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Hydroquinone–Benzonitrile System: Intramolecular Charge-Transfer and Computational Studies

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Abstract A novel intramolecular donor–acceptor system of hydroquinone–benzonitrile was synthesized. Its photo-induced intramolecular charge-transfer (ICT) transition was confirmed by (1) shift of its emission maximum with increasing solvent polarity, (2) high dipole moment for the ICT excited state calculated from the Lippert equation, and (3) its HOMO and LUMO. According to the extent of separation between HOMO and LUMO, it is suggested that substituent position (ortho, meta, or para) in the donor–acceptor biphenyls is not a key point for the photo-induced intramolecular charge transfer and the donor with two alkoxy or hydroxy groups has more photo-induced charge transfer transitions than the one with one alkoxy or hydroxy group. In other words, the hydroquinone–benzonitrile system displays more photo-induced charge transfer transitions than 4COB (4-cyano-4′-butyloxybiphenyl).

Keywords Intramolecular charge transfer · Excited state · Hydroquinone · Benzonitrile · Fluorescence

Introduction

Replacement of fossil energy with solar energy is one of ways to solve global warming and energy crisis, so efficient use of solar energy is a critical topic. The primary step to convert solar energy to chemical potential is photo-induced electron transfer [1].

Photo-induced intramolecular charge transfer (ICT) [2–6] has been a topic of continuing interest since the 1970s

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and it has potential applications in fluorescent solvatochromic probes [7], nonlinear optical materials [8], and electro-optic devices [9, 10]. Some photo-induced intramolecular charge-transfer biphenyls are known, such as biphenyls with amino or alkoxyl groups as electron donors and nitro or cyano groups as electron acceptors [11–15], but the biphenyl with hydroquinone as an electron donor and benzonitrile as an electron acceptor is still unknown. This article explores the properties of its ICT excited state by investigating solvent effect on its emission spectra and explores ICT transition of substituted biphenyls by means of their electronic configurations of HOMO and LUMO, which were calculated by density functional theory (DFT). We like to know if substituent position (ortho, meta, or para) in the donor–acceptor biphenyls is important for the photo-induced ICT transition and if the hydroquinone–benzonitrile system with two alkoxy or hydroxy groups has more photo-induced ICT transitions than 4COB (4-cyano-4′-butyloxybiphenyl) with one alkoxy group.

Experimental

General

All the reagents were obtained from commercial suppliers and used as received. Compound **1** was prepared according to the literature method [16]. All UV-visible absorption spectra were recorded on a Perkin Elmer Lamda 40 spectrophotometer with 10 μM solution of the compounds and all fluorescence emission spectra were recorded on a Perkin Elmer LS45 fluorescence spectrophotometer with similar solution concentrations in various solvents. Quantum yields were determined using quinine bisulfate as a standard (Φ=0.546 in 1 N H_2SO_4) [17].

2-(*p*-Cyanophenyl)-*p*-hydroquinone (2)

To a solution of **1** (0.6 g, 3 mmol) in 5 ml of chloroform was $Na_2S_2O_4$(aq) (1.3 g, 7.5 mmol in 5 ml of water) added. The solution was stirred vigorously for 30 min at room temperature. After filtration of the mixture, the precipitate was washed with water and dried at 50°C. The crude product was purified by column chromatography with a mobile phase of hexane/ethyl acetate (7:3) to obtain **2**: a light brown solid; yield: 82%; ^{1}H NMR (d[6]-DMSO) δ 6.65 (2H, m, PhH), 6.78 (1H, d, PhH, *J*=8.5 Hz), 7.70 (2H, d, PhH, *J*=8.2 Hz), 7.81 (2H, d, PhH, *J*=8.2 Hz); ^{13}C NMR (d[6]-DMSO) δ 109.15, 116.35, 116.70, 117.35, 119.31, 126.30, 130.04, 132.06, 143.88, 147.15, 150.46; IR (thin film) 2233 (CN), 1640 (C=O) cm^{-1}; HRMS (EI) m/z calculated for $C_{13}H_9NO_2$ 211.0628, found 209.0628.

