DOI 10.5012/bkcs.2011.32.2.664

Novel Synthesis of Hydrophilic Dipolar Chromophores using Dendronized Sulfonates

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Received December 22, 2010, Accepted January 17, 2011

A series of hydrophilic chromophores was synthesized through introduction of dendritic sulfonate anions using click chemistry. A dendron structure bearing several sulfonate groups enhances hydrophilicity of attached chromophores. A click triazole formation connects chromophores with hydrophilic groups. A neutral trichloroethyl sulfonate has versatile features such as easy introduction, chemical endurance for isolation or storage, and convenient transformation to a hydrophilic anion. Zinc and OH mediated cleavage of trichloroethyl group from the neutral sulfonate undergoes to generate a water-soluble sulfonate anion. The solubility was examined with different counter cations and in different pH media and thus increased with the number of attached sulfonate ion. Two hydrophilic chromophores of stilbene-derived and azobenzene-derived dipolar structures exhibit clear negative and positive solvatochromism in protic solvents, respectively.

Key Words: Hydrophilic chromophores, Sulfonate ion, Click chemistry, Dendronized sulfonates, Solvatochromism

Introduction

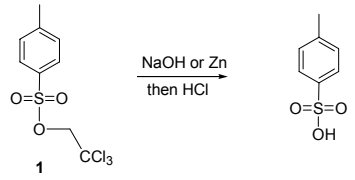
Dendrimers have emerged as an important class of drug encapsulating nanoparticles as a result of their unique architecture and macromolecular characteristics.[1] The most popular class of highly branched molecules, dendrimers, has been intensively studied for two decades. A lot of exciting results related to chemical architectures, synthetic routines, encapsulating properties, aggregation behavior, assembly in solution and surfaces in conjunction with prospective applications in drug delivery, nanocomposite materials, and catalytic systems have been reported.[2,3,4] Many potential applications of dendrimers are based on their unparalleled molecular uniformity, multifunctional surface and the presence of internal cavities. These specific properties make dendrimers suitable for a variety of high technology including biomedical and industrial applications.[3,5,6] Water-soluble optical chromophores have been issued for nanosized molecular switch, sensor, OLED and drug-delivery system.[7] Thus, water soluble dendrons were adapted for the water-media applications.[8] Organic chromophores were derived with ionic groups such as $-SO_3^-$ and $-NH_3^+$.[9]

Huisgen 1,3-dipolar cycloaddition of azide and alkyne yielding a triazole group is popularly known as click chemistry.[10,11] The advantages of employing click chemistry are extraordinary reliability, high conversion yield, atom-economy and functional group tolerance in addition to air and moisture tolerant reaction conditions.[12] We chose the click chemistry of triazole formation in this research to bind organic chromophore and water-solubilizing groups. Ionic sulfonates attached to dendrons make neutral chromophores soluble in water and examine optical property toward a solvent polarity.

