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Combined phase transfer catalysis and ultrasound to enhance tandem alkylation of azo dyes

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Abstract—Ultrasound has been found to enhance *N*-substitution against elimination in the reaction of carbazole-containing bromides **3** with a *Disperse Orange 3* derivative **2** under PTC condition. Upon using combined PTC and ultrasound conditions, a series of bifunctional molecules **1** have been prepared to possess charge-transporting agents and nonlinear optical chromophores in 2:1 ratio. © 2002 Published by Elsevier Science Ltd.

Effective synthetic methodology for multiple functions-containing molecules is essential in the development of fully-functionalized organic photorefractive materials,[1] which require a combination of several active components, including charge transporting (CT) agents and nonlinear optical (NLO) chromophores.[2–4] *Disperse orange 3* is an ideal starting material because of its inherent NLO property[5,6] and availability of an active amine group. Derivatization of the amine by CT-containing component can lead to single molecules with CT and NLO components in different ratios and therefore potentially with different properties. Previously, we have described the use of phase transfer catalysts[7] (PTC) alone to synthesize molecules with 1:1 CT–NLO components.[8] Here we fully disclose enhanced tandem alkylation of *Disperse Orange 3* under combined PTC and ultrasound conditions for the synthesis

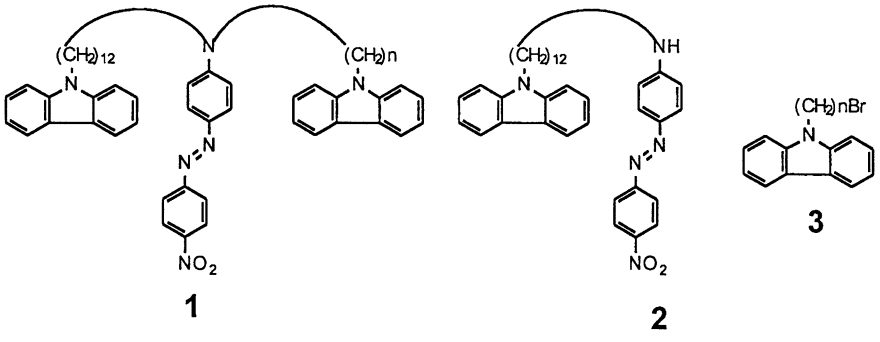
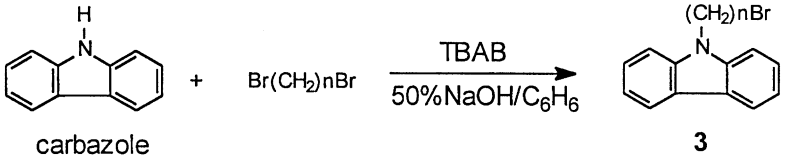


Figure 1. General structures of **1**–**3**.



Scheme 1.

Keywords: phase transfer; alkylation; azo compounds; polycyclic heterocyclic compounds; amines.

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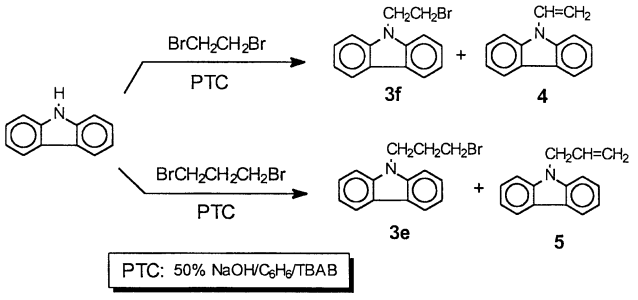
Table 1. Preparation of **3** from carbazole

Run	**3**	*n*	Yield (%) of **3**
1	**3a**	12	92
2	**3b**	10	82
3	**3c**	6	90
4	**3d**	4	88
5	**3e**	3	55
6	**3f**	2	12

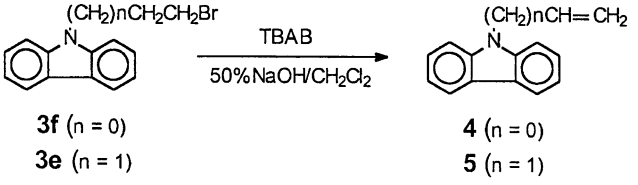


Scheme 2.

of single molecules **1**, which contain 2:1 CT–NLO components as well as tunable alkyl chains for desirable physical properties (Fig. 1).[9]

The synthetic approach to **1** uses the convergent method to tether carbazole derivative **3** to a carbazole-containing *Disperse Orange 3* derivative (**2**) by a flexible alkyl chain. First, carbazole derivatives **3** with various size of alkyl chain were prepared according to Scheme 1 under PTC conditions using *N*-Bu_4NBr (TBAB) as catalyst (Scheme 1).

Yields are chain-length dependent, and are moderate to high when $n \geq 4$ (Table 1). Shorter chains led to acceptable to low yields as evident when $n=2$ and 3. In these cases, elimination process is predominant, and the corresponding olefins **4** and **5** were isolated (Scheme 2). In particular, when $n=2$, only 12% substitution yield was obtained.



