Ionicity of Intramolecular Charge-Transfer Molecule D$^{\delta+}-\pi-$A$^{\delta-}$ Based on 1,3,3-Trimethyl-2-methyleneindoline and 7,7,8,8-Tetracyanoquinodimethane

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The *intramolecular* charge-transfer (CT) molecules linked by a π-bond (D$^{\delta+}-\pi-$A$^{\delta-}$; D, donor; A, acceptor; δ, degree of CT) have potentially been investigated as functional soft materials for dyes,[1] photovoltaic[2] and photochromic[3] materials, nonlinear optics,[4] rectifiers,[5] conductors,[6] and magnets.[7] Although the ionicity (δ) of the *intermolecular* CT compounds has been quantitatively discussed in a description of the electronic properties of organic (super)-conductors[8] and of their phase transitions (Peierls, Mott, charge order, neutral−ionic),[8,9] not very many quantitative experiments concerning functionality versus δ have been done for the *intramolecular* compounds except for a few cases,[4b,c] because of the difficulty in obtaining δ of D$^{\delta+}-\pi-$A$^{\delta-}$. Either a complete neutral or a zwitterionic ground state (δ = 0 or 1) has often been anticipated.[1−3,4a,d,5,7,10] We report here a simple method to evaluate the relative ionicity of D$^{\delta+}-\pi-$A$^{\delta-}$ molecules and discuss some functionality versus δ relations, exemplifying conventional D−π−A molecules 1-R (Chart 1), prepared by the reaction between 1,3,3-trimethyl-2-methyleneindoline (1) and R-TCNQ according to the procedures reported previously.[3,4d,5a]

The 1-R exhibits, in general, two peaks (labeled peaks A and B) between λ = 700−850 nm and two shoulders between λ = 550−700 nm in solution (Figure 1a) similar to those of the analogous compounds.[1,3,4d,5] Peak B is used in the following analysis because the intensity of peak A is sensitive to the solvent used. When the overlap of the peaks was significant, the positions of the peaks were determined by line deconvolution into four Gaussian bands.

In polar solvents, a hypsochromic band shift was observed for the 1-R derived from a strong acceptor in the TCNQ system, confirming that its ground state was ionic. However, in solvents less polar than chlorobenzene (PhCl), a bathochromic band shift was observed,[1,11] indicating a change of ground state from the ionic to neutral state. Consequently, we exclude the solvents having smaller Reichardt E_T values[12] than that of PhCl in the evaluation of δ so as not to mix opposite solvatochromic effects for each 1-R.

The examination of the transition energy of peak B ($h\nu_{CT}(B)$) in connection with the relative permittivity ϵ_r and E_T of solvent revealed that (1) E_T has a linear relation with $h\nu_{CT}(B)$ (eq 1, Figure 1b) but ϵ_r does not, and (2) the slope a of each line varies in good accordance with the redox potentials of R-TCNQ (Table 1).

$$h\nu_{CT}(B) = aE_T + b \qquad (1)$$

The CT energy for an ionic complex D$^{\delta+}$A$^{\delta-}$ (δ ≥ 0.5), $h\nu_{CT}^I$ (I: ionic, eq 2), is related to ϵ_r in terms of both the Coulomb attractive ($\sim$e$^2/\epsilon_r r$) and the solvation ($\Delta G \approx 1 - 1/\epsilon_r$) energies in solution.[14] Here I_D is the ionization potential of D, E_A is the electron affinity of A, r is the distance between D$^{\delta+}$ and A$^{\delta-}$, ΔG is the difference between the solvation energies for D^{0}A^0 and D^{1+}A^{1-}
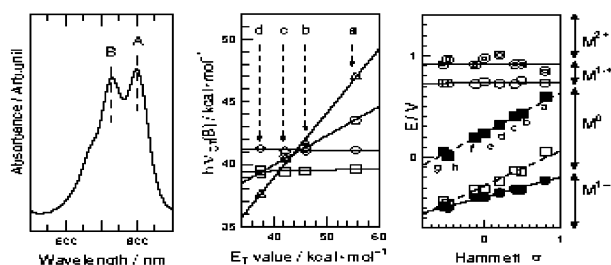
Figure 1. (a) Absorption spectrum of 1-CF$_3$ in PhCl. (b) Plot of transition energy of the peak B of 1-R (R = F$_4$(△), F$_2$(○), H(□), (MeO)$_2$ (◇)) vs E_T value (a, methanol; b, acetonitrile; c, acetone; d, PhCl). For other 1-R's, see the Supporting Information. (c) Plot of redox potentials of 1-R (◎, E_1; ○, E_2; ●, E_3) and corresponding TCNQs (■, □) vs Hammett σ.[13] The chemical species in the regions separated by solid lines are labeled by M^{2+}, M$^{•+}$, M^0, and M$^{•-}$ for M = 1-R (R = a, F$_4$; b, CF$_3$; c, F$_2$; d, F; e, H; f, Me; g, (MeO)$_2$; h, (EtO)$_2$).