2-(*p*-Cyanophenyl)-1,4-dimethoxybenzene (3)

To a solution of **2** (0.6 g, 3 mmol) in 5 ml of acetone were dimethylsulfate (1 ml, 10.6 mmol) and K_2CO_3 (1.7 g, 12 mmol) added. The solution was stirred under reflux for 4 h. After the reaction was complete, 15 ml of water was added into the solution and some solid precipitated. After filtration of the mixture, the precipitate was washed with water. The crude product was purified by column chromatography with a mobile phase of hexane/ethyl acetate (8:2) to obtain **3**: a white solid; yield: 88%; ^{1}H NMR (d[6]-DMSO) δ 3.77 (3H, s, CH₃), 3.81 (3H, s, CH₃), 6.87 (1H, m, PhH), 6.93 (2H, m, PhH, *J*=8.5 Hz), 7.62 (2H, d, PhH, *J*= 8.4 Hz), 7.98 (2H, d, PhH, *J*=8.4 Hz); ^{13}C NMR (d[6]-DMSO) δ 55.77, 56.13, 110.50, 112.64, 114.24, 116.46, 119.05, 129.39, 130.12, 131.72, 143.14, 150.51, 153.78; IR (thin film) 2,222 (CN), 1,640 (C=O) cm^{-1}; HRMS (EI) m/z calculated for $C_{15}H_{13}NO_2$ 239.0946, found 239.0945.

Results and discussion

According to the literature method [16], aryl-*p*-benzoquinone **1** was prepared by reaction of *p*-benzoquinone with *p*-cyanobenzene-diazonium chloride, which was made *in situ* by treating *p*-aminobenzonitrile with nitrous acid. Then, reduction of **1** with sodium hydrosulfite generated aryl-*p*-hydroquinone **2** in 82% yield. Treatment of **2** with dimethylsulfate gave aryl-1,4-dimethoxybenzene **3** in 88% yield. This way to prepare **3** is better than the previous method [18] (Scheme 1).

As shown in Fig. 1, according to Platt's notation [19] the absorption of hydroquinone at 290 nm is assigned ^1L_b transition and the absorption at 225 nm is attributed to ^1L_a state; the absorption of benzonitrile at 270 nm is due to ^1L_b transition and the absorption at 222 nm is assigned ^1L_a
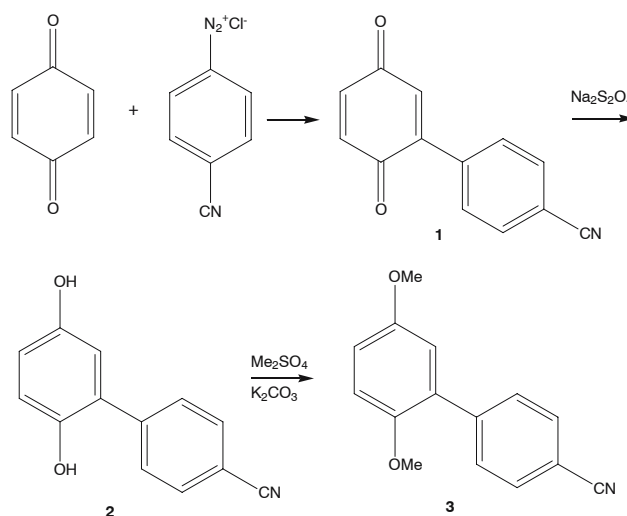

Scheme 1

state. Electronic absorption spectrum of a mixture of benzonitrile (e-acceptor) and hydroquinone (e-donor) in cyclohexane is almost the same as the summation of electronic absorption spectra of the individual components, indicating that there is no evident photo-induced intermolecular charge-transfer absorption for this mixture. On the other hand, the structureless absorption at around 320 nm for the electronic absorption spectrum of **2**, which has benzonitrile and hydroquinone connected by a carbon–carbon bond, displays around 29 nm bathochromic shift as compared with the absorption spectrum of the mixture of benzonitrile and hydroquinone in cyclohexane. According to assignments for absorption spectra of other biphenyls [11, 15], the absorption at 320 nm for **2** is assigned a charge-transfer transition (CT band) to the lowest Franck–Condon excited state (^{1}CT). The H (hidden) band at around 300 nm is associated with the forbidden ^1L_b state. The A band at around 270 nm is produced by the ^1L_a state. The B band at around 245 nm is due to ^1B_b state. The C band at around 200 nm is assigned the ^1B_a transition. Electronic absorption of **2** and **3** were measured in 5 solvents with a wide range of solvent polarity, and the results are shown in Table 1. The charge-transfer absorption maximum of **2** and **3** was 20 and 7 nm bathochromic shift, respectively, from a solvent of cyclohexane to a solvent of DMSO. This is consistent with the results found in other donor–acceptor biphenyls [11]. According to Franck–Condon principle, absorption of light occurs in around 10^{-15} s, which is too short for substrates and solvents to move. That is why absorption spectra are less sensitive to solvent polarity than emission spectra.