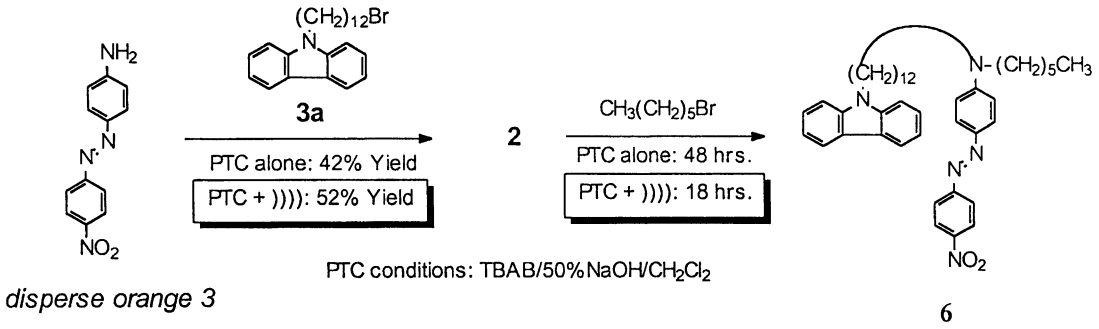
Scheme 3.

Carbazole-containing *Disperse Orange 3* (**2**), which is a bifunctional molecule was obtained by treatment of *Disperse Orange 3* with **3a** under PTC condition.[8]

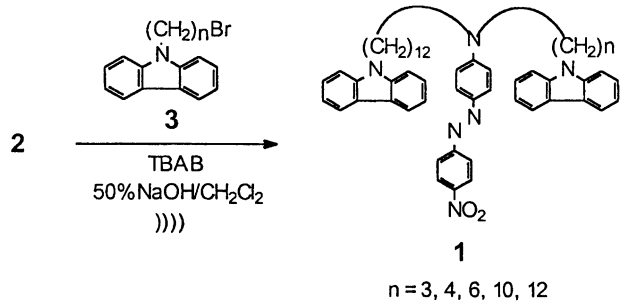
The initial approach to the preparation of **1** only used the PTC[10] condition (50% $NaOH/CH_2Cl_2$/TBAB). Treatment of **2** with **3** gave **1** in just 20–25% yields. The reactions required more than 100 h to complete as monitored by TLC. Moreover, the reaction of **2** with **3f** failed to produce desirable substituted product **1f** in synthetically meaningful yields. Despite the fact that **2** can be easily *N*-alkylated in moderate to good yields with classical alkyl bromides,[8] the PTC condition alone is found to be inadequate for the present reaction. Thus, the use of carbazole-containing alkyl bromide suffered generally low yield and long reaction time.

A side reaction from the halide **3** was a source of the problem. In the PTC condition, **3** was found to undergo elimination reaction and form the corresponding olefins. For example, the bromide **3f** gave 9-vinylcarbazole **4** while **3e** gave 9-(2-propene)carbazole **5** (Scheme 3).

Competition from elimination prompted us to investigate if *N*-substitution reaction under PTC conditions can be improved in the presence of ultrasound.[10,11] Application of ultrasound has been reported in the alkylation of thiocyanate,[12] diazacoronand,[13] and indole.[14] There is no elimination situation reported in those cases. Since there are two competitive reactions in the present systems, ultrasound may promote either elimination or substitution or both. Although several scenarios are possible, the critical issue is whether the use of ultrasound can selectively accelerate the substitution. When this happens, the significance is that a shorter reaction time will likely help control elimination process. To test ultrasound effects, two model reactions were examined first using structurally closely related amine. In one reaction, ultrasound has been found to dramatically enhance yields. *N*-alkylation of *Disperse Orange 3* with **3a** afforded **2** in 52% yield under both PTC and ultrasound conditions (Scheme 4). That is 10% increase in the yield as opposed to 42% yield under PTC conditions without the ultrasound assistance. In the second one, ultrasound has been found to significantly shorten reaction times. *N*-alkylation of **2** with 1-bromohexane for the synthesis of compound **6** only took 18 h to complete under both PTC and ultrasound conditions (Scheme 4). Otherwise, it would take 48 h without ultrasound.



Scheme 4.



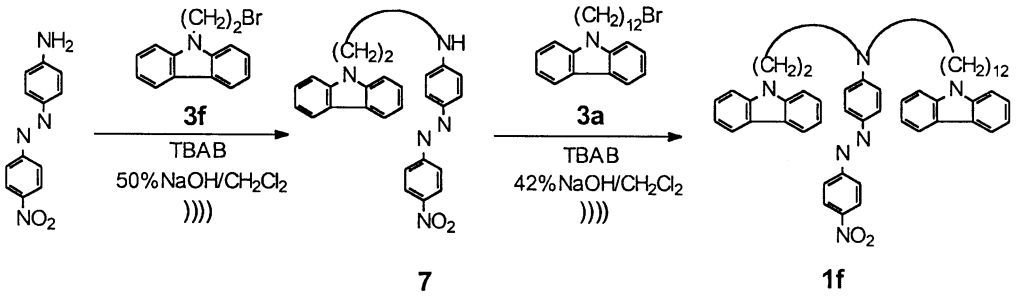
Scheme 5.

