An Excellent Fluorescent Dye with a Twistable Aromatic Chain and Its Axially Chiral Crystals

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A new organic fluorescent dye, 2,4-dichloro-6-[*p*-(*N*,*N*-diethylamino)biphenylyl]-1,3,5-triazine (DBQ), with an electron withdrawing−donating pair bridged by a twistable aromatic chain has been synthesized. DBQ exhibits high fluorescence quantum yields (0.96 in hexane and 0.71 in THF), high extinction coefficients, and an excitation window extending up to ~480 nm. Due to the strong intramolecular charge transfer character, DBQ shows obviously solvent-dependent Stokes shifts with a value as high as 6360 cm^{-1} in THF and controllable fluorescence emission in the visible region from "blue" to "orange". The axially chiral structures of DBQ crystals were clearly revealed by the X-ray analyses and CD spectroscopy measurements. Two enantiomers of DBQ were obtained by spontaneous resolution upon crystallization without any chiral auxiliary. The low rotation barriers around the interannular bonds in DBQ molecules resulted in an efficient and selective multiplication of each of the chiral structures when DBQ crystallized in THF at room temperature in the presence of an enantiopure crystal seed, leaving racemized DBQ molecules in the solution. The special crystalline properties of DBQ provided a new approach to the design and synthesis of organic chiral crystals. The photophysical properties of DBQ make it promising in the preparation of new fluorescent probes with high sensitivity.

Introduction

Organic fluorescent dyes with electron withdrawing−donating pairs usually exhibit intramolecular charge transfer (ICT) character, and some of them have proved to be efficient fluorescent probes and sensors in photochemistry and photobiology[1] since their fluorescence is sensitive to changes in polarity, viscosity, or temperature of the environment. In order for a molecule to function as a highly sensitive fluorescent probe or sensor, it should have a high molar extinction coefficient, a large Stokes shift, and a high quantum yield, which ensure a high fluorescence emission capability, less self-quenching, and small measurement errors caused by excitation light and background fluorescence. Many dye molecules possessing the ICT character exhibit large Stokes shifts in polar solvents; however, their fluorescence quantum yields in these solvents are quite low.

Yang and co-workers[2] reported a series of arylethynyl-substituted 9,10-anthraquinones. The emission spectra of these compounds in polar solvents, such as CH_2Cl_2, have characteristic charge-transfer bands with considerably large Stokes shifts of 5782−9529 cm^{-1}. However, low fluorescence quantum yields (<6%) of these dyes were observed as a limitation. Peng et al.[3] later reported two heptamethine cyanine dyes that have excellent photophysical properties, such as emission fluorescence in the near-infrared region, high molar extinction coefficients ($\epsilon_{max} >$ 50 000 M^{-1} cm^{-1}), large Stokes shifts, and relatively high fluorescence quantum yields. The Stokes shifts of the dyes are about 2497 cm^{-1} in ethanol with fluorescence quantum yields of about 0.44. However, as the Stokes shifts of the dyes increase to 3401 cm^{-1} in water, the fluorescence quantum yields drop to 0.07. Since the Stokes shift and the fluorescence quantum yield are both crucial parameters for applications such as fluorescence probes, design and synthesis of new fluorescence molecules that simultaneously meet these requirements are of significance.

On the other hand, chiral materials are of significance in nonlinear optical materials,[4] enantioselective synthesis,[5] asymmetric catalysis,[6] and chiral separation.[7] The enantiopure crystals can be obtained via either enantioselective synthesis with enantiopure chiral species or spontaneous resolution upon crystallization without any chiral auxiliary.[8] However, spontaneous resolution is not a common phenomenon due to the lack of homochiral intermolecular interactions between neighboring chiral units to extend the chirality to high dimensionality.[9] Moreover, it was generally accepted that a successful spontaneous resolution required a sufficiently high enantiomerization barrier of the two enantiomers (>96 kJ/mol at 25 °C) for avoiding a rapid racemization process.[10]

Recently, we reported two D-π-A-type chromophores which exhibited excellent sensitization properties for the Eu^{III} fluorescence. The "antenna" ligand consists of a *N*,*N*-diethylamino group as the electron-donating group, a phenylene group as the π-bridge, and a moiety containing a triazinyl group as the electron-withdrawing group.[11] Herein we report the synthesis and photophysical properties of a novel organic fluorescent dye, 2,4-dichloro-6-[*p*-(*N*,*N*-diethylamino)biphenylyl]-1,3,5-triazine (DBQ), with a *N*,*N*-diethylamino group as an electron-donating moiety, a biphenylene group as a π-bridge, and a 2,4-dichloro-1,3,5-triazinyl group as an electron-withdrawing moiety (Scheme 1). DBQ simultaneously exhibits high fluorescence quantum yields, high molar extinction coefficients, and large Stokes shifts in many relatively low polar solvents ($\Delta f(\epsilon,n) <$ 0.250). It also shows obviously solvent-dependent Stokes shifts and controllable fluorescence emission in the visible region from "blue" to "orange". Two enantiomers were obtained via

