahedral coordination. The synthesis of such a hybrid ligand is important for the development of a magnetic–conductive-conjugated molecular system. In this study, we report the synthesis of a π-conjugated donor (D)–accepter (A)-type *N*,*N*,*N*-tridentate ligand **1** with a reducible site receptive to both electrical and chemical reactions. A π–d interaction could work between the localized d spin and the delocalized π electron generated by reduction of the *p*-naphthoquinone (*p*-NQ) moiety when a transition-metal complex is formed. Furthermore, this quinone-type complex has the ability to give rise to MLCT (metal-to-ligand charge transfer) by coordination to metal and the quinonic accepter unit.[4] In order to characterize such composite molecule **1**, we examine spectroscopic and voltammetric data in comparison with the results of molecular orbital calculations.

We have synthesized the precursor **4** by a previously reported method[3] which the phosphate mediated cross-coupling reaction with triethyl phosphite as shown in Scheme 1. 3-(2-Pyridyl)-4,5-diazafluoren-9-one (**2**)[3] with 4,9-diacetyloxynaphtho[2,3-*d*]-1,3-dithiole-2-thione (**3**)[5] were allowed to react in triethyl phosphite–dry toluene at 80–90 °C for 2 h under argon atmosphere, affording **4** in 65% yield.[3] Preparation of the functionalized quinone derivative of **1** followed a reported procedure.[5d] Subsequent methanolysis using sodium methoxide in THF–MeOH afforded the hydronaphthoquinone derivative after treatment with *p*-toluenesulfonic acid (PTSA•H_2O). This derivative was oxidized using 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), providing us with **1** in 59% yield as a slightly soluble light green powder.[6]



Scheme 1.

A chloroform solution of **1** showed a broad absorption spectral band centered at 615 nm in the wavelength range of 500–800 nm which can be due to a weak intramolecular charge-transfer (ICT) interaction in cooperation with the conjugation involving both donor and accepter moieties.[6] In order to inquire into the origins of ICT, geometry optimization of **1** was performed using Gaussian 98 at the B3LYP/6-31G(d) level.[7] The HOMO and LUMO orbitals are characterized by large contribution from the $S_2C{=}C$ site and the quinone moiety, respectively.[6] The ICT band of **1** therefore appears to be assigned as a charge transfer from the HOMO of the donor part to the LUMO of the acceptor part.

The polarized nature of push–pull compounds like **1** is indicated by the solvent effect of the ICT band.[5,8] The spectra of **1** in twelve standard solvents were measured in the UV–visible region. **1** clearly shows a typical negative solvatochromism, which is revealed by the hypsochromic shift of the ICT absorption band with increasing polarity of the solvent.

Figure 1 shows that there is a fairly good relationship between the frequency (ν_{ICT}) and the relative permittivity (ε_{γ}); such an effect is more sensitive to halogenated solvents than non-halogenated ones. The observed negative solvatochromism

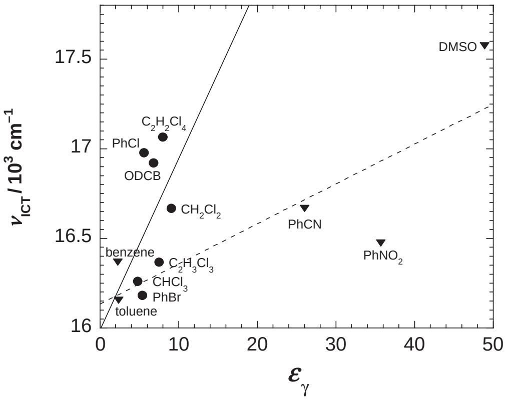


Figure 1. Solvent polarity dependence of wavenumber for the charge-transfer absorption band of **1** in solution. ●: halogenated solvents, ▼: non-halogenated solvents.

of **1** is indicative of a highly polar ground state which has a configuration corresponding to a zwitterionic form (D^+–A^-), and an excited state with decreased polarity; i.e., $\mu_g > \mu_e$, where μ_g and μ_e are dipole moments in the ground state and the excited state, respectively.[8]