Table 2. Yields for the preparation of **1**

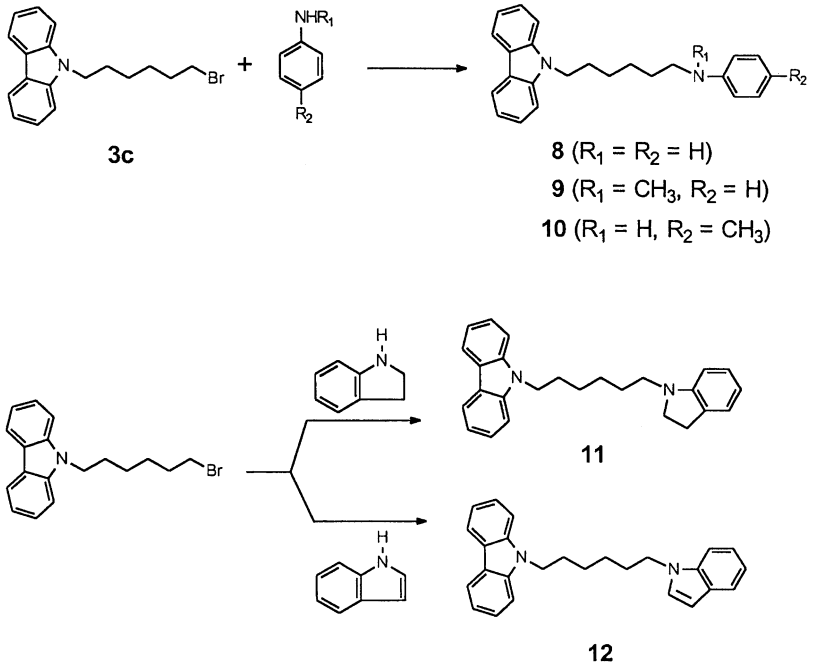
Run	1	*n*	Yield (%)
1	**1a**	12	40
2	**1b**	10	45
3	**1c**	6	52
4	**1d**	4	47
5	**1e**	3	48
6	**1f**	2	<2

The ultrasound strategy worked well when it was applied to prepare **1a–e** (Scheme 5, Table 2). The reaction was carried out in aqueous and methylene chloride phases, and TBAB used as catalyst. The yields have been generally improved up to 40–52%. For example, **1c** was obtained in 52% from the reaction of **3c** with **2**. As monitored by TLC, all the reactions are usually completed in less than 40 h. Compared with the results from the conditions without ultrasound (generally 20–25% yields and more than 100 h), the present results have showed impressive enhancement of reaction rate and improvement on the yield. With shorter reaction time needed, the elimination reaction has been effectively reduced.

There is one exception: this ultrasound approach does not work well for the synthesis of **1f** although it does lead to the formation of the desirable product. The reaction of **2** with β-bromoethylenecarbazole **3f** under PTC and ultrasound conditions produced **1f** in only less than 2% yield. The predominant elimination of *N*-(β-bromoethyl)carbazole gave *N*-vinylcarbazole **4** as a major product. Most likely, high reactivity of **3f** to elimination is caused by the proximity of carbazole that can stabilize carbanion in E1cB mechanism[15] and thus promotes elimination reaction.



Scheme 6.



Scheme 7.

Table 3. Comparison results using PTC with or without ultrasound present

Compound	Without ultrasound			With ultrasound		
	Time (h)	Temp (°C)	Yield (%)	Time (h)	Temp (°C)	Yield (%)
8	72	40	34.0	72	40	66.9
9	48	75	77.1	48	75	86.3
10	48	75	65.9	48	75	80.6
11	72	40	39.7	50	40	40.8
12	24	75	85.4	16	75	92.9

PTC: 50% NaOH/C_6H_6/TBAB.

To effectively tackle the problem, consideration is given to the reactivity of amine groups. The current amine **2** used in the reaction is a secondary amine. A primary amine is usually more reactive than a secondary amine. By and large, the use of a primary amine would effectively enhance the reactivity in *N*-alkylation, which will in turn reduce elimination process. Thus, a new approach has been devised accordingly in which the reaction of *N*-(β-bromoethyl)-carbazole (**3f**) with *Disperse Orange 3*, a primary amine, is carried out first. Indeed, *N*-alkylation has been significantly improved. This new strategy led to **7** in 25% yield. The subsequent *N*-alkylation of **7** with **3a** led to the formation of the desirable product **1f** in 10% yield (Scheme 6).

A combination of PTC with ultrasound obviously provides a more efficient synthetic approach that is needed for the preparation of a series of new bifunctional target molecules. We have further expanded this strategy to a series of amine compounds to examine generality of the advantages. Treatment of **3c** with aniline for 72 h under PTC condition only gave **8** in 34% yield (Scheme 7, Table 3). The yield was dramatically improved to 67% when both PTC and ultrasound were used. Reactions using other aniline derivatives such *N*-methylaniline and 4-methylaniline also showed yield improvement under both PTC and ultrasound conditions. Compound **9** was obtained in 86% yield with ultrasound compared to 77% yield without ultrasound. The yield of compound **10** was also improved by 15% in case of ultrasound. When indoline was used, the reaction time for completion was much shorter (by 22 h) under a combined condition. In case of indole, both short reaction time and higher reaction yield were obtained, 16 h and 93% yield vs. 24 h and 85% yield without ultrasound. These results demonstrate that a combined condition has general effectiveness on versatile types of amine substitutions.

The glass transition temperature (T_g) of **1** has been determined using differential scan calorimetry (DSC, heating rate 10°C in air, Table 4). Since the C_{12} alkyl chain is fixed in the molecule, the T_g is mainly tuned by the other flexible chain which varies from C_2 to C_{12}. The T_g's respond well to the flexible alkyl chain length. The correlation between the even number of the alkyl chain carbons and the T_g is shown in Fig. 2. The use of the flexible alkyl chain from C_2 to C_{12} can fine-tune the overall T_g range between −20 and 94°C. The lowest T_g (−20.7°C) is registered when the flexible chain is C_{12}. From C_{12} to C_{10}, the T_g moves up by 17.3 to −3.4°C. Similarly, from C_6 to C_4, the T_g change is by 15.9°C. The most dramatic change is obtained from C_4 to C_2, by 79.3°C.