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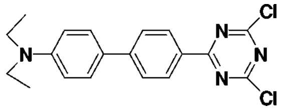
SCHEME 1: Molecular structure of 2,4-Dichloro-6-[*p*-(*N*,*N*-diethylamino)biphenylyl]-1,3,5-triazine



spontaneous resolution of DBQ without any chiral auxiliary. The axial chirality of the obtained DBQ enantiomers was revealed by X-ray analyses and CD spectroscopy measurements. The spontaneous resolution property and the low rotation barriers around the interannular bonds of DBQ provide an uncommon opportunity to efficiently and selectively multiply each chiral structure of the two DBQ enantiomers via the crystallization of DBQ in solutions in the presence of an enantiopure crystal seed under mild conditions.

Experimental Section

Synthesis. ***4-Bromo-4′-(N,N-diethylamino)biphenyl (1).*** 4-Amino-4′-bromobiphenyl (2.0 g, 8.1 mmol) was dissolved in glacial acetic acid (110 mL) in a round-bottomed flask. The obtained solution was cooled to 15 °C, and $NaBH_4$ (3.5 g, 92.5 mmol) was added pelletwise. The obtained mixture was warmed to room temperature and another 92.5 mmol of $NaBH_4$ was added in a similar fashion. The mixture was heated at 85 °C for about 40 min, and then neutralized with a dilute aqueous solution of NaOH. Product **1** was extracted with dichloromethane and the obtained solution was dried over anhydrous magnesium sulfate. After solvent evaporation under vacuum, the residue was purified by column chromatography on silica gel with chloroform as the eluent to afford product **1** with a yield of 84%. EI MS m/z M^+ 303.

2,4-Dichloro-6-[p-(N,N-diethylamino)biphenylyl]-1,3,5-triazine (2). **2** was synthesized according to the previously reported process[11c] with some modification. A solution of **1** (1.2 g, 4.0 mmol) in 20 mL of dry THF was kept in a bath of dry ice and acetone. Air in the bottle was replaced with Ar and *n*-butyllithium (6.4 mmol in 4.0 mL hexane) was added dropwise to the THF solution of **1** under stirring. The obtained solution was added dropwise to cyanuric chloride (1.0 g, 5.4 mmol) at −78 °C under stirring to obtain a mixture that was slowly warmed to room temperature. The mixture was concentrated by evaporation under vacuum, and then the residue was purified by column chromatography on silica gel with dichloromethane as the eluent. After recrystallization from petroleum ether, product **2** was obtained as orange crystal grains with a yield of 54%. Mp 199−200 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.501 (d, $J = 8.3$ Hz, 2H, Ph−H), 7.713 (d, $J = 8.4$ Hz, 2H, Ph−H), 7.599 (d, $J = 8.6$ Hz, 2H, Ph−H), 6.761 (d, $J = 8.6$ Hz, 2H, Ph−H), 3.427 (q, $J = 7.0$ Hz, 4H, NCH_2CH_3), 1.217 ppm (t, $J = 7.6$ Hz, 6H, NCH_2CH_3); EI MS m/z M^+ 372. Anal. Calcd for $C_{19}H_{18}N_4Cl_2$: C, 61.13; H, 4.86; N, 15.01. Found: C, 60.94; H, 5.05; N, 14.92. Crystal data for **2**: $C_{19}H_{18}N_4Cl_2$, $M = 373.27$, monoclinic, $P2(1)$, $a = 7.6007(2)$ Å, $b = 7.3647(2)$ Å, $c = 16.1100(4)$ Å, $V = 899.61(4)$ Å^3, $T = 20(2)$ °C, $Z = 2$, μ(Mo Kα) = 0.71 cm^{-1}, 4109 reflections measured, 3237 observed reflections [$I > 2\sigma(I)$] used in all of the calculations, $R = 0.0350$, $R_w = 0.0865$.

Spectroscopic Measurements. UV/vis absorption and photoluminescence measurements were carried out on an absorption spectrometer (CARY 1E, Varian) and a fluorescence spectrophotometer (F-4500, Hitachi), respectively, at ambient conditions, using 10 mm cells. The CD spectra were recorded on a circular dichroism chiroptical spectrometer (J-810, Jasco) at 20 °C.