In order to characterize the electronic structure of **1**, the redox potentials ($E_{1/2}$) were measured with differential pulse voltammetry (DPV) under following two conditions: A [start at −0.5 to +1.3 V, n-Bu_4NBF_4 0.1 M in $CH_2Cl_2/CH_3CN = 9/1$ (v/v), $v = 100\,\mathrm{mV\,s^{-1}}$, 298 K] and B [start at 0 to −1.3 V, n-Bu_4NBF_4 0.1 M in ODCB/$CH_3CN = 19/1$ (v/v), $v = 50\,\mathrm{mV\,s^{-1}}$, 291 K].[6] Condition A gave a one-electron oxidation wave at $E_{1/2}{}^{\mathrm{ox}} = +1.13$ V (vs. SCE) corresponding to the successive generation of cation radical ($\mathbf{1}^{+\bullet}$) species of the 1,3-dithiole ring–diazafluorene moiety.[3,9] Two reduction processes were examined for the p-NQ moiety, including the first one-electron reduction wave at $E_{1/2}{}^{\mathrm{red1}} = -0.29$ V ($\mathbf{1}^{-\bullet}$)[10] and a poorly resolved second reduction wave at $E_{1/2}{}^{\mathrm{red2}} \approx -1$ V ($\mathbf{1}^{2-}$).[6] The HOMO–LUMO gap (1.42 eV) of **1** is calculated from the difference between the first oxidation peak ($E_{1/2}{}^{\mathrm{ox}}$) and first reduction peak ($E_{1/2}{}^{\mathrm{red1}}$). On the other hand, condition B gave two reduction processes for anion radical ($\mathbf{1}^{-\bullet}$) and dianion ($\mathbf{1}^{2-}$) species of the p-NQ moiety at −0.29 ($E_{1/2}{}^{\mathrm{red1}}$) and −1.19 V ($E_{1/2}{}^{\mathrm{red2}}$) (vs. SCE), respectively.[5b,6]

The thermodynamic stability of the anion radical ($\mathbf{1}^{-\bullet}$) in a two-step reduction process can be evaluated from $\log K_{\mathrm{comp}}$, where K_{comp} is the equilibrium constant for the following comproportionation reaction:

$$\mathbf{1}^{2-} + \mathbf{1} \overset{K_{\mathrm{comp}}}{\rightleftharpoons} 2(\mathbf{1}^{-\bullet}) \qquad (1)$$

The values of $\log K_{\mathrm{comp}}$ are calculated from the differences between the first two reduction potentials ($\Delta E = E_{1/2}{}^{\mathrm{red1}} - E_{1/2}{}^{\mathrm{red2}}$) using the relation of $\Delta E = (2.0303RT/nF) \log K_{\mathrm{comp}}$ ($n = 1$, $T = 291$ K)[11] and summarized in Table 1. On the basis of comparison among these values, the stability of the anion radical ($\mathbf{1}^{-\bullet}$) is estimated to be as similar as that of p-$BQ^{-\bullet}$ and higher than that of $TCNQ^{-\bullet}$.[11]

Chemical reduction of **1** with Cu metal in dichloromethane containing $P(Ph)_4Br$ lead to disappearance of the ICT band and appearance of bands at 412, 430, 455, and 530 nm due to the anion radical ($\mathbf{1}^{-\bullet}$);[12] the intensity of these bands increased for 5 h. The color of the solution changed from blue-green (**1**) to yellow ($\mathbf{1}^{-\bullet}$). In addition, the anion-radical salt [$\mathbf{1}^{-\bullet}\cdot P(Ph)_4{}^+$] immediately deactivated in the course of a few hours.[6] An anion-radical salt ($\mathbf{1}^{-\bullet}\cdot Na^+$) with a long half-life can be efficiently prepared by the action of a mixture of 28% NaOMe in methanol solution on **1** in dichloromethane at 293 K.[6] The electron paramagnetic resonance (EPR) spectrum measured of the anion radical ($\mathbf{1}^{-\bullet}$) showed a strong broad signal without any detectable hyperfine structure at $g = 2.0029$ under this condition.[6]

Table 1. The differential pulse voltammetry data of **1** and quinoide molecules[a]

Compound	$E_{1/2}{}^{\mathrm{red1}}$/V	$E_{1/2}{}^{\mathrm{red2}}$/V	ΔE/V	$\log K_{\mathrm{comp}}$
1	−0.29	−1.19	0.87	15.1
p-BQ[b]	−0.39	−1.28	0.89	15.4
DCNQ[c]	−0.39	−1.20	0.81	14.0
TNQ[d]	−0.27	−1.00	0.73	12.6
AQ[e]	−1.07	−1.52	0.45	7.8
2[6]	−1.00	−1.52	0.52	9.0
TCNQ[f]	+0.39	−0.32	0.71	12.3

[a]All data measured under condition B.[6] [b]p-BQ = 1,4-Benzoquinone. [c]DCNQ = 2,3-Dichloro-1,4-naphthoquinone. [d]TNQ = 4,9-Dioxo-4,9-dihydronaphtho[2,3-*d*]-1,3-dithiole-2-thione. [e]AQ = anthraquinone. [f]TCNQ = 7,7,8,8-tetracyanoquinodimethane.

Currently, we are trying to prepare more stable anion-radical species ($\mathbf{1}^{-\bullet}$) and transition-metal complexes of using **1** as a ligand.

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