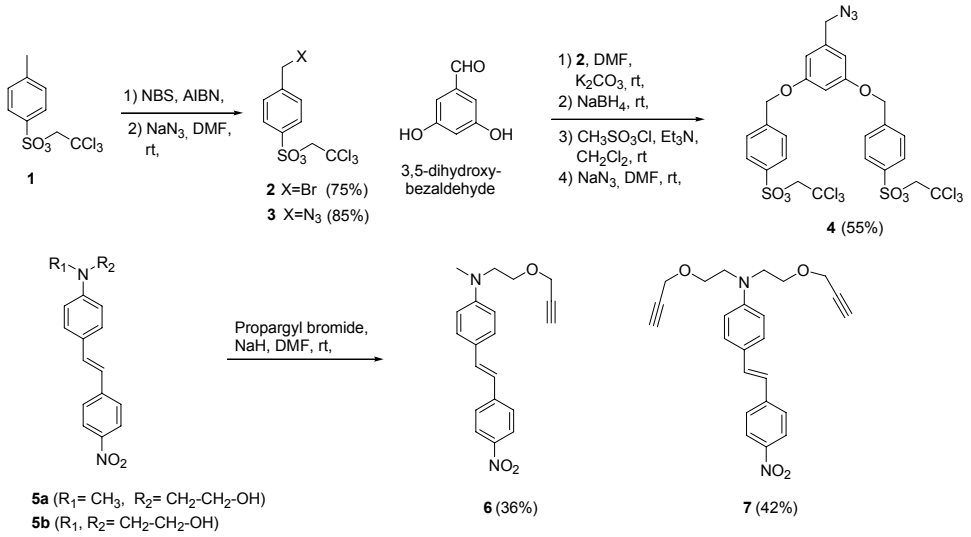
Results and Discussion

Synthesis. We have demonstrated a simple and elegant synthetic method for water-soluble chromophores based on click chemistry. In the approach, the construction of the chromophores takes place in a stepwise manner, starting from the core and building up towards the molecule using two basic operations. The one is formation of the chromophores and derivation for the click reaction. The other is the introduction of sulfonate groups to give sulfonate anion. Aliphatic sulfonates were very frequently introduced for water solubility of molecules and were attachable in a final synthetic step owing to their reactivity and excellent water solubility.[13] We assumed that an aromatic sulfonate such as phenyl sulfonate can reduce the synthetic limitation with hydrophilicity.

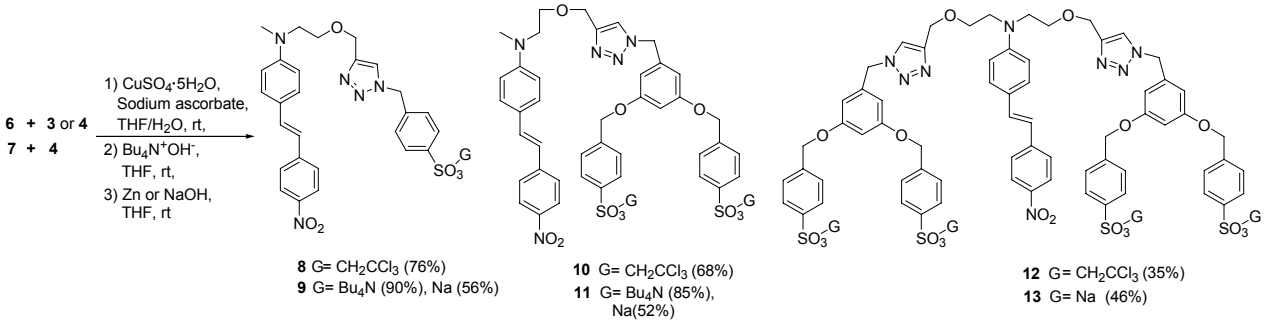
Recently, some articles reported the use of trichloroethyl group (TCE) to protect a sulfonate group. The TCE was readily removed using zinc dust.[14] A basic study was performed with trichloroethyl tosylate as shown in Scheme 1. The cleavage of the sulfonate bond was suggested in two ways. The hydrolysis of alkyl sulfonates by a S_N2 reaction hardly occurred due to a strong S-O strength, whereas benzene sulfonate of 1,1,1-trichloroethanol was observed to readily generate a sulfonate anion.[15] It is attributed to a good leaving ability of trichloroethoxy group. The alkaline hydroxide is too reactive to synthesize dendrimers with ester- or amide-repeated connection. The hydrolysis by zinc is hypothetically initiated by metal insertion reaction onto C-Cl bond and followed by leaving a sulfonate group through β-elimination. Zinc reduction of 2,2,2-trichloroethyl group results in the cleavage of the C-O bond. In spite of no detection of a volatile 1,1-dichloroethene, the explanation was feasible through the generation of toluene sulfonic