Fluorescence quantum yields were determined according to the method described by Demas and Crosby[12] and the results were obtained according to eq 1, in which subscripts S and R denote the sample and the reference, respectively, A represents the absorbance, D represents the intensity of fluorescence, and n represents the refractive index of the solvents:

$$\Phi_S = \left[\frac{A_R {n_S}^2 D_S}{A_S {n_R}^2 D_R}\right]\Phi_R \qquad (1)$$

Fluorescence quantum yields of DBQ in different solvents were measured at 20 °C with perylene ($\Phi = 0.75$ in toluene),[13] acridine yellow ($\Phi = 0.57$ in methanol),[13] rhodamine 6G ($\Phi = 0.86$ in methanol),[13] and 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran (DCM, $\Phi = 0.57$ in *n*-propanol)[14] as the references.

Results and Discussion

Molecular Structure and Spontaneous Resolution of DBQ. It was found that two kinds of chiral crystal grains could be obtained from simple crystallization of DBQ in THF at room temperature. The circular dichroic (CD) spectra of the two kinds of enantiopure crystal grains of DBQ in KBr are shown in Figure 1a, which are designated as (+) and (−) crystals by the sign of ellipticity at 500 nm.

The molecular structure of DBQ in a crystal grain was determined by X-ray analyses. An ORTEP drawing with the corresponding atom labeling scheme is shown in Figure 2. The crystallographic data show that DBQ, with its $-N(CH_2-)_2$ moiety of the *N*,*N*-diethylamino group being coplanar with the phenylene ring of the substituted aniline group, adopts a helicodal configuration twisting around its interannular C(10)−C(9) and C(4)−C(3) bonds, with twist angles of 25.1° and 15.5° for C(11)−C(10)−C(9)−C(8) and C(5)−C(4)−C(3)−N(3), respectively. The bond lengths of C(10)−C(9) (1.52 Å) and C(4)−C(3) (1.50 Å) are much longer than that of a C=C bond (1.34 Å) but close to that for a C−C bond (1.54 Å),[15] which indicates the small π-overlap of the three twistingly arranged six-membered rings of a DBQ molecule in the crystal.

Brock and Minton[16] have investigated the structures of biphenyl molecules. They found that the torsion angles Ψ of the interannular C−C bonds of those molecules are all close to 0° in the solid state due to the crystal-packing effect.[17] However, DBQ molecules adopt helicodal configurations in its crystals, resulting in its axial chirality.

Spontaneous resolutions of axially chiral molecules, whose chirality is only derived from the rotation around the interannular bonds, have been intensively investigated.[18] 1,1′-Binaphthyl is a well-known example for this case and has attracted much attention.[7a,19] It was reported that the half-life of 1,1′-binaphthyl enantiomers in the enantiomerization process in several solvents was about 10 h at 25 °C. Therefore, the rotation around the interannular bond was sufficiently restricted, which allowed the spontaneous resolution of the enantiomers in solution at room temperature.

Different from 1,1′-binaphthyl, on the molecular chain of the axially chiral DBQ molecule, there is no substituted group that exerts large steric hindrance for the rotation around the interannular bonds, implying a low rotation barrier of DBQ molecules in solution. The racemization process of the chiral DBQ molecules occurred fast when an enantiopure DBQ crystal grain was dissolved in THF at room temperature as revealed