Table 4. Thermal properties of bifunctional molecules **1**

	1a	**1b**	**1c**	**1d**	**1e**	**1f**
n	12	10	6	4	3	2
Mp (°C)	−13.3	0.0	80.8	114.7	105.3	126.0
T_g (°C)	−20.7	−3.4	−1.4	14.5	29.3	93.8

As the flexible chain is short (for example when *n*=2 and 4), this unit acts as a pendent group to the main chain which consists of *Disperse Orange 3* and C_{12} carbazole units. As the chain becomes longer, both this one and the fixed C_{12} alkyl chain are branched out from *Disperse Orange 3* unit (Fig. 3).[16] One of the reasons why the current T_g changes so differently according to chain length is probably because these two types of molecular geometry offer different relaxation mechanisms.[17]

The melting temperatures (T_m) determined by DSC (heating

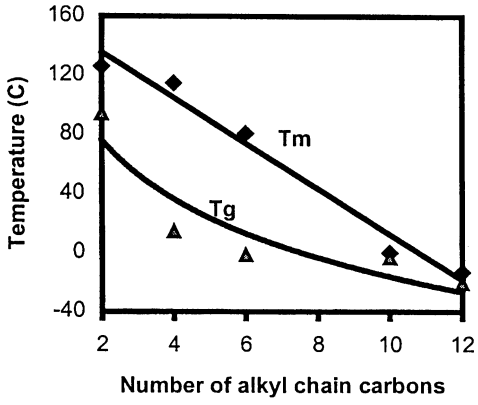


Figure 2. Correlation between flexible chain and T_g and T_m of compound **1**.

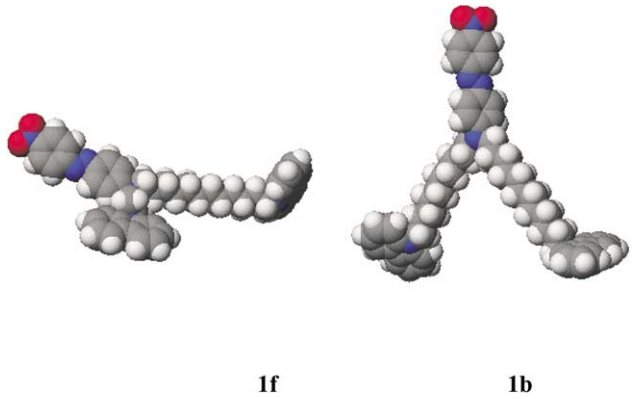


Figure 3. Molecular geometry of **1b** and **1f** in minimum energy.

rate 10°C min^{-1} in air, Table 4) also showed a good response to the length of the flexible alkyl chain. The correlation between the alkyl chain carbons and T_m is presented in Fig. 2. The lowest T_m of −13.3°C is registered in **1a** with a C_{12} chain, and the highest T_m of 126.0°C in **1f** with a C_2 chain. It is noted that **1b** (C_{10}) had a T_m of 0°C. The correlation of T_g or T_m is established only with the even-number carbons of the flexible alkyl chain. The odd-number carbon alkyl chain showed a deviation as a result of even–odd carbon number effect, which has been observed in a series of bifunctional compounds with 1:1 CT–NLO components.[8]

In conclusion, a more efficient synthetic methodology has been developed for the preparation of a series of new bifunctional molecules. The ultrasound effect, in combination with PTC conditions has enhanced *N*-substitution against elimination in the reaction of carbazole-containing bromide with *Disperse Orange 3* derivatives. In particular, with ultrasound assistance, the reaction takes place under mild condition, requires relatively shorter time, and gives moderate yields of substitution product. These advantages prove to be rather general in the substitution reactions of a variety of other amine substrates.

1. Experimental

Disperse Orange 3 was purchased from Acros and Aldrich, and used as received. The dye contents are 95 and 90%, respectively. All other chemicals and solvents were purchased from Adrich and used as received. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a Bruker instrument with TMS as an internal standard for reference. Elemental analysis was performed at Atlantic Microlab at Norcross, Georgia. High resolution MS was obtained in VG Instruments 70SE using electron impact (EI) ionization. DSC and melting point measurement was carried out at Seiko 220C in air with a rate of 10°C min^{-1}.

Ultrasound was generated using Bransonic B-2200R-4 ultrasonic bath, which was filled with water, level of which was always kept less than an inch from the top. Temperature was controlled by circulating water through coiled tubes that were placed in the bottom of the bath. This convenient setup was used for all the ultrasound reactions except for the syntheses of compounds **8**–**12**, for which ultrasound was generated using Autotune Series High Intensity Ultrasonic Processor (750 W) with 25% amplitude and a 13 mm microtip probe.

1.1. Preparation of 3

3a and **3c** were prepared according to the procedure reported previously.[8] **3b**,[18,19] **3d**,[18,19] **3e**,[18,19] and **3f**[19] were prepared in a way similar to that for **3a** and **3c**. **4**[20] and **5**[21] are obtained during the preparation of **3f** and **3e**, respectively.

1.1.1. Compound 3b. ^{1}H NMR ($CDCl_3$/TMS) δ 1.19–1.32 (12H, m); 1.75–1.81 (4H, m); 3.33 (2H, t, J=7.1 Hz); 4.22 (2H, t, J=7.1 Hz); 7.19 (2H, t, J=8.0 Hz); 7.35 (2H, d, J=8.0 Hz); 7.42 (2H, t, J=8.1 Hz); 8.07 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$/TMS): δ 27.7, 28.6, 29.1, 29.4, 29.8, 29.8, 33.3, 34.4, 43.5, 109.1, 119.4, 120.4, 123.3, 126.1, 140.9.

