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Phase Transfer Catalysis for Tandem Alkylation of Azo Dyes for the Synthesis of Novel Multifunctional Molecules

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Abstract—Potentially photorefractive molecules, which possess both a charge transfer component and a nonlinear optical chromophore, were prepared by the direct *N*-monoalkylation of Disperse Orange 3 (**1**) with a carbazole alkyl bromide (**2**) utilizing phase transfer catalysis. Further *N*-alkylation of the remaining active N–H with alkyl halides with various chain lengths allowed the thermal properties of the Disperse Orange 3 derivatives to be fine-tuned. © 2000 Elsevier Science Ltd. All rights reserved.

Direct alkylation of 4-(4-nitrophenylazo) aniline (Disperse Orange 3, **1**) with a carbazole-containing halide has not been reported despite the increasing importance of the potential electro-optical properties expected for such products.[1] Derivatives of Disperse Orange 3 have been pursued actively for application in nonlinear optical materials based upon the donor–space–acceptor (D–π–A) motif in the structure.[2–4] Moreover, the recent development of organic photorefractive materials requires molecules that possess multiple functional groups such as charge transporting and nonlinear optical groups.[5,6] Commercially available Disperse Orange 3, which inherently exhibits nonlinear optical properties, is an ideal starting material for such applications because the active primary amine at Disperse Orange 3 can be readily derivatized. Herein we report the tandem alkylation of Disperse Orange 3 under phase transfer catalysis conditions in the synthesis of a new series of bifunctional molecules **7**. These molecules incorporate a carbazole tethered to a 4-nitrophenylazoaniline by a C_{12} alkyl chain. A second flexible alkyl chain has also been introducted into **7** to fine-tune its physical properties. The carbazole component is a well-known charge-transporting agent as indicated by the wide use of its polymeric counterpart such as poly(9-vinylcarbazole) (PVK)[7,8] in photoconducting devices.

The *N*-alkylation of aromatic amines is usually carried out by the treatment of an amine with an alkyl halide in the presence of a base, usually potassium carbonate, and in some cases, with the addition of potassium iodide to promote the reaction. However, in a similar manner, attempts to *N*-alkylate Disperse Orange 3 gave only low yields of the desired product (Scheme 1), indicating that the commonly used methodology is not effective. *N*-Alkylation of **1** with carbazole-containing bromide **2** was best realized when potassium carbonate was used as base in *n*-BuOH or *i*-PrOH with a 2.5:1 ratio of **1** to **2** (Table 1). The reaction was relatively slow, requiring long reaction times (up to 5 days) to give only a 20% yield of **3**. Attempts to improve the yield by utilizing other high boiling solvents were not fruitful. For example, no reaction was observed in 1,2-dimethoxyethane, while only trace amounts of the desired product (yield <2%) were formed in DMF.

In order to seek milder reaction conditions and improve reaction efficiency, phase transfer conditions were investigated in hope that phase transfer catalysis (PTC)[9–13] would be effective in the *N*-alkylation of Disperse Orange 3. Two catalysts were examined for their effectiveness for *N*-alkylation of carbazole (Scheme 2). Tetrabutylammonium bromide, Bu_4NBr (TBAB) was found to be more effective than benzyltriethylammonium bromide (TBEA)[14] in the alkylation of carbazole with 1,6-dibromohexane (Scheme 2). Most significantly, the PTC condition using TBAB turns out to work quite well for alkylation of large molecules such as Disperse Orange 3 by **2**.

When a 1:1 ratio of **1** and **2** was treated in 50% aqueous $NaOH/CH_2Cl_2$ at room temperature with TBAB (Scheme 1), a mixture of mono- and di-substitution products (**3**, 10% *and* **4**, 25%, entry 1, Table 2) was obtained. This result

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

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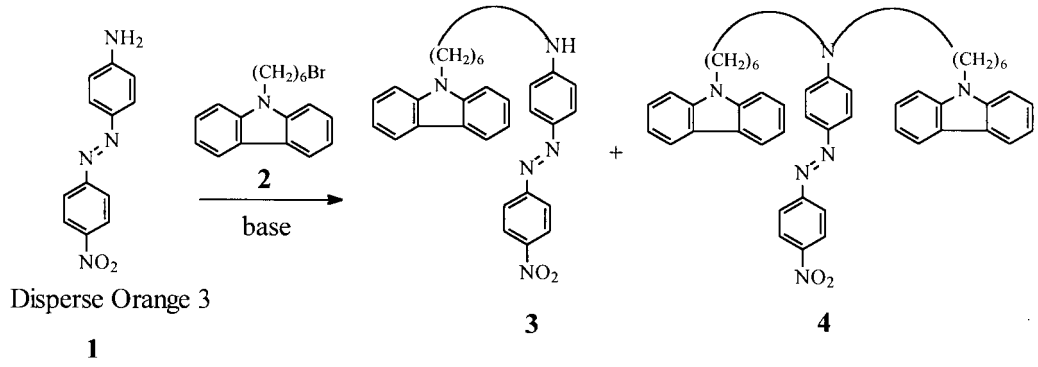


Scheme 1.