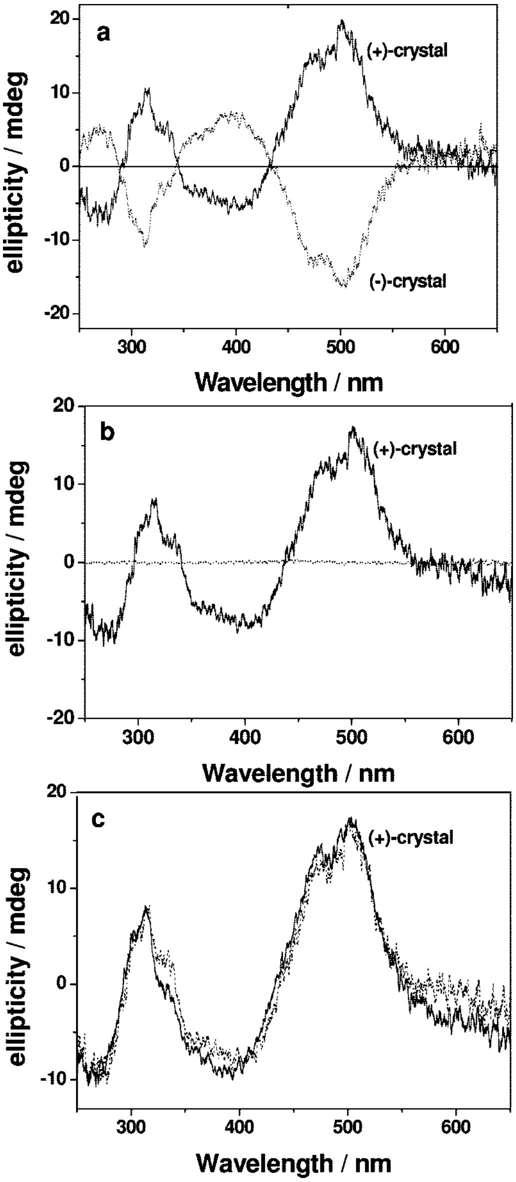


Figure 1. (a) CD spectra of two kinds of enantiopure crystal grains of DBQ in KBr. A mixture of 200 μg of DBQ and 200 mg of KBr was well ground and formed into a disk with a radius of 5 mm for the measurement. (b) CD spectra of the DBQ enantiopure crystal grain in KBr (solid line) and DBQ dissolved in THF (2.0×10^{-5} M) (dotted line). (c) CD spectra of the initial DBQ crystal seed (dotted line) and the big DBQ crystal grain (solid line) in KBr. The big crystal grain was obtained via crystallization of DBQ in THF in the presence of the enantiopure crystal seed.

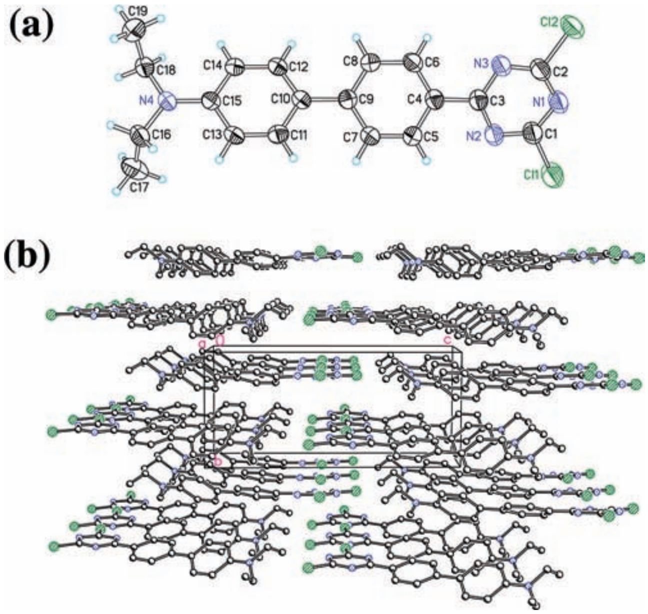


Figure 2. Molecular structure of DBQ obtained from a crystal grain ($0.53 \times 0.45 \times 0.07$ mm^3 in size) (a) and its crystal packing (b).

by the CD spectrum of the obtained solution (Figure 1b, measured immediately after the crystal grain was dissolved). To the best of our knowledge, DBQ is a rare example for axially chiral molecules with low rotation hindrance which are capable of spontaneous resolution. We believe that the intermolecular interaction between DBQ molecules in the enantiopure crystals is the main reason for the spontaneous resolution of DBQ.

The low chain-rotation racemization barrier and spontaneous resolution property of DBQ crystals imply that the crystallization-induced multiplication of the chiral structure of DBQ should be efficient under mild conditions. Fortunately, this idea was confirmed by the following experiment. A thin enantiopure DBQ crystal seed ($1.00 \times 1.00 \times 0.07$ mm^3 in size) was put into a saturated THF solution of DBQ (5.0 mL). After 6 days the single crystal grew to be a thick one, $4.80 \times 4.80 \times 0.25$ mm^3 in size. During this crystallization process, DBQ molecules in the solution remained racemic. CD spectra measurements on the initial crystal seed and the obtained big crystal grain proved that they have the same chirality (Figure 1c). This property of DBQ affords a facile approach to the selective and efficient multiplication of the chiral structures.