Electronic emission spectra of **2** and **3** were measured in 5 solvents with a wide range of solvent polarity, and the results are shown in Figs. 2, 3, and Table 1. The fluorescence maximum of **2** and **3** was 80 and 60 nm bathochromic shift, respectively, from a solvent of cyclohexane to a solvent of

Fig. 1 Electronic absorption spectra of benzonitrile (*dashed line*), hydroquinone (*dotted line*), a mixture of benzonitrile and hydroquinone (*solid line*), and **2** (**—·—**) in cyclohexane
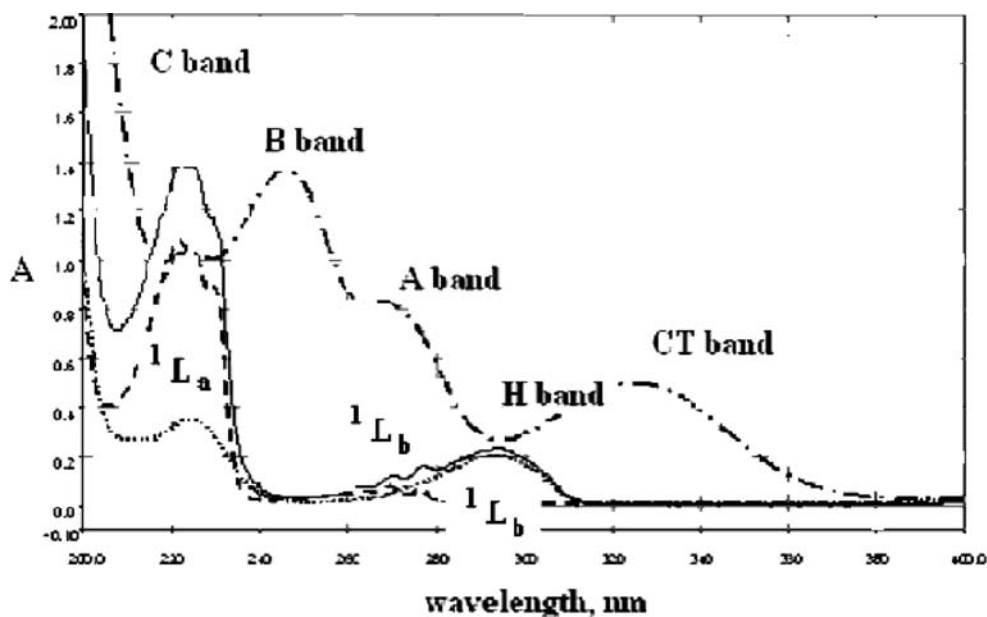
DMSO (Table 1). These bathochromic shifts are as significant as another intramolecular donor–acceptor biphenyl system of 4COB (4-cyano-4′-butyloxybiphenyl), which has the emission maximum be bathochromically shifted 52 nm from a solvent of hexane to a solvent of acetonitrile [12].

The existence of ICT can be determined very well by testing shift of emission maximum of the substrate with increasing solvent polarity [20]. Therefore, the following two ways have been used to identify the ICT for **2** and **3**.

One of the most effective ways to evaluate solvent effects on emission processes is to plot emission energies of a substrate versus an empirical solvent polarity parameter of $E_T(30)$ [7, 21–23]. The parameter is based on well-defined charge-transfer processes, and the molecules within which the ICT occurs translate the sum of solvent interactions into easily measured emission energies. It was reported that a plot of emission energies of a substrate against $E_T(30)$ of solvents with a slope greater than 0.5 suggests charge transfer [21]. The fluorescence maximum of **2** and **3** can be converted to emission energies (E_F) in kcal/mol, which are plotted against $E_T(30)$ of solvents in Figs. 4 and 5. The slopes of the two plots for **2** and **3** are −1.0 and −0.7, respectively, suggesting that ICT occurs upon photo-excitation of **2** and **3**.