1.1.2. Compound 3d. ^{1}H NMR ($CDCl_3$/TMS) δ 1.88–1.95 (2H, m); 2.03–2.10 (2H, m); 3.38 (2H, t, J=6.3 Hz); 4.36 (2H, t, J=6.2 Hz); 7.22 (2H, t, J=8.1 Hz); 7.40 (2H, d, J=8.1 Hz); 7.47 (2H, t, J=8.2 Hz); 8.10 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 28.1, 30.7, 33.5, 42.6, 108.9, 119.4, 120.8, 123.3, 126.1, 140.7.

1.1.3. Compound 3e. ^{1}H NMR ($CDCl_3$/TMS) δ 2.34–2.39 (2H, m); 3.30 (2H, t, J=6.2 Hz); 4.41 (2H, t, J=6.2 Hz); 7.22 (2H, d, J=8.0 Hz); 7.44 (4H, m); 8.04 (2H, d, J=8.1 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 31.2, 32.2, 41.4, 109.0, 119.8, 120.9, 123.4, 126.3,.140.8.

1.1.4. Compound 3f. ^{1}H NMR ($CDCl_3$/TMS) δ 3.64 (2H, t, J=8.0 Hz); 4.66 (2H, t, J=8.0 Hz); 7.25 (2H, t, J=8.0 Hz); 7.40 (2H, d, J=8.1 Hz); 7.46 (2H, t, J=8.2 Hz); 8.08 (2H, d, J=8.1 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 28.5, 45.1, 108.8, 120.0, 120.7, 123.6, 126.4, 140.4.

1.1.5. Compound 4. ^{1}H NMR ($CDCl_3$/TMS) δ 5.15 (1H, d, J=9.2 Hz); 5.53 (1H, d, J=16.0 Hz); 7.27 (1H, dd, J=16.1, 9.1 Hz); 7.29 (2H, t, J=8.1 Hz); 7.46 (2H, t, J=8.0 Hz); 7.64 (2H, d, J=8.0 Hz); 8.05 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 102.5, 111.0, 120.8, 124.4, 126.7, 130.0, 139.8.

1.1.6. Compound 5. ^{1}H NMR ($CDCl_3$/TMS) δ 4.87 (2H, m); 5.02 (1H, d, J=16.2 Hz); 5.13 (1H, d, J=10.3 Hz); 5.97 (1H, m); 7.22 (2H, m); 7.35 (2H, d, J=8.0 Hz); 7.44 (2H, m); 8.09 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 41.4, 102.5, 108.9, 119.4, 120.8, 123.3, 126.7, 130.0, 140.7.

1.2. Synthesis of 1

The carbazole-containing alkyl bromide **3** (1.6 mmol) was added into a methylene chloride solution (3 mL) of *Disperse Orange 3* derivative **2** (230 mg, 0.4 mmol), followed by the addition of 50% NaOH aqueous solution (10 mL). The flask containing this mixture was immersed in an ultrasound bath in a way that surface of the mixture in the flask was below that of water. No external heat was provided, but the temperature in the bath would arise slowly as ultrasound was generated in a continuous fashion. Bath temperature was controlled at 40°C using circulating water, and the reaction was run for approximately 40 h. The reaction was periodically monitored by TLC. Upon cooling, the mixture was poured into water. Organic substrates were extracted with methylene chloride (3×30 mL). The combined organic solvent was washed with water. After removal of the solvent, the residue was purified by chromatography on silica column (petroleum ether/hexane/methylene chloride, (v/v): 1/2/3). In case without ultrasound, the mixture was stirred with a magnetic stirring bar, and the temperature was controlled in an oil bath. The workup procedure was the same.

1.2.1. Compound 1a. ^{1}H NMR ($CDCl_3$/TMS) δ 1.23–1.31 (32H, m); 1.62 (4H, m); 1.83–1.86 (4H, m); 3.35 (4H, t, J=7.1 Hz); 4.28 (2H, t, J=7.0 Hz); 6.67 (2H, d, J=8.0 Hz); 7.21 (4H, t, J=8.0 Hz); 7.39 (4H, d, J=8.0 Hz); 7.45 (4H, t,

J=8.0 Hz); 7.89 (4H, m); 8.10 (4H, d, J=8.0 Hz); 8.29 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 27.5, 27.7, 27.8, 29.4, 29.8, 29.8, 30.8, 43.5, 51.7, 109.0, 111.7, 119.1, 120.7, 120.9, 122.9, 123.2, 125.1, 125.9, 140.8, 143.7, 147.6, 152.1, 157.0. Anal. calcd: C: 79.26, H: 7.98; Found: C: 79.00, H: 7.91.

1.2.2. Compound 1b. ^{1}H NMR ($CDCl_3$/TMS) δ 1.23–1.29 (28H, m); 1.59 (4H, m); 1.83–1.86 (4H, m); 3.31 (4H, t, J=7.1 Hz); 4.28 (2H, t, J=7.1 Hz); 6.66 (2H, d, J=8.1 Hz); 7.21 (4H, t, J=8.0 Hz); 7.40 (4H, d, J=8.0 Hz); 7.44 (4H, t, J=8.1 Hz); 7.86 (4H, d, J=8.0 Hz); 8.10 (4H, t, J=8.0 Hz); 8.32 (2H, d, J=8.1 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 27.4, 27.7, 27.8, 29.4, 29.8, 29.9, 29.9, 30.0, 43.5, 51.7, 109.2, 111.9, 119.1, 121.0, 123.3, 123.1, 125.1, 126.0, 126.8, 140.9, 143.7, 147.6, 152.1, 157.4. Anal. calcd C: 79.05, H: 7.78; Found: C: 79.19, H: 7.75.