Spectroscopy and Solvatochromism Properties of DBQ. The solvent polarity is scaled by the orientational polarizability $\Delta f(\epsilon,n)$:[20]

$$\Delta f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

where ϵ is the dielectric constant and n is the refractive index of the solvent. The solvents listed in Table 1 can be sorted into three categories: nonpolar solvents (nos. 1−5), dipolar solvents (nos. 6−14), and nondipolar solvents (nos. 15−17) which have near-zero dipolar moments for their symmetrical structures, and large high-order multipole moments owing to the polar bonds.[21]

The absorption spectra of DBQ in several solvents are shown in Figure 3. In nonpolar solvents, such as hexane and cyclohexane, the absorption spectra show some fine structures, which is probably due to the vibrational effect.[22] In the dipolar and nondipolar solvents, however, the peak shape tends to be symmetrical. The molar extinction coefficients at the absorption maxima of DBQ are high ($\epsilon_{\max} > 29\,000$ M^{-1} cm^{-1}) in the solvents listed in Table 1. The plot of the frequencies at the absorption maxima versus $\Delta f(\epsilon,n)$ of the solvents (Figure 5), with a near-zero slope, indicates that the solvent polarity has only a slight influence on the absorption maximum position of DBQ.

The emission spectra of DBQ in some solvents are shown in Figure 4a, which illustrates the obviously solvent-dependent fluorescence emission of DBQ. As observed in the absorption spectra, emission spectra of DBQ show vibrational structures in nonpolar solvents, such as cyclohexane (Figure 4b). The peaks at 21 863 and 20 730 cm^{-1} and the shoulder at 19 539 cm^{-1} are attributed to the transitions from the lowest vibrational level of the first excited state to the nth ($n = 0-2$) vibrational level

TABLE 1: Solvent Properties and Photophysical Data of DBQ at 20 °C[a]

no.	solvent	$\Delta f(\epsilon,n)$	$10^{-3}\upsilon_{abs}$ [cm^{-1}]	$10^{-4}\epsilon_{max}$ [M^{-1} cm^{-1}]	$10^{-3}\upsilon_{em}$ [cm^{-1}]	$\Delta\upsilon$ [cm^{-1}]	Φ_F
1	pentane	0.001	24.45/23.31	3.22	22.22/21.05	1090	0.96
2	hexane	0.000	24.39/23.26	3.29	22.08/20.92	1180	0.96
3	cyclohexane	0.000	24.15/22.99	3.45	21.83/20.70	1160	0.95
4	heptane	0.000	24.27/23.15	3.47	22.08/20.83	1070	0.89
5	octane	0.000	24.21/23.09	3.44	21.98/20.79	1110	0.89
6	dibuthyl ether	0.097	23.47	3.54	19.42	4050	0.79
7	$CHCl_3$	0.149	22.94	2.95	17.51	5420	0.56
8	diethyl ether	0.163	23.70	3.51	18.66	5040	0.87
9	ethyl acetate	0.201	23.04	3.12	17.24	5800	0.29
10	THF	0.210	23.31	3.51	16.95	6360	0.71
11	methyl acetate	0.215	23.42	2.98	16.95	6470	0.079
12	CH_2Cl_2	0.218	22.88	3.45	16.89	5990	0.67
13	DMSO	0.264	23.04	3.03	17.24	5800	0.017
14	acetonitrile	0.306	23.53	2.92	17.21	6320	0.077
15	benzene	0.003	23.20	3.12	19.08	4120	0.77
16	toluene	0.014	23.26	3.61	19.16	4100	0.76
17	1,4-dioxane	0.021	23.70	3.62	18.59	5110	0.88

[a] ϵ, static dielectric constant (25 °C), and n, refractive index (25 °C) were taken from ref 33. $\Delta f(\epsilon,n)$, orientational polarizability of the solvent; υ_{abs}, the frequency at the absorption maximum; ϵ_{max}, molar extinction coefficient at the absorption maximum; υ_{em}, the frequency at the emission maximum; $\Delta\upsilon$ ($\Delta\upsilon = \upsilon_{abs} - \upsilon_{em}$), Stokes shift; and Φ_F, fluorescence quantum yield. The uncertainty of Φ_F is 10%.

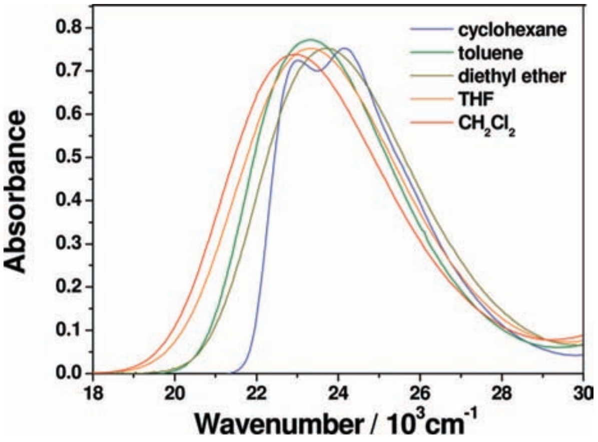


Figure 3. UV−vis absorption spectra of DBQ in the solvents with different polarities at 2.0×10^{-5} M.

of the ground state, respectively. However, the emission spectrum loses the vibrational feature with the increase in solvent polarity.