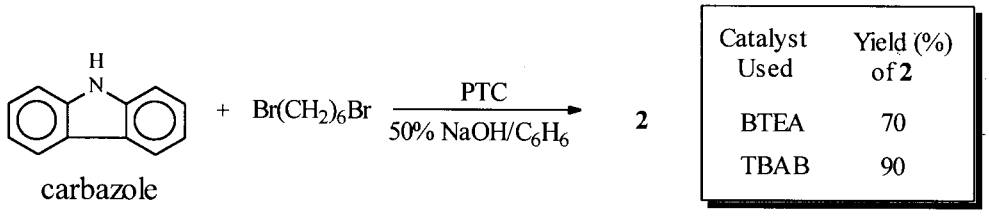
Table 1. Reaction of *N*-(6-bromohexyl)carbazole with 4-(4-nitrophenylazo)aniline

Entry	Method	Ratio **1**:**2**	Reagents	Solvent	*T* (°C)	Time (days)	Yield (%)	
							3	**4**
1	A	5:1	K_2CO_3/KI	*n*-BuOH	Reflux	2	12	–
2	A	2.5:1	K_2CO_3/KI	*n*-BuOH	Reflux	5	20	Trace
3	A	2.5:1	K_2CO_3/KI	*i*-PrOH	Reflux	5	20	Trace
4	A	2.5:1	K_2CO_3/KI	*c*-HxOH	Reflux	2	Trace	–
5	A	3:1	K_2CO_3/KI	DMF	Reflux	2	Trace	–
6	A	2.5:1	K_2CO_3/KI	$(CH_3OCH_2)_2$	Reflux	3	–	–

prompted us to consider how the ratio of **1** to **2** critically effects the *N*-monoalkylation of **1**. The use of an excess of **1** has been found effective to suppress the formation of the di-substitution product **4**. For example, treatment of **1** and **2** in a 3:1 ratio gave **3** in 25% yield and **4** in 5% yield. When the ratio of **1**:**2** is increased to 5:1, a moderate yield of 42% (isolated yield) of **3** was obtained, with less than 1% of di-substitution product **4**. A ratio of **1**:**2** higher than 5:1 complicates the separation without increasing yields. The reaction was achieved at room temperature and within 48 h, suggesting that the present method (method B, Table 2) using PTC condition is much more efficient than method A (Table 1). Thermally driven reactions in method A led to a lot of unidentified insoluble materials while PTC promoted reactions in method B led to much less undesirable by-products.

In addition, direct *N*-alkylation of a prime amine by an alkyl halide in a basic condition is generally a poorly selective reaction, and is often challenged by the formation of mixtures of mono- and di-subsitution products as well as quaternary salts.[15,16] The method B clearly provides high selectivity in *N*-monoalkylation under PTC conditions in moderate yields. To our surprise, the azo unit in Disperse Orange 3 is highly tolerant with PTC promoted basic conditions and maintains its entity intact during the reaction.