Chart 1. Chemicals in Text
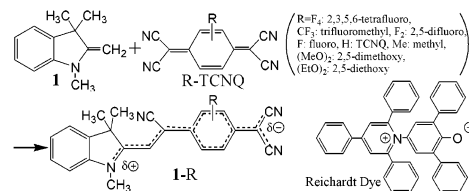
Table 1. Slope in Eq 1 and Estimated CT Degree of 1-R

	R							
	F$_4$	CF$_3$	F$_2$	F	H	Me	(MeO)$_2$	(EtO)$_2$
$a(\times 10^{-2})$	56.3	23.6	23.4	4.19	0.89	−0.75	−0.45	−0.85
δ^a	1.00	0.71	0.71	0.54	0.51	0.49	0.50	0.49

^{a} Direct use of peak B (use of peak B by deconvolution of the spectrum causes a scatter of δ by −0.00−0.03).

states, and X is the resonance stabilization energy.

$$h\nu_{CT}^I = -I_D + E_A + (2\delta - 1)e^2/\epsilon_r r - (2\delta - 1)\Delta G + X \quad (2)$$

It is reasonably expected that $h\nu_{CT}^I \approx h\nu_{CT}^N$ at δ = 0.5, where $h\nu_{CT}^N$ is for a neutral complex D$^{\delta+}$A$^{\delta-}$ (δ ≤ 0.5), resulting in a practically ϵ_r-independent CT energy.[15] We presume that eq 2 for a D$^{\delta+}$A$^{\delta-}$ complex is valid for a D$^{\delta+}-\pi-$A$^{\delta-}$ molecule as well.

The E_T values are the *intramolecular* CT energies of the zwitterionic Reichardt dye (Chart 1, δ = 1) in various solvents[12] and are formulated by eq 3, where r', $\Delta G'$, and X' represent the same meaning for the corresponding terms in eq 2

$$E_T = -I_{D-\pi-A} + E_{D-\pi-A} + e^2/\epsilon_r r' - \Delta G' + X' \quad (3)$$

Equations 2 and 3 afford an apparent linear relation between $h\nu_{CT}$ and E_T provided that δ is insensitive to E_T. If δ is a function

of E_T, a quadratic behavior is expected in a plot of $h\nu_{CT}^I$ versus E_T, contrary to the observed linear behavior in Figure 1b.

To go further, we need information about $(I - E)$ of **1**-R. Figure 1c compares the redox potentials of **1**-R and respective R-TCNQ with the Hammett σ values.[13] Every **1**-R exhibits three one-electron redox steps. The first two, in the $+0.7-1.0$ V range (E_1, ◎; E_2, ○), are insensitive to the σ values, showing that these two are mainly associated with the D-part. Their much more positive values than those of $E_{1/2}^{0/1-}$ of the corresponding R-TCNQ (■) confirm that these steps are ascribed to essentially $M^{2+}(D^{2+}-\pi-A^0) \rightleftharpoons M^{\bullet+}(D^{\bullet+}-\pi-A^0) \rightleftharpoons M^0(D^0-\pi-A^0)$; here M represents a whole D$-\pi-$A molecule. The third E_3 at -0.25 to -0.50 V (●) shows a linear dependence on the σ value with both a much more negative magnitude and a less steep slope as compared to $E_{1/2}^{1-/2-}$ of the corresponding R-TCNQ (□), indicating that this step is ascribed to $M^0(D^0-\pi-A^0 \leftrightarrow D^{\bullet+}-\pi-A^{\bullet-}) \rightleftharpoons M^{\bullet-}$(mainly $D^{\bullet+}-\pi-A^{2-}$). Therefore, Figure 1c indicates that the $(I - E)$ process of M^0, $M^{\bullet+} \rightleftharpoons M^0 \rightleftharpoons M^{\bullet-}$, which corresponds to the separation between E_2 and E_3 (ΔE), varies weakly with the σ value ($\Delta E = -0.21\sigma + 1.12$), and this implies that the $(I - E)$ term in eq 3 is a linear function of δ. Hence, eq 3 is modified to eq 4.