Figure 5 shows the good correlation ($R = 0.989$) between the frequencies at the emission maxima (υ_{em}) and $\Delta f(\epsilon,n)$ in the nonpolar and dipolar solvents with the values of $\Delta f(\epsilon,n)$ less than 0.25. The emission peaks show considerable red-shifts with increasing $\Delta f(\epsilon,n)$ in this polar region, and the difference between the peak positions in pentane and dichloromethane is as high as 5330 cm^{-1}. The good linear relationship between υ_{em} and $\Delta f(\epsilon,n)$, and the significant red-shifts of υ_{em} in the relatively low polar region ($\Delta f(\epsilon,n) < 0.25$) indicate that the stabilization effect on the excited states of DBQ of polar solvents is pronounced, suggesting a high dipole moment of the DBQ excited state.

However, in the more polar region ($\Delta f(\epsilon,n) > 0.25$), the profile of the correlation curve between υ_{em} and $\Delta f(\epsilon,n)$ reaches a plateau. The υ_{em} values in DMSO ($\Delta f(\epsilon,n) = 0.264$) and acetonitrile ($\Delta f(\epsilon,n) = 0.306$) no longer show any red-shift relative to that in CH_2Cl_2 ($\Delta f(\epsilon,n) = 0.218$). This unexpected phenomenon might be caused by the drastic increase in the twist angles around the chiral axis of the preponderant configuration of DBQ, which decreases the delocalization extent of the π-electrons in DBQ and counteracts the stabilization effect of high polar solvents on DBQ. As expected, such a phenomenon cannot be observed for Coumarin 153[21,23−26] with a rigid structure (Figures S1 and S2 in the Supporting Information).

As shown in Figure 5, the υ_{em} values in three nondipolar solvents listed in Table 1, i.e., benzene, toluene, and 1,4-dioxane, stray away from the linear relationship. The reason is that these solvents are nondipolar solvents with high-order multipole moments.[21,24]

As listed in Table 1, the Stokes shift changes remarkably with the change of solvents. Usually, the relationship between Stokes shift and $\Delta f(\epsilon,n)$ can be given by the Lippert−Mataga equation[20]

$$\Delta\upsilon = \upsilon_{abs} - \upsilon_{em} = \frac{1}{4\pi\epsilon_0}\frac{2}{hca_w^{\ 3}}(\mu_e - \mu_g)^2 \Delta f(\epsilon, n) + \text{constant} \quad (3)$$

where υ_{abs} and υ_{em} are the frequencies at the absorption and emission maxima, respectively, h is Plank's constant, c is the speed of light in vacuum, ϵ_0 is the dielectric constant of vacuum, a_w is the radius of the solvent cavity, and μ_e and μ_g are the excited state dipole moment and ground state dipole moment, respectively.

Figure 6 shows the good linear correlation ($R = 0.992$) of the Stokes shift of DBQ with $\Delta f(\epsilon,n)$ in nonpolar and dipolar solvents with the values of $\Delta f(\epsilon,n)$ less than 0.25. The deviation of the data in nondipolar solvents, DMSO and acetonitrile is due to the same reason as that for the emission. From its slope (2.41×10^4), the static dipole moment difference $\Delta\mu$ ($\Delta\mu = \mu_e - \mu_g$) of DBQ is estimated to be 28.6 D based on the assumption[27] that the solvent cavity radius a_w is equal to 7.0 Å, which is a half of the optimized distance between the two farthest atoms of the molecule in the direction of charge separation. The large value of $\Delta\mu$ confirmed that the excited state of DBQ has a CT character.[28,29]

Fluorescence Quantum Yields of DBQ. The fluorescence quantum yields (Φ_F) of DBQ determined at 20 °C in several solvents are listed in Table 1. As listed in Table 1, the Φ_F values of DBQ are high in the solvents with $\Delta f(\epsilon,n)$ less than 0.250, excluding two esters (methyl acetate and ethyl acetate). Moreover, in some solvents such as THF, CH_2Cl_2, and 1,4-dioxane,