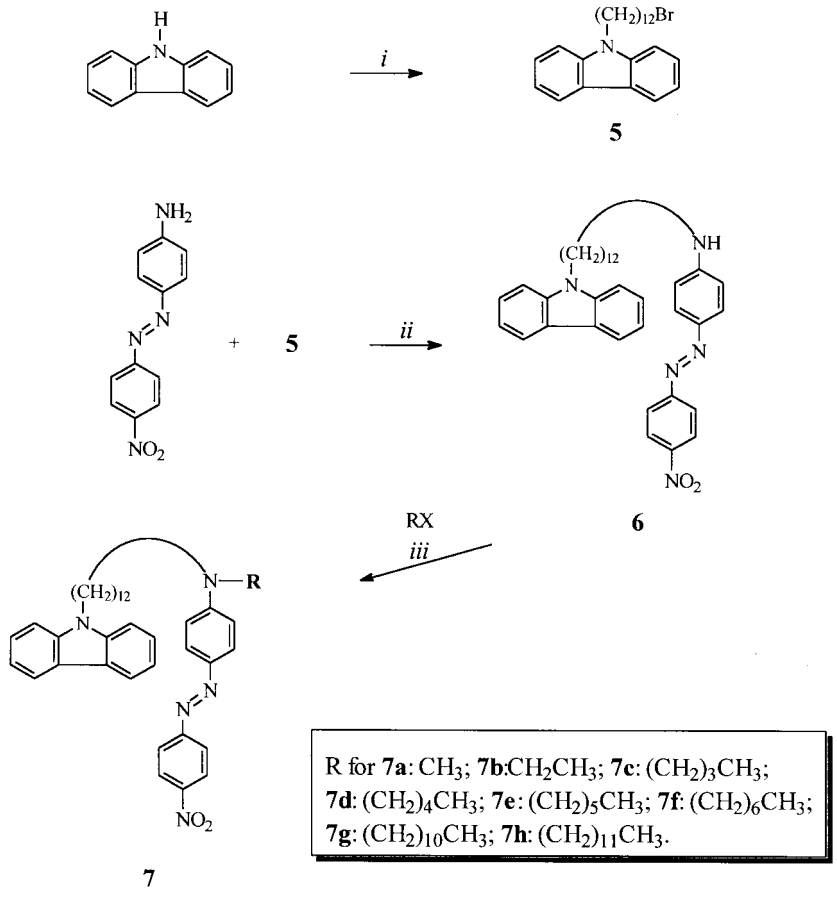
The target molecules **7a**–**h** were synthesized successfully by tandem alkylation of Disperse Orange 3, in three steps from carbazole (Scheme 3). Treatment of 1,12-dibromododecane with carbazole in 50% aqueous NaOH/benzene with TBAB as a PTC gave **5** in 92% yield. The reaction



Scheme 2.

Table 2. Reaction of *N*-(6-bromohexyl)carbazole with 4-(4-nitrophenylazo)aniline

Entry	Method	Ratio **1**:**2**	Reagents	Solvent	*T* (°C)	Time (h)	Yield (%)	
							3	**4**
1	B	1:1	TBAB/NaOH	CH_2Cl_2/H_2O	rt	48	10	25
2	B	2:1	TBAB/NaOH	CH_2Cl_2/H_2O	rt	48	15	12
3	B	3:1	TBAB/NaOH	CH_2Cl_2/H_2O	rt	48	25	5
4	B	5:1	TBAB/NaOH	CH_2Cl_2/H_2O	rt	48	42	Trace



Scheme 3. *i*: $Br(CH_2)_{12}Br$/TBAB/50% NaOH/benzene; *ii*: TBAB/50% NaOH/CH_2Cl_2; *iii*: TBAB/50% NaOH/benzene.

of **5** with Disperse Orange 3 under PTC conditions in 1:5 ratio led to the formation of **6** in 43% yield. **6** was further alkylated with aliphatic halides under PTC conditions to give the requisite compounds **7**.

A series of alkyl halides have been used to *N*-alkylate **6** under PTC conditions to fine-tune the physical properties of **7**. Benzene has been found to be the solvent of choice as the organic phase under the PTC conditions (Scheme 3). When the alkyl chains longer than ethyl were used, mild reaction conditions (40°C) led to the best yields (55–90%). When methyl and ethyl groups are used, the reaction temperature needs to be controlled at 20–25°C in order to eliminate some unidentified side reactions that led to slightly lower yields of the desired products. The optimized reaction conditions gave excellent yields (91–97%, Table 3). In all the cases except methyl, the alkyl bromide was used. In the methyl case, MeI was used, and a 10:1 ratio of the halide to **6** proved to be the best for yields of **7**. Although excess halides have been used in this step, the formation of quaternary salts was not observed.

The glass transition temperatures (T_g) of **6** and **7** were determined using differential scanning calorimetry (DSC, heating rate 10°C min^{-1} in air). Selected data summarized in Table 4 revealed that the T_g was significantly influenced by H-bonding and the size of alkyl chains. The parent compound **6** (R=H) exhibits a T_g at 92.0°C. The substitution of H with a methyl group, or an ethyl group lowers the T_g to −5.3°C (**7a**), and −3.2°C (**7b**), respectively. The compound **7h** with the longest dodecyl alkyl chain exhibits a T_g of −29.5°C. The dramatic decrease of T_g from H (**6**) to methyl (**7a**) suggests that H-bonding may be present in the parent compound. The N–H group found in **6** would be able to

Table 3. Preparation of **7** from **6** in TBAB/NaOH conditions

Compound	RX used	Reaction temperature (°C)	Yield (%)
7a	CH_3I	rt	97
7b	C_2H_5Br	rt	91
7c	C_4H_9Br	40	90
7d	$C_5H_{11}Br$	40	89
7e	$C_6H_{13}Br$	40	71
7f	$C_7H_{15}Br$	40	75
7g	$C_{11}H_{23}Br$	40	55
7h	$C_{12}H_{25}Br$	40	60