Another quantitative relationship between the ICT fluorescence maximum and solvent polarity is provided by the Lippert equation [24].

$$\nu_{abs} - \nu_{flu} = (2/hc)\left[(\mu_E - \mu_G)^2 \big/ a^3\right](\Delta f) + constant$$

where

$$\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)],$$

Table 1 Photophysical data of **2** and **3** in five solvents with a wide range of solvent polarity

Compound	Solvent ($\Delta f, E_T(30)$)	Absorption spectra			Fluorescence spectra		
		λ_{max}/nm	ν_{max}/cm^{-1}	ε_{max}	λ_{fl}/nm	ν_{fl}/cm^{-1}	Φ_{fl}
2	Cyclohexane (0.001,30.9)	320	31,250	5,537	384	26,040	0.20
2	THF (0.2075,37.4)	334	29,940	7,894	424	23,580	0.33
2	CH$_3$CN (0.3047,45.6)	326	30,670	7,873	436	22,940	0.30
2	DMF (0.276,43.2)	339	29,500	6,767	458	21,830	0.20
2	DMSO (0.2624,45.1)	340	29,410	8,148	464	21,550	0.19
3	Cyclohexane (0.001,30.9)	318	31,450	10,975	376	26,040	0.30
3	THF (0.2075,37.4)	322	31,060	10,683	404	24,750	0.45
3	CH$_3$CN (0.3047,45.6)	320	31,250	10,446	430	23,260	0.43
3	DMF (0.276,43.2)	324	30,860	10,321	432	23,150	0.56
3	DMSO (0.2624,45.1)	325	30,770	10,107	436	22,940	0.71

**Fig. 2** Electronic emission spectra of **2** in five solvents with a wide range of solvent polarity. λ_{ex}=320 nm
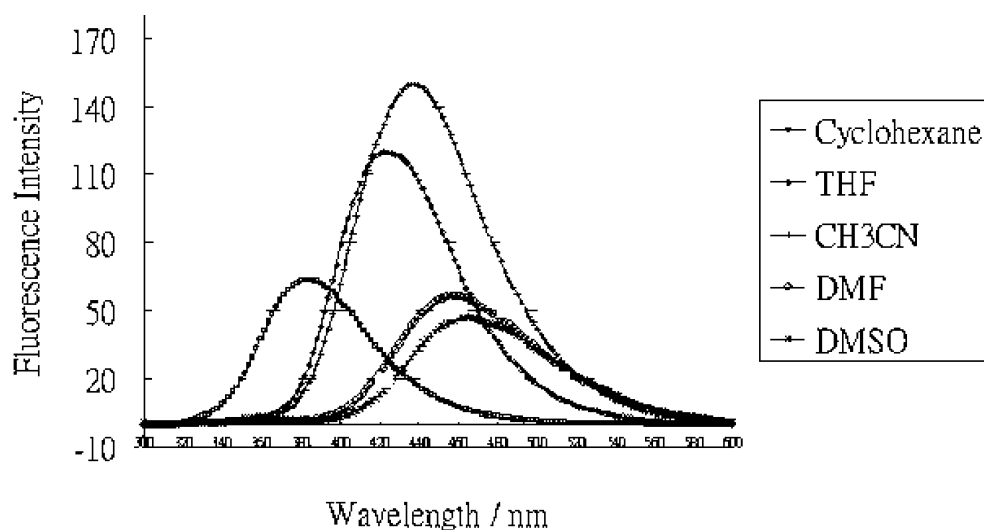
a and $(\nu_{abs}-\nu_{flu})$ are the radius and the Stokes shift of substrate, μ_E is dipole moment for excited state of substrate, μ_G is dipole moment for ground state of substrate, and ε and n are dielectric constant and refractive index of solvents. Plots of the Stokes shift of **2** and **3** against the orientation polarizability (Δf) of the five solvents are shown in Figs. 6 and 7. Observed linear correlations between the Stokes shift of **2** and **3** and the Δf illustrate the adherence of the experimental data to the Lippert equation. The dipole moment and radius of ground states were calculated to be 8.25 D and 4.77 Å for **2** and 8.12 D and 5.36 Å for **3** at HF/6-31+G* level [25]. According to the Lippert equation and the linear plots in Figs. 3 and 4, the dipole moment of excited states of **2** and **3** was calculated to be 18.07 and 21.86 D, respectively, confirming that ICT takes place upon photo-excitation of **2** and **3**.