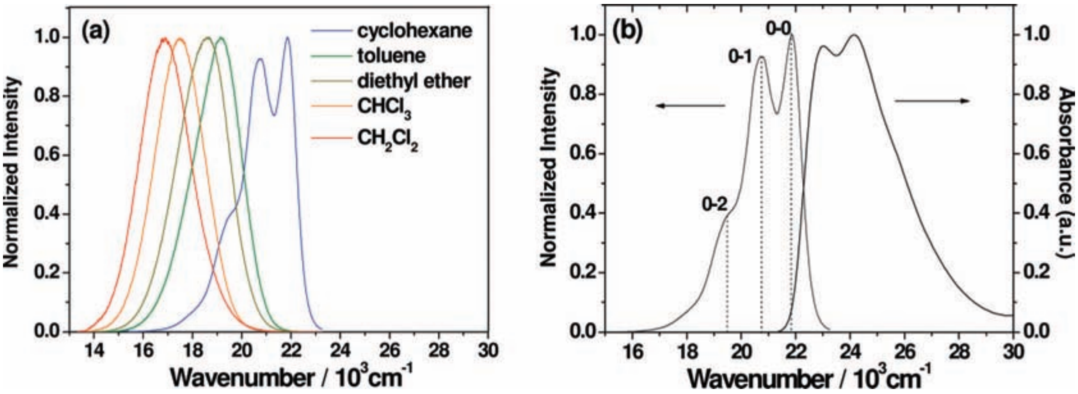


Figure 4. (a) Emission spectra of DBQ in the solvents with different polarities at 2.0×10^{-5} M ($\lambda_{ex} = 420$ nm). (b) UV−vis absorption spectrum and emission spectrum ($\lambda_{ex} = 420$ nm) of DBQ in cyclohexane at 2.0×10^{-5} M. The vertical dotted lines show the corresponding frequencies of the three estimated transitions contributed to the emission.

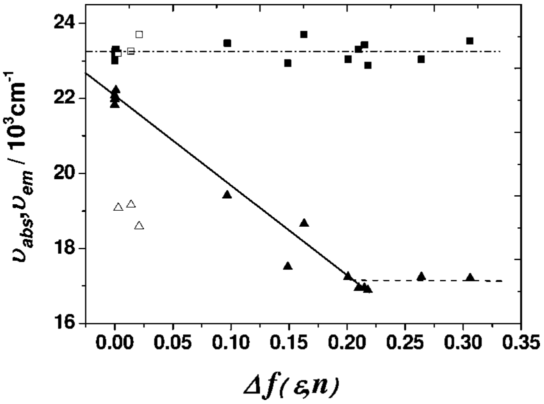


Figure 5. Frequencies at absorption maxima (■, □) and emission maxima (▲, △) of DBQ plotted versus $\Delta f(\epsilon,n)$. The solid line is fitted to υ_{em} in nonpolar and dipolar solvents with $\Delta f(\epsilon,n)$ less than 0.250, i.e., excluding the data in the nondipolar solvents shown as open symbols, DMSO, and acetonitrile.

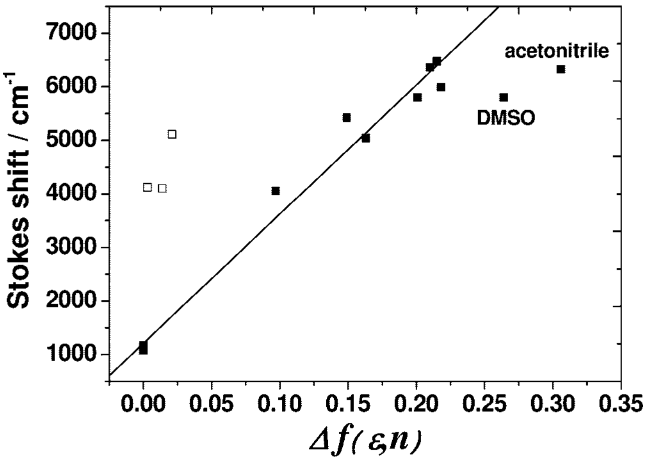


Figure 6. Correlation of Stokes shift of DBQ with $\Delta f(\epsilon,n)$. The line is fitted to the Stokes shifts in nonpolar and dipolar solvents with $\Delta f(\epsilon,n)$ less than 0.250, i.e., excluding the data in the nondipolar solvents shown as open symbols, DMSO, and acetonitrile.

TABLE 2: Fluorescence Quantum Yields of DBQ and TA in Different Solvents at Room Temperature

solvents	Φ_F[a] TA[b]	DBQ
cyclohexane	0.81	0.95
toluene	0.54	0.76
benzene	0.62	0.77
diethyl ether	0.42	0.87
THF	0.03	0.71
dichloromethane	0.03	0.67

[a] The uncertainty of Φ_F is 10%. [b] Data for TA in the different solvents are cited from ref 30.

DBQ synchronously exhibits high Φ_F and large Stokes shifts, with a Stokes shift of 6360 cm^{-1} and a Φ_F value of 0.71 in THF.