Table 4. Thermal properties of compunds **6** and **7**

Compound	R	T_g (°C)	T_m (°C)	T_d (°C)
6	H	92.0	110.7	291.8
7a	CH_3	−5.3	61.9	289.6
7b	C_2H_5	−3.2	81.6	288.8
7c	C_4H_9	−8.4	30.7	289.1
7d	C_5H_{11}	−8.9	21.5	250.5
7e	C_6H_{19}	−21.3	15.5	272.5
7h	$C_{12}H_{25}$	−39.7	−29.5	294.6

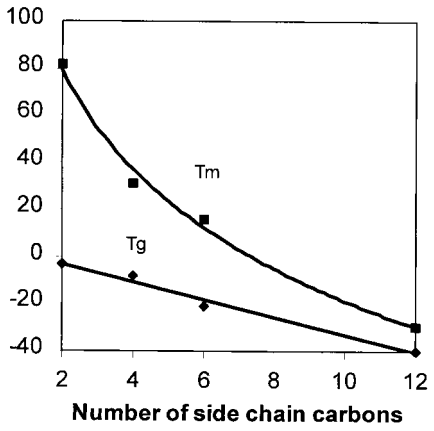


Figure 1. Correlation between tunable side chain and T_g as well as T_m.

participate in H-bonding, but, when the H is replaced with an alkyl group, no H-bonding would occur. The use of longer alkyl chain ultimately leads to lower T_g. In increasing alkyl group length from methyl to dodecyl, the length of alkyl chains may be reasonably viewed as a force for the T_g drop. It is found that a general trend correlates well between even-numbered carbons and T_g as shown in Fig. 1. In contrast to the general trend, odd-numbered carbons had abnormal deviation (not shown). These striking differences may imply the odd–even number effect.[17] Accordingly, **7a** (R=Me, T_g −5.3°C) shows a lower T_g than **7b** (R=Et, T_g −3.2°C). **7d** (R=C_5H_{11}) has a T_g (−8.9°C) that is close to the T_g (−8.4°C) of **7c** (R=C_4H_9).

The melting temperatures (T_m) of compounds **7** determined by DSC revealed that the T_m dropped substantially upon the N-substitution of **6**. The parent compound **6** exhibited a T_m of 110.7°C. The T_m dropped 48.8°C from **6** to the methyl analogues (**7a**). As the alkyl chain increases, the T_m decreases in general. However, the drop does not entirely correspond to the chain length. It was found that the correlation only existed between even-numbered carbons and T_m. The odd-number carbons has a significant deviation. For this reason, the T_m drops 61.9°C from **6** to **7a** (R=Me) as opposed to 81.6°C from **6** to **7b** (R=Et). These important findings from the T_m are in accord with those from the T_g, once again indicating that the H-bonding plays a critical role along with the odd–even number effect.

It is interesting to note that the difference between T_g and T_m for a given compound is influenced significantly by the alkyl group. The difference between T_m and T_g in **6** (R=H) is 19°C while it is 67°C in **7a** (R=Me). Compound **7b** (R=Et) has the largest separation of 85°C. With an increase in the chain length, the separation becomes smaller. For instance, the difference is only about 10°C in compound **7h**, which has a dodecyl group.

Table 5. Electonic absorption and nonlinear optical properties of selected compounds

Compound	λ_{max} (nm)	$\mu\beta$ (10^{-48} esu)
6	453	570
7c	455	930

It is also found that the T_m does not drop as dramatically as the T_g from **6** to the methyl analogue **7a**. The T_m drops 48.8°C while the T_g does 97.3°C. But, in the series, **7**, the T_g drop is much less than the T_m drop as the chain length increases. For instances, the change of the T_g is only 5.2°C as opposed to 50.9°C of the T_m change from **7b** to **7c**.

The onset of thermal decomposition temperatures (T_d) determined by DSC revealed that both **6** and **7** are highly thermally stable. The parent compound **6** did not start to decompose until 291.8°C while its alkyl substituted derivatives **7** exhibited the T_d in the range of 250–280°C (see Table 4). Surprisingly, the use of long alkyl chains does not compromise the thermal stability. For example, **7c** with a C_4 chain had a T_d of 289.1°C while **7a** with a C_1 chain gave a T_d of 289.6°C. These two temperatures are incredibly comparable despite the chain length difference. The most significant result is from **7h** with a C_{12} chain that exhibited an impressive T_d of 294.6°C. These results clearly indicate that the chain length has little effect on the nature of thermal stability and all the compounds show high thermal stability.