In contrast to dual fluorescence of dimethylaminobenzonitrile (DMABN) [19], emission spectra of **2** and **3** in Figs. 2 and 3 show only one emission peak with increasing solvent polarity, and emission energies of **2** and **3** are linearly correlated with solvent polarity of $E_T(30)$ with slopes of 1.0 and 0.7. It implies that only one emission state exists for **2** and **3** and this emissive excited state is polar and highly stabilized by polar solvents in comparison with its ground state. Because slopes of the linear correlations between their emission energies and solvent polarity of $E_T(30)$ are more than 0.5, it means the emissive excited state is as polar as a charge-transfer excited state [21]. Ground-state biphenyl is twisted, but its relaxed emission state is planar [19]. However, a substituent of OH or OMe at ortho-position of **2** and **3** inhibits a planar excited-state structure. Therefore, it is clear that the

Fig. 3 Electronic emission spectra of **3** in five solvents with a wide range of solvent polarity. λ_{ex}=320 nm
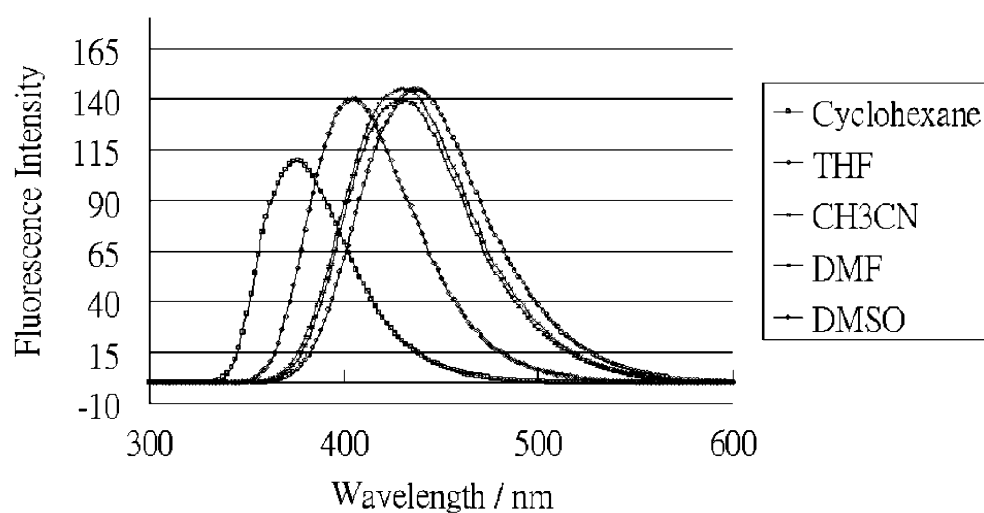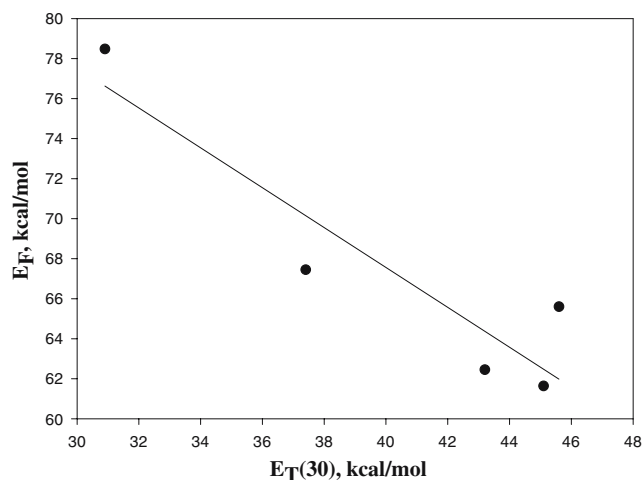
Fig. 4 A plot of emission energy (E_F) of **2** against the solvent polarity parameter of $E_T(30)$ (kcal/mol) (linear correlation coefficient $r^2=0.85$)

Fig. 6 Lippert plot of **2** in five solvents with a wide range of solvent polarity (linear correlation coefficient $r^2=0.90$)

emission state of **2** and **3** is a twisted and relaxed charge-transfer excited state (^{1}CT).