The photophysical properties of a series of dyes, which share the same *N*,*N*-dialkylamino electron-donating groups connecting with different linear π-conjugated moieties, have been intensively investigated.[30−32] The fluorescent dye *N*,*N*-diethyl-4-(dichloro-1,3,5-triazinyl)aniline (TA) reported by Cowley and Pasha[30] has the same electron-donating and electron-withdrawing groups with DBQ. The only difference between TA and DBQ is that the former has a phenylene π-bridge, while DBQ possesses a biphenylene π-bridge. However, it is surprise to us that different from DBQ, the Φ_F values of TA decrease dramatically with the solvent polarity increasing as listed in Table 2. In THF, the Φ_F and Stokes shift values of TA are 0.03 and 2580 cm^{-1}, respectively. The low Φ_F values of TA in polar solvents have been ascribed to the formation of a nonradiative state, in which the *N*,*N*-diethylamino group is twisted with respect to the phenylene ring of the substituted aniline group.[30]

Cao and co-workers[31] later reported a hemicyanine dye 4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium (HR). The Φ_F values of HR are also low in polar solvents, with a value of 0.02 in CH_2Cl_2. On the basis of the calculation results about the rotation barriers around the chemical bonds in HR, the authors concluded that the rotation of the *N*,*N*-dimethylamino group around the $C-N(CH_3)_2$ bond in HR is difficult. The calculation results suggest that the rotations around the aniline−ethylene bond and the pyridyl−ethylene bond in HR are the main channels for the formation of the nonradiative states which cause the low Φ_F values of HR.

Whereas DBQ exhibited high Φ_F values and large Stokes shifts even in polar solvents such as THF, CH_2Cl_2, and $CHCl_3$, the high Φ_F values and low racemization energy barrier of DBQ suggest that the exhausted energy in the nonradiative transitions relative to the rotations around the $C-N(CH_2-)_2$ bond and the interannular bonds in DBQ molecules takes a low portion of the whole excitation energy of DBQ molecules in the solvents with $\Delta f(\epsilon,n)$ less than 0.250. The low Φ_F values of DBQ in methyl acetate and ethyl acetate might be caused by some specific solvent effects. In the high polar solvents DMSO and acetonitrile, the Φ_F

values of DBQ are merely about 1.7% and 7.7%, respectively. This phenomenon might be explained by the speculation that in DMSO and acetonitrile the exhausted energy in the nonradiative transitions relative to the rotations around the interannular bonds or the C$-$N(CH$_2-$)$_2$ bond in DBQ molecules take an important portion of the whole excitation energy of DBQ molecules.

Conclusions

We have reported the synthesis and photophysical properties of a novel organic fluorescent dye, 2,4-dichloro-6-[*p*-(*N*,*N*-diethylamino)biphenylyl]-1,3,5-triazine (DBQ). The chirality of DBQ molecules in crystals, as revealed by the X-ray analyses and CD spectroscopy measurements, is derived from the twist around the interannular bonds in the molecules. The racemization process of DBQ was revealed to be fast in solutions under mild conditions, while spontaneous resolution of DBQ occurred without any chiral auxiliary. The spontaneous resolution property and the low rotation barriers around the interannular bonds of DBQ provided an efficient method for selectively multiplying each chiral structure of the two DBQ enantiomers under mild conditions. The special crystalline properties of DBQ provided a new approach to the design and synthesis of organic chiral crystals.

The static dipole moment difference of DBQ is estimated to be 28.6 D. DBQ exhibits excellent photophysical properties including large molar extinction coefficients, obviously solvent-dependent Stokes shifts, and high fluorescence quantum yields even in some polar solvents where DBQ exhibits large Stokes shifts. In THF the Stokes shift of DBQ reaches 6360 cm^{-1}, and the fluorescence quantum yield remains as high as 0.71. Using this phenomenon, the fluorescence band positions of DBQ can be exactly controlled in the visible region from “blue” to “orange” by selecting appropriate solvents. In view of the uncommon photophysical properties of DBQ, we believe it is promising in the development of novel fluorescent probes for the chemical and biological sensors. Moreover, due to the controllable fluorescence emission and the high fluorescence quantum yields, DBQ can be used as a convenient reference for determining the fluorescence quantum yields of various samples with different emission bands in a wide wavelength region.

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Supporting Information Available: Crystallographic data in CIF files for DBQ and table of photophysical data, molecular structure, emission spectra, linear relationship of v_{em} and Δv with $\Delta f(\epsilon,n)$ for Coumarin 153. This material is available free of charge via the Internet at http://pubs.acs.org.

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