The second-order nonlinear optical property is characterized by $\mu\beta$, the scalar product of the dipole moment (μ) and the molecular first-order hyperpolarizability (β). The data of selected compounds are listed in Table 5 along with electronic absorption (in chloroform). The second-order nonlinearity was determined by electric field induced second-harmonic generation (EFISH) at a fundamental wavelength of 1907 nm using a quartz reference (nonlinear optical coefficient d_{11}=0.27 pm/V).[18,19] The molecules clearly show nonlinear optical properties, most significantly, with a big difference in $\mu\beta$ values between the two molecules. Since the molecular nonlinearity can be directly influenced by the strength of donors, acceptors, and/or conjugation pathway, it is understandable that **7c** has a higher molecular nonlinearity than **6** when the N-substitution effect is considered. With *N*,*N*′-di-substituted amino group, **7** possesses a stronger amino donating group, thus, leading to a higher $\mu\beta$ value. In contrast, the aryl amino group in **6** is mono-substituted. Therefore, the N-substitution by alkyl groups provides not only a wide range of thermal properties, but also enhanced molecular nonlinearity.

In view of this and T_g, T_m, and T_d results, it is clear that the use of variable length of alkyl chain has been effective to fine-tune thermal properties such as T_g and T_m without compromising thermal stability as determined by T_d. Thus, compounds **6** and **7a**–**h** could provide potential photorefractive molecules with a wide range of T_g but consistent high thermal stability and enhanced molecular nonlinearity. In host–guest photorefractive materials system, where active organic components are guest and polymeric matrices are host, these compounds could be used as compatible guests in polymeric host matrices with different T_g.

In conclusion, phase transfer catalysis conditions with TBAB were found to be effective in the *N*-alkylation of Disperse Orange 3. A tandem *N*-alkylation strategy has been used to prepare bifunctional molecules with tunable alkyl chains. Alkyl groups have been found to effectively adjust physical properties such as phase transition

temperatures without compromising thermal stability of the compounds.

Experimental

Disperse Orange 3 (**1**) was purchased from Acros and Aldrich, and was used as received. The dye contents are 95 and 90%, respectively. All other chemicals and solvents were purchased from Aldrich or Fisher Scientific and were used as received. ^{1}H and ^{13}C NMR data were acquired on a Bruker 400 MHz spectrometer. Elemental analysis was performed by Atlantic Microlab, Norcross, Georgia. DSC measurement was carried out on Seiko 220C in air with a rate of 10°C min^{-1}. Silica gel used for column chromatography was purchased from Scientific Absorbents, Inc.

The second-order nonlinearity was evaluated by the EFISH method according to a reported procedure,[18] using a pulsed Nd-YAG laser (200 mJ, 10 Hz) that was wavelength-shifted to λ=1.907 μm with a Hydrogen Raman cell. The second-harmonic intensity was detected by a photomultiplier tube. The β values were calibrated against a reference sample of 2-methyl-4-nitroaniline (MNA) in dioxane, using a crystalline quartz as a reference.

Synthesis of 2 and 5 using TBAB as PT catalyst

General procedure. To a mixture of TBAB (80 mg, 0.25 mmol), and aqueous 50% sodium hydroxide (3 mL) was added a solution of carbazole (1.0 g, 6.0 mmol) and dibromide (18 mmol) in benzene (3 mL). The mixture was stirred at room temperature overnight and then poured into water. The organic components were extracted with dichloromethane (3×25 mL). The organic phase was washed with water and dried over sodium sulfate. After removal of solvent, the residue was purified by column chromatography. The elution of the top band by dichloromethane/hexane (1:5, v/v) gave the bromide-containing carbazole.

2. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36–1.50 (m, 4H), 1.76–1.87 (m, 2H), 1.88–1.92 (m, 2H), 3.34 (t, *J*=8 Hz, 2H), 4.30 (t, *J*=8 Hz, 2H), 7.22 (t, *J*=8 Hz, 2H), 7.38 (d, *J*=8 Hz, 2H), 7.46 (t, *J*=8 Hz, 2H), 8.09 (d, *J*=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.9, 28.3, 29.2, 30.0, 34.0, 43.3, 109.0, 119.2, 120.8, 123.3, 126.0, 140.8.

5. yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22–1.39 (m, 16H), 1.80–1.87 (m, 4H), 3.40 (t, *J*=8 Hz, 2H), 4.27 (t, *J*=8 Hz, 2H), 7.39 (d, *J*=8 Hz, 2H), 7.46 (t, *J*=8 Hz, 2H), 8.09 (d, *J*=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.7, 28.6, 29.14, 29.6, 29.8, 29.8, 30.0, 33.2, 34.49, 43.5, 109.0, 119.1, 120.7, 123.2, 126.0, 140.9.