$$h\nu_{CT}^I = (2\delta - 1)(e^2/\epsilon_r r' - \Delta G' + C_1) + (X' - C_2) \quad (4)$$

To evaluate δ, we need the magnitude of a slope a_1 of a plot of $h\nu_{CT}$ versus E_T for the **1**-R of $\delta = 1$, then eq 4 is expressed as

$$h\nu_{CT}^I = (e^2/\epsilon_r r' - \Delta G' + C_1) + (X' - C_2) = a_1 E_T + b_1 \quad (5)$$

The ratio a/a_1 ($\approx 2\delta - 1$) then gives the ionicity δ on the reasonable assumption that the r' and $\Delta G'$ values do not vary significantly among the **1**-R molecules. By taking the δ of **1**-F$_4$ as 1, the relative CT degree δ is calculated (Table 1).

The relation between the estimated δ values in solution and the $E_{1/2}^{0/1-}$ of R-TCNQ is utilized for the synthesis of new **1**-R for desired δ. Also, the relation of their redox properties such as that in Figure 1c is utilized to elucidate the ionicity$-$functionality relation of a D$-\pi-$A unimolecule.

Interestingly the δ of **1**-H is close to 0.5, consistent with E_T-insensitive CT energy (Figure 1b, □), giving rise to nearly the same electronic structures between the ground $D^{\delta+}-\pi-A^{\delta-}$ and its excited $D^{(1-\delta)+}-\pi-A^{(1-\delta)-}$ states by *intramolecular* electron transfer. Thus, **1**-H is expected to be useful for the intermolecular electron transport but inactive for intramolecular rectification, in which a molecule with a high δ value like **1**-F$_4$ is required. As for an indicator of solvent[1,12] having a wide solvatochromic effect, a system not only with a large slope in Figure 1b but also with a small r' value is important according to eq 4. As for a photovoltaic material, which requires a stable charge-separated state, the **1**-R system is not adequate because it exhibits a spontaneous relaxation of the charge-separated state to the neutral one as observed in Figure 1c.

The estimated δ has a fairly good relation with the difference of the dipole moments of ground (μ_g) and excited (μ_e) states or the molecular hyperpolarizability (β), calculated on the basis of the molecular structures.[16] So far, the structural analysis of **1**-R (R = F$_2$, F, H, (MeO)$_2$, (EtO)$_2$) has been exploited, and the μ_g(D), μ_e(D), and β(10^{-30} cm^5 esu^{-1}) values of (25.5, 10.2, -401), (24.5, 10.1, -382), (20.6, 13.9, -218), (15.6, 15.5, -53.6), and (16.2, 15.5, -66.4), respectively, were evaluated. The calculated ($\mu_g - \mu_e$) decreases with decreasing δ and approaches zero when δ becomes $0.49-0.50$ as is expected from $(\mu_e - \mu_g) = (1 - 2\delta)er'$. The β values behave in excellent agreement with eq 6 (Figure 2)
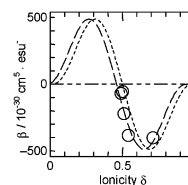
Figure 2. Circles indicate the relation between the molecular hyperpolarizability β and ionicity (δ) of **1**-R (R = F$_2$, F, H, (MeO)$_2$, (EtO)$_2$). Dotted and dashed lines represent eq 6 with a coefficient of 1.3×10^5 and horizontally shifted by 0 and -0.05, respectively.

$$\beta \propto \mu_{ge}^2(\mu_e - \mu_g) \propto \delta^3(1 - \delta)^3(1 - 2\delta) \quad (6)$$

which is derived from the equation proposed by Ducuing *et al.*[17] Here μ_{ge} is the transition dipole moment between ground and excited states. The agreement observed in Figure 2 confirms the validity of the estimated δ values and is in good accordance with those of recent works on the polyene dyes in terms of bond-length alternation[4b] or mixing between the limiting-resonance forms,[4c] both of which reflect the ionicity of D$-\pi-$A indirectly. For the β value the δ values of $0.25-0.35$ and $0.65-0.75$ are required as well as a large r' value and much concentrated D and A moieties per unit volume.

In summary, we reported a simple method to evaluate the relative ionicity δ and discussed the functionality versus δ relations for the *intramolecular* CT molecules $D^{\delta+}-\pi-A^{\delta-}$.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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