1.2.3. Compound 1c. ^{1}H NMR ($CDCl_3$/TMS) δ 1.24–1.35 (20H, m); 1.56 (4H, m); 1.58–1.92 (4H, m); 3.28 (4H, t, J=7.2 Hz); 4.28 (4H, m); 6.62 (2H, d, J=8.1 Hz); 7.21 (4H, m); 7.39 (4H, d, J=8.1 Hz); 7.44 (4H, t, J=8 Hz); 7.86 (2H, d, J=8.0 Hz); 7.89 (2H, d, J=8.0 Hz); 8.09 (4H, t, J=8.0 Hz); 8.31 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 27.4, 27.6, 27.6, 27.7, 29.3, 29.8, 29.9, 43.3, 43.5, 51.4, 51.7, 109.0, 109.2, 111.6, 119.2, 119.4, 120.7, 120.8, 123.1, 123.2, 125.1, 125.9, 126.0, 126.70, 140.8, 143.7, 147.7, 151.9, 157.4. Anal. calcd C: 78.61, H: 7.39; Found: C: 78.37, H: 7.21.

1.2.4. Compound 1d. ^{1}H NMR ($CDCl_3$/TMS) δ 1.22–1.36 (16H, m); 1.51 (2H, m); 1.71 (2H, m); 1.82–1.88 (2H, m); 1.96–1.99 (2H, m); 3.20 (2H, t, J=7.1 Hz); 3.28 (2H, t, J=7.1 Hz); 4.29 (2H, t, J=7.0 Hz); 4.37 (2H, t, J=7.0 Hz); 6.60 (2H, d, J=8.0 Hz); 7.22 (4H, m); 7.39 (4H, d, J=8.1 Hz); 7.47 (4H, t, J=8.1 Hz); 7.84 (2H, d, J=8.1 Hz); 7.90 (2H, d, J=8.0 Hz); 8.10 (4H, t, J=8.1 Hz); 8.31 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 25.7, 26.9, 27.3, 27.6, 27.7, 29.4, 29.8, 30.1, 43.2, 43.5, 51.2, 51.6, 108.9, 109.0, 111.7, 119.1,119.2, 120.7, 120.9, 122.9, 123.2, 123.4, 125.1, 125.9, 126.1, 126.7, 140.7, 140.8, 143.7, 147.7, 151.8, 157.3. Anal. calcd C: 78.36, H: 7.08; Found: C: 78.47, H: 6.88.

1.2.5. Compound 1e. ^{1}H NMR ($CDCl_3$/TMS) δ 1.21–1.30 (16H, m); 1.54 (2H, m); 1.85 (2H, m); 2.25 (2H, m); 3.26 (2H, t, J=7.1 Hz); 3.38 (2H, t, J=7.0 Hz); 4.29 (2H, t, J=7.0 Hz); 4.42 (2H, t, J=7.0 Hz); 6.50 (2H, d, J=8.0 Hz); 7.24 (4H, m); 7.43 (8H, m); 7.75 (2H, d, J=8.1 Hz); 7.88 (2H, d, J=8.1 Hz); 8.09 (2H, d, J=8.0 Hz); 8.12 (2H, d, J=8.0 Hz); 8.30 (2H, d, J=8.1 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 26.9, 27.2, 27.2, 27.3, 27.7, 27.8, 29.4, 29.7, 29.8, 29.9, 40.9, 43,5, 5.1, 51.8, 108.9, 109.0, 111.7, 119.09, 119.7, 121.0, 121.0, 123.0, 123.2, 123.5, 125.1, 125.9, 126.3, 126.6, 140.7, 140.8, 144.0, 147.8, 151.6, 157.2. Anal. calcd C: 78.23, H: 6.95; Found: C: 78.47, H: 6.98.

1.2.6. Synthesis of 7. 3f (1 g, 3.65 mmol) was added to a mixture that contained methylene chloride (20 mL), *Disperse Orange 3* (1.35 g, 5.6 mmol), TBAB (250 mg, 0.73 mmol), and 50% aqueous NaOH (10 mL). The reaction was run in the ultrasonic bath filled with water so that the content of the reaction flask was immersed in water. The reaction was run at 45°C for 12 h. Water (20 mL) was added and the organic layer was separated. The combined organic solvent was washed with water. The residue was purified by chromatography on silica column three times to give analytical pure sample **7** (400 mg, 25%). **7**: ^{1}H NMR ($CDCl_3$/TMS) δ 3.81 (2H, t, J=6.4 Hz); 4.60 (2H, t, J=6.4 Hz); 6.64 (2H, d, J=8.1 Hz); 7.26 (2H, t, J=8.1 Hz); 7.35 (2H, d, J=8.0 Hz); 7.44 (2H, t, J=8.2 Hz); 7.89 (2H, d, J=8.1 Hz); 7.94 (2H, d, J=8.0 Hz); 8.12 (2H, d, J=8.0 Hz); 8.34 (2H, d, J=8.1 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 42.3, 42.7, 108.8, 112.8, 120.0, 121.0, 123.4, 123.5, 126.1, 126.7, 140.8, 145.5, 148.1, 151.5, 156.9. Anal. calcd C: 71.71, H: 4.86; Found: C: 71.56, H: 4.95.