Synthesis of 3

Method A. To a solution of the bromide **2** (330 mg, 1 mmol) and Disperse Orange 3 (625 mg, 2.5 mmol) in 50 mL of solvent (*n*-butanol) was added dry potassium carbonate (350 mg) and potassium iodide (20 mg). The mixture was heated to reflux for 2–5 days as monitored by TLC until **2** was almost gone. Upon cooling, the mixture was poured into water, and extracted with methylene chloride. The organic solvent was removed and the residue was purified by column chromatography on silica gel. The elution of the top purple band by methylene chloride/hexane (1:1 v/v) gave **4**, followed by elution of the first orange band to give **3**.

Method B. To a solution of the bromide **2** (660 mg, 2 mmol) and Disperse Orange 3 (2.5 g, 10 mmol) in 10 mL of methylene chloride was added 50% aqueous NaOH solution (10 mL) and TBAB (100 mg). The mixture was stirred at room temperature for 2 days (or monitored by TLC until **2** was no longer observed). The mixture was poured into water, and extracted with methylene chloride. The organic solvent was removed and the residue was purified by column chromatography on silica gel. The elution of the top purple band by methylene chloride/hexane (1:1 v/v) gave **4**, followed by elution of the first orange band to give **3**.

3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43–1.44 (m, 4H), 1.61 (m, 2H), 1.92 (m, 2H), 3.17 (t, *J*=7 Hz, 2H), 4.34 (t, *J*=7 Hz, 2H), 6.59 (d, *J*=8 Hz, 2H), 7.23 (t, *J*=8 Hz, 2H), 7.36 (d, *J*=8 Hz, 2H), 7.44 (t, *J*=8 Hz, 2H), 7.85 (d, *J*=8 Hz, 2H), 7.91 (d, *J*=8 Hz, 2H), 8.10 (d, *J*=8 Hz, 2H), 8.33 (d, *J*=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.2, 27.5, 29.3, 29.6, 43.3, 43.69, 109.0, 112.5, 119.2, 120.8, 123.4, 123.3, 125.1, 126.0, 126.8, 140.8, 145.1, 147.9, 152.6, 157.12. Anal. Calcd for $C_{30}H_{29}N_5O_2$: C, 73.30; H, 5.95. Found: C, 73.03; H, 5.78.

4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31(m, 4H), 1.37 (m, 4H), 1.52 (m, 4H), 1.87 (m, 4H), 3.20 (t, *J*=7 Hz, 4H), 4.31 (t, 7 Hz, 4H), 6.56 (d, *J*=8Hz, 2H), 7.21 (t, *J*=8 Hz, 4H), 7.37 (d, *J*=8 Hz, 4H), 7.44 (d, *J*=8 Hz, 4H), 7.44 (t, *J*=8 Hz, 4H), 7.80 (d, *J*=8 Hz, 2H), 7.91 (d, *J*=8 Hz, 2H), 8.08 (d, *J*=8 Hz, 4H), 8.30 (d, *J*=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.2, 27.6, 29.4, 43.3, 51.4, 109.2, 111.6, 119.2, 120.8, 112.9, 123.3, 125.1, 126.2, 126.7, 140.8, 143.8, 147.7, 151.8, 157.3. Anal. Calcd for $C_{48}H_{48}N_6O_2$: C, 77.81; H, 6.53. Found: C, 77.58; H, 6.41.

Synthesis of 6

The method B for synthesis of **3** is applied to the preparation of **6**.

6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.37 (m, 16H); 1.62 (m, 2H); 1.88 (m, 2H); 3.20(t, *J*=7 Hz, 2H); 4.29 (t, *J*=7 Hz, 2H); 6.64 (d, *J*=8 Hz, 2H); 7.22 (t, *J*=8 Hz, 2H); 7.40 (d, *J*=8 Hz, 2H); 7.44 (t, *J*=8 Hz, 2H), 7.86 (d, *J*=8 Hz, 2H); 7.90 (d, *J*=8 Hz, 2H); 8.09 (d, *J*=8 Hz, 2H); 8.30 (d, *J*=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.4, 27.7, 29.4, 29.7, 29.8, 29.9, 43.5, 43.9, 109.03, 111.5, 119.1, 120.7, 123.2, 125.0, 125.9, 126.8, 140.8, 140.8, 145.0, 147.9, 152.7, 157.1. Anal. Calcd for $C_{36}H_{41}N_5O_2$: C, 75.10; H, 7.18; N, 12.16. Found: C, 75.32; H, 7.32; N, 11.75.