Fluorescence quantum yields for the ^{1}CT emission of **4** and **5** decrease with increasing solvent polarity in dioxane–water mixtures, but they are not affected by heavy-atom effect [26, 27]. This fluorescence quenching was attributed to intramolecular charge recombination in polar solvents, converting ^{1}CT into the ground state (S_0). However, fluorescence quantum yields for the ^{1}CT emission of **6** with a rigid frame are much more than those of **7**, a twistable homolog of **6**, and the latter drops much more than the former with increasing solvent polarity [28]. This was explained by very efficient IC radiationless deactivation of the ^{1}CT state in **7**. On the other hand, as shown in Table 1, as dielectric constant of solvent increases,
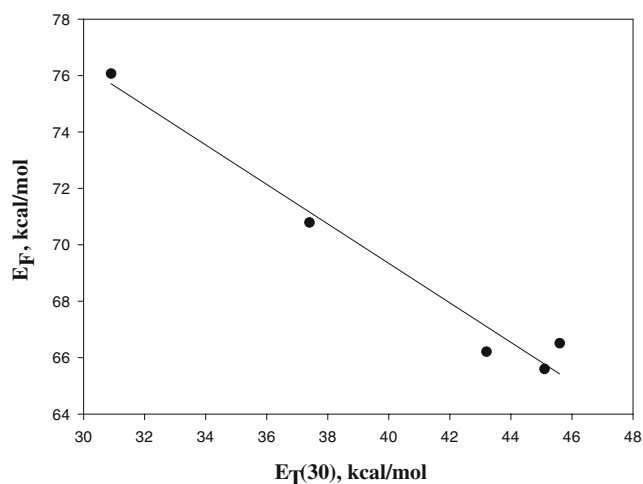
fluorescence quantum yield for the ^{1}CT emission of **2** decreases, which is consistent with the above literature results [26–28], but that of **3** increases, which is consistent with another literature results [12]. In general, fluorescence quantum yields for the ^{1}CT emission of **2** are smaller than those of **3**. These trends don't include the solvent of cyclohexane because of poor solubility of **2** and **3** in cyclohexane. We suggest that in the absence of hydrogen-