1.2.7. Synthesis of 1f from 7. 3a (304 mg, 0.73 mmol) in 1 mL of methylene chloride was added to a mixture of **7** (160 mg, 0.37 mmol) and TBAB (24 mg, 0.074 mmol) in methylene chloride (5 mL) and 42% NaOH aqueous solution (3 mL). The reaction was run under ultrasonic bath at 45°C for 10 h. Water (10 mL) was added and the organic layer was separated. The combined organic layer was washed with water, and dried over Na_2SO_4. Upon removal of the solvent, the residue was purified on silica column (hexane/methylene chloride, (v/v): 2/3) for five times to get analytical pure sample. **1f**: ^{1}H NMR ($CDCl_3$/TMS) δ 1.08–1.30 (16H, m); 1.84 (4H, m); 2.87 (2H, t, J=7.1 Hz); 3.86 (2H, t, J=6.3 Hz); 4.27 (2H, t, J=7.2 Hz); 4.57 (2H, t, J=7.1 Hz); 6.75 (2H, d, J=8.0 Hz); 7.21 (4H, m); 7.42 (8H, m); 7.95 (4H, d, J=8.1 Hz); 8.09 (4H, d, J=8.0 Hz); 8.34 (2H, d, J=8.1 Hz). ^{13}C NMR ($CDCl_3$/TMS) δ 27.1, 27.4, 27.7, 29.4, 29.6, 29.7, 29.8, 29.8, 30.8, 40.8, 43.5, 49.7, 52.2, 108.7, 109.0, 111.8, 119.1, 119.8, 120.7, 121.0, 123.1, 123.2, 123.5, 125.1, 125.9, 126.3, 126.8, 140.6, 140.8, 144.3, 147.9, 151.3, 157.2. Anal. calcd C: 78.09, H: 6.82; Found: C: 77.78, H: 7.01.

1.3. General procedure for preparation of compounds 8–12

To a mixture tetra(*n*-butylammonium) bromide (TBAB) (140 mg, 0.43 mmol), **3c** (0.66 g, 2 mmol,), and aromatic amine (2 mmol for compounds **8–10** and 3 mmol for **11–12**) was added sequentially benzene (10 mL), and 50% aqueous NaOH (10 mL). The mixture was stirred at 40 or 75°C for 16–72 h without ultrasound (see Table 3), and then poured into water (50 mL). A crude product was extracted with methylene chloride (3×30 mL). The combined organic solvent was washed with water and dried over Na_2SO_4. Upon the removal of the solvent, the residue was purified by column chromatography on silica gel with ether/hexanes (v/v) 1/8.

In case of ultrasound, the same mixture was charged in a pearl-shaped flask. A microchip probe was inserted into the solution, approximately 1.5 in. away from the bottom. Continuous ultrasound generated was used for the reaction, for which the period was indicated in Table 3. The temperature was controlled by an oil bath. No mechanical stirring was applied. The reaction was monitored periodically by TLC and GC-MS. The workup was essentially the same as described above.

1.3.1. Compound 8. ^{1}H NMR ($CDCl_3$/TMS/TMS): δ 8.09 (2H, d, J=8.0 Hz); 7.43 (4H, m); 7.19 (4H, m); 6.67 (1H, s); 6.54 (2H, d, J=8.0 Hz); 4.28 (2H, t, J=7.0 Hz); 3.50 (1H, br); 3.03 (2H, t, J=7.0 Hz); 1.86 (2H, m); 1.53 (2H, m); 1.39 (8H, m). ^{13}C NMR ($CDCl_3$/TMS): δ 148.5, 140.5, 129.3, 125.7, 123.0, 120.5, 118.9, 118.8, 117.3, 112.8, 108.7, 43.9, 43.0, 29.5, 29.0, 27.2, 27.1. HRMS (EI): calcd M^+ for $C_{24}H_{26}N_2$, 342.2096, Found, 342.2103.

1.3.2. Compound 9. ^{1}H NMR ($CDCl_3$/TMS/TMS): δ 8.13 (2H, d, J=8.0 Hz); 7.47 (4H, m); 7.24 (4H, m); 6.70 (3H, m); 4.32 (2H, t, J=7.0 Hz); 3.27 (2H, t, J=7.0 Hz); 2.89 (3H, s); 1.91 (2H, m); 1.56 (2H, m); 1.40 (4H, m). ^{13}C NMR ($CDCl_3$/TMS): δ 149.3, 140.4, 129.1, 125.6, 122.8, 120.3, 118.7, 115.9, 112.1, 108.6, 52.6, 42.9, 38.2, 28.9, 27.2, 26.9, 26.5. HRMS (EI): calcd M^+ for $C_{25}H_{28}N_2$, 356.2253, Found, 356.2283.

1.3.3. Compound 10. ^{1}H NMR ($CDCl_3$/TMS, ppm): δ 8.13 (2H, d, J=8.0 Hz); 7.47 (4H, m); 7.27 (2H, m); 7.00 (2H, d, J=8.0 Hz); 6.52 (2H, d, J=8.0 Hz); 4.32 (2H, t, J=7.0 Hz); 3.34 (1H, br); 3.06 (2H, t, J=7.1 Hz); 2.26 (3H, s); 1.91 (2H, m); 1.57 (2H, m); 1.44 (4H, m). ^{13}C NMR ($CDCl_3$/TMS): δ 146.1, 140.4, 129.7, 126.2, 125.6, 122.8, 120.3, 118.7, 112.8, 108.6, 44.1, 42.8, 29.4, 28.9, 27.1, 26.9, 20.4. HRMS (EI): calcd M^+ for $C_{25}H_{28}N_2$, 356.2253, Found, 356.2303.