General synthesis of 7

Compound **6** (230 mg, 0.4 mmol) was added to a mixture of

benzene (2 mL) containing the alkyl halide (4 mmol), 50% aqueous sodium hydroxide solution (10 mL) and TBAB (32 mg, 0.1 mmol). The mixture was stirred at 40°C (or room temperature for methyl and ethyl groups) until **6** was no longer detected by TLC (~18–24 h). The mixture was diluted with water (20 mL), and the organic layer was extracted with methylene chloride (20 mL) and washed with water. After removal of solvents, the residue was purified by column chromatography on silica gel with elution with CH_2Cl_2/hexane (1:1 v/v) to give **7**.

7a. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.31 (m, 16H); 1.54 (m, 2H); 1.86 (m, 2H); 3.07 (s, 3H); 3.42 (t, J=7 Hz, 2H); 4.28 (t, J=7 Hz, 2H); 6.72 (d, J=8 Hz, 2H); 7.22 (t, J=8 Hz, 2H); 7.39 (d, J=8 Hz, 2H); 7.44 (t, J=8 Hz, 2H); 7.87 (d, J=8 Hz, 2H); 7.90 (d, J=8 Hz, 2H); 8.09 (d, J=8 Hz, 2H); 8.31 (d, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.4, 27.4, 27.7, 29.4, 29.8, 29.8, 9.8, 29.9, 39.0, 43.5, 53.1, 109.2, 111.7, 119.1, 120.7, 122.9, 123.1, 125.1, 125.6, 126.6, 140.8, 143.9, 147.7, 152.9, 157.3. Anal. Calcd for $C_{37}H_{43}N_5O_2$: C, 75.35; H, 7.35. Found: C, 75.06; H, 7.62.

7b. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21–1.32 (m, 19H); 1.62 (m, 2H); 1.86 (m, 2H); 3.37 (t, J=7 Hz, 2H); 3.47 (t, J=7 Hz, 2H); 4.29 (t, J=7 Hz, 2H); 6.73 (d, J=8 Hz, 2H); 7.22 (t, J=8 Hz, 2H); 7.39 (d, J=8 Hz, 2H); 7.44 (t, J=8 Hz, 2H); 7.87 (d, J=8 Hz, 2H); 7.90 (d, J=8 Hz, 2H); 8.09 (d, J=8 Hz, 2H); 8.31 (d, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.8, 27.5 27.7, 28.0, 29.35, 29.8, 29.8, 29.8, 29.9, 43.5, 45.8, 51.1, 109.2, 111.7, 119.1, 120.7, 122.9, 123.1, 125.1, 125.9, 126.6, 140.8, 143.9, 147.7, 152.9, 157.3. Anal. Calcd for $C_{38}H_{45}N_5O_2$; C, 75.59; H, 7.51. Found: C, 75.35; H, 7.50.

7c. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J=7 Hz, 3H); 1.23–1.38 (m, 18H); 1.60 (m, 4H); 1.86 (m, 2H); 3.34 (m, 4H); 4.29 (t, J=7 Hz, 2H); 6.70 (d, J=8 Hz, 2H); 7.22 (t, J=8 Hz, 2H); 7.39 (d, J=8 Hz, 2H); 7.43 (t, J=8 Hz, 2H); 7.86 (d, J=8 Hz, 2H); 7.88 (d, J=8 Hz, 2H); 8.08 (d, J=8 Hz, 2H); 8.28 (d, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3, 20.7, 27.5, 27.7, 27.8, 29.4, 29.8, 29.8, 29.9, 29.9, 29.9, 43.5, 51.4, 51.9, 109.0, 111.3, 119.1, 120.7, 122.9, 123.2, 125.1, 125.9, 126.8, 140.8, 143.7, 147.6, 152.1, 157.4. Anal. Calcd for $C_{40}H_{49}N_5O_2$: C, 76.04; H, 7.82. Found: C, 75.92; H, 7.80.

7d. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J=7 Hz, 3H); 1.25–1.37 (m, 20H); 1.62 (m, 4H); 1.86 (m, 2H); 3.36 (m, 4H); 4.29 (t, J=7 Hz, 2H); 6.69 (d, J=8 Hz, 2H); 7.21 (t, J=8 Hz, 2H); 7.40 (d, J=8 Hz, 2H); 7.45 (t, J=8 Hz, 2H); 7.86 (d, J=8 Hz, 2H); 7.89 (d, J=8 Hz, 2H); 8.09 (d, J=8 Hz, 2H); 8.30 (d, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.4 22.9, 27.1, 27.5, 27.7, 27.8, 29.4, 29.6, 29.8, 29.8, 29.9, 29.9, 29.9, 43.5, 51.7, 109.0, 111.6, 119.1, 120.7, 122.8, 123.2, 125.1, 125.9, 126.7, 140.8, 143.7, 147.6, 152.1, 157.4. Anal. Calcd for $C_{41}H_{51}N_5O_2$: C, 76.24; H, 7.96 Found: C, 75.40; H, 7.87.