Fig. 5 A plot of emission energy (E_F) of **3** against the solvent polarity parameter of $E_T(30)$ (kcal/mol) (linear correlation coefficient $r^2=0.97$)
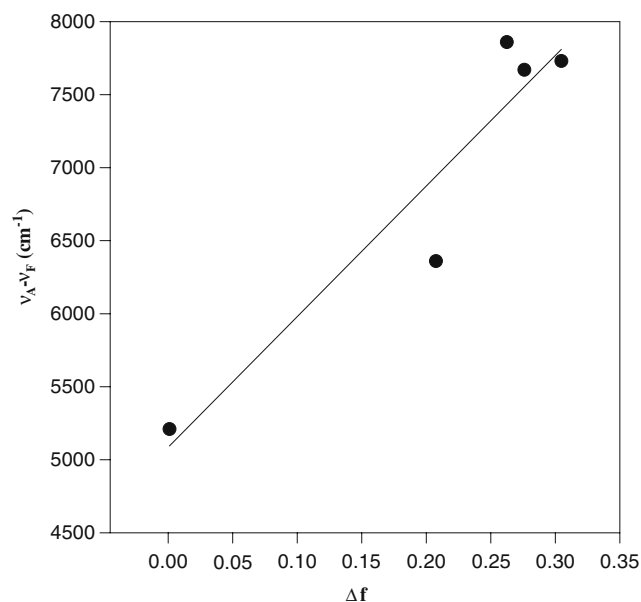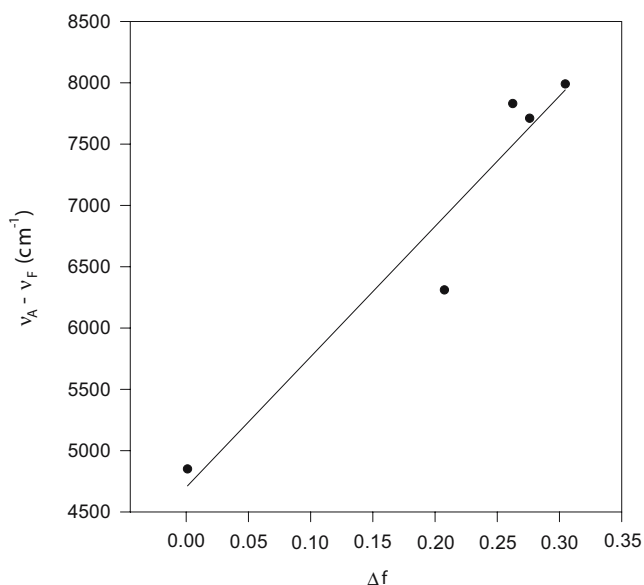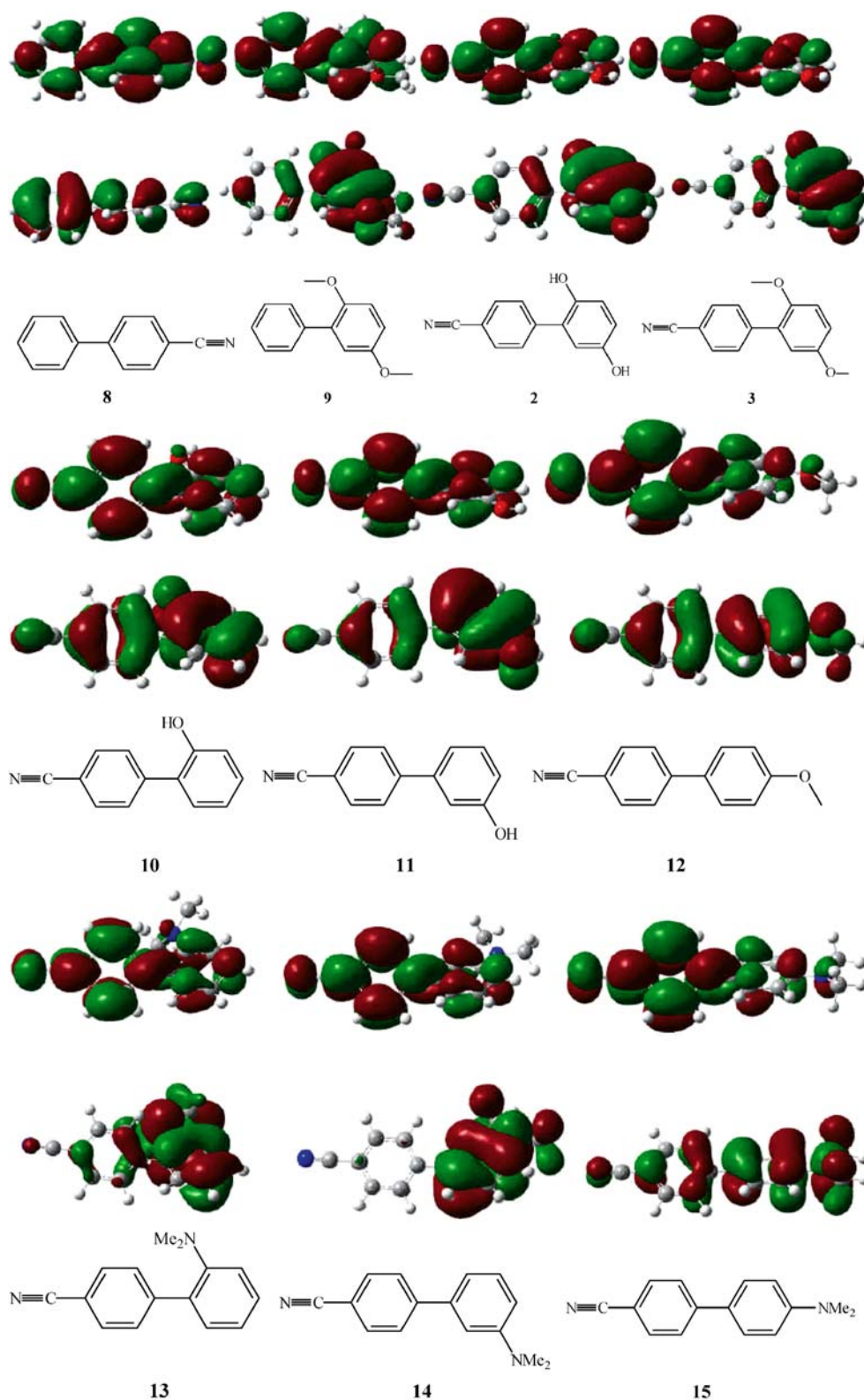