1.3.4. Compound 11. ^{1}H NMR ($CDCl_3$/TMS, ppm): δ 8.12 (2H, d, J=8.1 Hz); 7.45 (4H, m); 7.25 (2H, m); 7.05 (2H, m); 6.64 (1H, m); 6.41 (1H, d, J=8.1 Hz); 4.33 (2H, t, J=7.1 Hz); 3.29 (2H, t, J=7.1 Hz); 3.02 (2H, t, J=7.1 Hz); 1.92 (2H, m); 1.57 (2H, m); 1.44 (4H, m). ^{13}C NMR ($CDCl_3$/TMS): δ 152.6, 140.3, 129.9, 127.1, 125.5, 124.3, 122.8, 120.3, 118.7, 117.2, 108.5, 106.7, 52.9, 49.0, 42.9, 28.9, 28.5, 27.1, 26.9. HRMS (EI): calcd M^+ for $C_{26}H_{28}N_2$, 368.2253, Found, 368.2274.

1.3.5. Compound 12. ^{1}H NMR ($CDCl_3$/TMS): δ 8.07 (2H, d, J=8.0 Hz); 7.60 (1H, d, J=8.1 Hz); 7.42 (2H, m); 7.31 (2H, d, J=8.0 Hz); 7.21 (4H, m); 7.08 (1H, t, J=8.1 Hz); 6.99 (1H, d, J=3 Hz); 6.45 (1H, d, J=3 Hz); 4.22 (2H, t, J=7.1 Hz); 4.01 (2H, t, J=7.1 Hz); 1.79 (4H, m); 1.32 (4H, m). ^{13}C NMR ($CDCl_3$/TMS): δ 140.3, 135.9, 128.5, 127.6, 125.6, 122.8, 121.5, 120.9, 120.3, 119.2, 118.7, 109.3, 108.6, 100.9, 46.1, 42.7, 30.0, 28.7, 26.8, 26.7. HRMS (EI): calcd M^+ for $C_{26}H_{26}N_2$, 366.2096, Found, 366.2094.

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References

1. (a) Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127. (b) Zhang, Y.; Burzynski, R.; Ghosal, S.; Casstevens, M. K. *Adv. Mater.* **1996**, *8*, 111–125.
2. Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060.
3. Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.
4. Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *Chem. Commun.* **1993**, 90.
5. (a) Hayden, L.; Sauter, G.; Ore, F.; Pasillas, P.; Hoover, J.; Lindsay, G.; Henry, R. *J. Appl. Phys.* **1990**, *68*, 456. (b) Kang, C.-S.; Winkelhahn, H.-J.; Schulze, M.; Neher, D.; Wegner, G. *Chem. Mater.* **1994**, *6*, 2159–2166.
6. (a) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Science* **1995**, *268*, 1604–1606. (b) Miller, R. D.; Lee, V. Y.; Twieg, R. J. *Chem. Commun.* **1995**, 245–246.
7. For general reviews on PTC: (a) *Phase-Transfer Catalysis: Mechanisms and Syntheses*, Halpern, M. E., Ed.; American Chemical Society: Washington, DC, 1997. (b) *Phase Transfer Catalysis: Fundamentals, Applications, and Industrial Perspectives*, Starks, C., Liotta, C. L., Halpern, M., Eds.; Chapman and Hall: New York, 1994. (c) *Phase Transfer Catalysis in Organic Synthesis*, Weber, W. P., Gokel, G. W., Eds.; Springer: New York, 1977.
8. Li, X.; Mintz, E. A.; Bu, X. R.; Zehnder, O.; Bosshard, C.; Günter, P. *Tetrahedron* **2000**, *56*, 5785.
9. Part of this work was communicated previously in: Li, X.; Santos, J.; Bu, X. R. *Tetrahedron Lett.* **2001**, *41*, 4057.
10. (a) Suslick, K. S. *Ultrasound: Its Chemical, Physical and Biological Effects*; VCH: Weinheim, 1998. (b) Luche, J.-L. *Synthetic Organic Sonochemistry*; Plenum: New York, 1998.
11. Mason, T. J.; Luche, J.-L. In *Chemistry Under Extreme or Non-Classical Conditions*, Eldik van, R., Hubbard, C. D., Eds.; Wiley: New York, 1996.
12. Reeves, W. P.; McClusky, J. V. *Tetrahedron Lett.* **1983**, *24*, 1585.
13. Jurczak, J.; Ostaszewski, R. *Tetrahedron Lett.* **1988**, *29*, 959.
14. Davidson, R. S.; Patel, A. M.; Safdar, A.; Thornthwaite, D. *Tetrahedron Lett.* **1983**, *24*, 5907.
15. March, J. *Advanced Organic Chemistry*; 4th ed.; Wiley: New York, 1992 p. 992.
16. The structure is refined by performing a pre-optimization calculation in mechanics using augmented MM3, followed by an optimized geometry calculation in MOPAC using PM3 parameters in Cache WorkSystem (version 4.4), Fujitsu Limited, and Oxford Molecular Limited.
17. *Physical Properties of Polymers*, Mark, J. E., Eisenberg, A., Graessley, W. W., Mandelkern, L., Samulski, E. T., Koenig, J. L., Wignall, G. D., Eds.; 2nd ed., American Chemical Society: Washington, DC, 1993 Chapter 2.
18. Katayama, H.; Ito, S.; Yamamoto, M. *J. Phys. Chem.* **1992**, *96*, 10115.
19. Oshima, R.; Wada, T.; Kumanotani, J. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3135.
20. Aldrich catalog.
21. Heller, J.; Hewett, W. A. *Makromol. Chem.* **1964**, *73*, 48.