7e. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7 Hz, 3H); 1.24–1.33 (m, 22H); 1.63 (m, 4H); 1.86 (m, 2H); 3.36 (m, 4H); 4.29 (t, J=7 Hz, 2H); 6.68 (d, J=8 Hz, 2H); 7.21 (t, J=8 Hz, 2H); 7.40 (d, J=8 Hz, 2H); 7.45 (t, J=8 Hz, 2H); 7.86 (d, J=8 Hz, 2H); 7.89 (d, J=8 Hz, 2H); 8.09 (d, J=8 Hz, 2H); 8.30 (d, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.4, 23.0, 27.1, 27.5, 27.7, 27.8, 29.4, 29.8, 29.8, 29.9, 29.9, 29.2, 32.0, 43.5, 51.7, 109.0, 111.6, 119.1, 120.7, 122.9, 123.2, 125.0, 125.9, 126.7, 140.8, 143.7, 147.6, 152.1, 157.4. Anal. Calcd for $C_{42}H_{53}N_5O_2$: C, 76.44; H, 8.095. Found: C, 76.30; H, 8.13.

7f. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7 Hz, 3H), 1.24–1.35 (m, 24H), 1.54–1.64 (m, 4H), 1.87 (m, 2H), 3.39 (t, J=7 Hz, 4H), 4.29 (t, J=7 Hz, 2H), 6.68 (d, J=8 Hz, 2H), 7.22 (t, J=8 Hz, 2H), 7.39 (d, J=8 Hz, 2H), 7.47 (t, J=8 Hz, 2H), 7.88 (t, J=8 Hz, 4H); 8.09 (t, J=8 Hz, 2H), 8.30 (t, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.5, 23.0, 27.5, 27.7, 27.8, 29.4, 29.5, 29.8, 29.8, 29.9, 29.9, 29.9, 30.8, 32.2, 43.5, 51.7, 109.0, 111.6, 119.1, 120.7, 122.9, 123.2, 125.1, 125.9, 126.7, 140.8, 143.7, 147.6, 152.1, 157.4.

7g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J=7 Hz, 3H), 1.24–1.30 (m, 32H), 1.63 (m, 4H,), 1.87 (m, 2H), 3.36 (t, J=7 Hz, 4H), 4.28 (t, J=7 Hz, 2H), 6.68 (d, J=8 Hz, 2H), 7.22 (t, J=8 Hz, 2H), 7.39 (d, J=8 Hz, 2H), 7.45 (t, J=8 Hz, 2H), 7.87 (t, J=8 Hz, 2H), 7.89 (d, J=8 Hz, 2H), 8.09 (t, J=8 Hz, 2H), 8.30 (t, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.5, 23.1, 27.5, 27.7, 27.8, 29.4, 29.7, 29.8, 29.9, 30.0, 32.3, 43.5, 51.7, 109.0, 111.6, 119.1, 120.7, 122.9, 123.2, 125.1, 125.9, 126.8, 140.8, 143.70, 147.6, 152.1, 157.4.

7h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7 Hz, 3H); 1.26–1.32 (m, 32H); 1.62 (m, 4H); 1.86 (m, 2H); 3.36 (m, 4H); 4.29 (t, J=7 Hz, 2H); 6.68 (d, J=8 Hz, 2H); 7.21 (t, J=8 Hz, 2H); 7.40 (d, J=8 Hz, 2H); 7.45 (t, J=8 Hz, 2H); 7.86 (d, J=8 Hz, 2H); 7.89 (d, J=8 Hz, 2H); 8.09 (d, J=8 Hz, 2H); 8.30 (d, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.4, 23.1, 27.4, 27.7, 27.8, 29.4, 29.8, 29.8, 29.9, 29.9, 32.0, 32.3 43.5, 51.7, 109.0, 111.6, 119.1, 120.7, 122.9, 123.4, 125.0, 125.9, 126.7, 120.8, 143.7, 147.6, 152.1, 157.4. Anal. Calcd for $C_{48}H_{65}N_5O_2$: C, 77.48; H, 8.81. Found: C, 77.43; H, 8.92.

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