Fig. 7 Lippert plot of **3** in five solvents with a wide range of solvent polarity (linear correlation coefficient $r^2=0.93$)

Fig. 8 HOMO (*middle*) and LUMO (*top*) of **2**, **3**, **8~15** at B3LYP/6-31+G* level

bonding between **3** and solvents, stabilization of the ^{1}CT state of **3** by polar aprotic solvents makes photo-induced electron transfer between the excited donor and acceptor easier and faster, leading to a better fluorescence quantum yield for the ^{1}CT emission. We also suggest that in the presence of hydrogen-bonding between **2** and solvents, stabilization and hydrogen-bonding of the ^{1}CT state of **2** by polar aprotic solvents makes IC radiationless deactivation

of the ^{1}CT state faster, causing a smaller fluorescence quantum yield for the ^{1}CT emission.
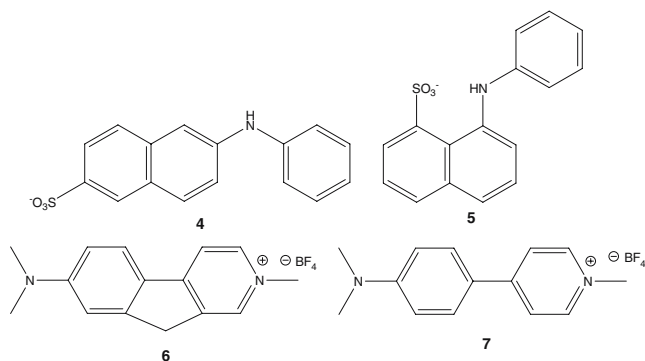
It was reported ICT property of a molecule could be predicted by its HOMO and LUMO [20]. Therefore, **2**, **3**, **8~15** were optimized and their HOMO and LUMO were obtained at level of B3LYP/6-31+G* [25] (Fig. 8). HOMO and LUMO of **8** are both localized on the whole molecule. HOMO of **9** is localized on the donor moiety and its LUMO is spread over the whole molecule with the major part on the donor moiety. Therefore, it is not expected to have ICT upon photo-excitation of **8** and **9**. Conversely, HOMO of **2** and **3** is located on the donor moiety and their LUMO is spread over the whole molecule with the major part on the acceptor moiety. Therefore, **2** and **3** are expected to have ICT upon photo-excitation, and this is consistent with the experimental results. HOMO and LUMO of **10**, **11**, and **12** are mainly located on the donor and acceptor moieties, respectively, and they both overlap more or less, so photo-induced intramolecular charge transfer is expected in these molecules. The extent of separation between HOMO and LUMO in **10~12** is about the same, but it is poorer than that in **2** and **3**. It implies that substituent position (ortho, meta, or para) in the donor–acceptor biphenyls is not a key point for the intramolecular charge transfer and the donor with two alkoxy or hydroxy groups has more charge transfer transitions than the one with one alkoxy or hydroxy group. As a result, **2** and **3** display more photo-induced charge-transfer transitions than **10~12**. Similar phenomena are also found in **13**, **14**, and **15**, but the extent of separation between HOMO and LUMO in **13**, **14**, and **15** is much greater than that in **10**, **11**, and **12**. In other words, **13**, **14**, and **15** display more photo-induced charge-transfer transitions than **10~12**, too. It can be rationalized by the fact that NMe$_2$ substituent is a better e-donor than OR substituent [1].

Conclusion

Intramolecular charge-transfer (ICT) transition of hydroquinone-benzonitrile was confirmed by (1) shift of its emission maximum with increasing solvent polarity, (2) high dipole moment for the ICT excited state calculated from the Lippert equation, and (3) its HOMO and LUMO. Substituent position (ortho, meta, or para) in the donor–acceptor biphenyls is not a key point for the photo-induced intramolecular charge transfer. The hydroquinone–benzonitrile system with two alkoxy or hydroxy groups has more photo-induced ICT transitions than 4COB (4-cyano-4′-butyloxybiphenyl) with one alkoxy group.

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