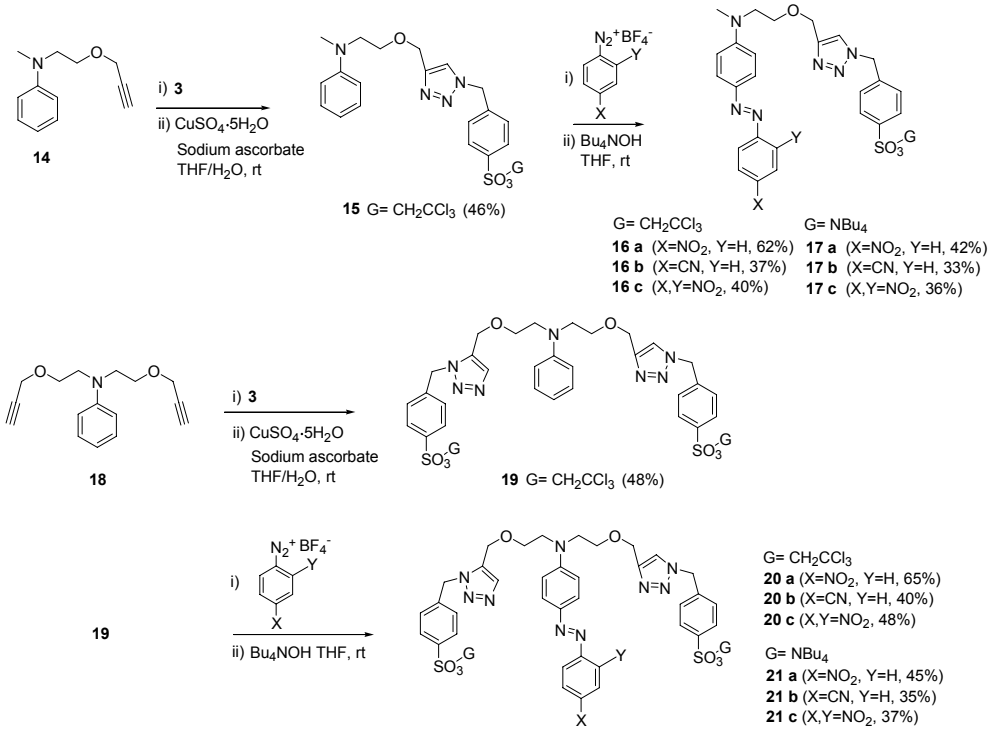
Scheme 1. Hydrolysis of TCE group from sulfonate



Scheme 2. Synthesis of azide and propargyl derivatives



Scheme 3. Synthesis of stilbene-cored chromophores



Scheme 4. Synthesis of azobenzene cored chromophores

acid. Toluene alkylsulfonate derivative **1** was synthesized simply by treatment of toluene sulfonly chloride with 2,2,2-trichloroethanol with 75% yield.

Radical bromination of **1** with *N*-bromosuccinimide (NBS) gave the bromide derivative **2** and treatment of NaN_3 afforded azide derivative **3** in 85% yield. The synthesis of alkyl sulfonate attached azide **4** was begun with alkylation using 3,5-dihydroxy benzaldehyde. A series of alkylation, $NaBH_4$ reduction, methylation, and azidation was successively performed to give azide **4** as shown in Scheme 2. Chromphores **5** (dialkylamino-nitro-stilbene, DANS) was prepared by the according to literature.[16] Propargyl derivatives **6** and **7** were prepared through propargyl alkylation of DANS chromophores.

Coupling reactions with using propargyl derivatives (**6**,**7**) and azide chromophores (**3**,**4**) underwent in the presence of $CuSO_4{\cdot}5H_2O$ and sodium ascorbate in THF/H_2O to form triazole-linked chromophores **8**, **10**, **12** in moderate yields. The triazole formation gave a selective 1,3-adduct as expected with a known Huisgen 1,3-dipolar cycloaddition reaction.[10] The coupled chromophores were further treated with zinc dust or tetrabutylammonium hydroxide to yield the corresponding ionic sulfonates of chromophores. The hydrolysis was completely occurred and confirmed with ^{1}H-NMR analysis which showed disappearance of methylene peaks (4.6 ppm, -CH_2-CCl_3 in $CDCl_3$) after the reaction.

Final dipolar chromophores (**9**, **11**, **13**) with one, two, and four sulfonates were generated with two different salts as shown in Scheme 3. The hydrolysis with sodium hydroxide required longer reaction periods of several days than that with tetrabutylammonium hydroxide. The former was isolated with sodium salts of sulfonates, while the latter was isolated with tetrabutylammonium salts.

Propargyl derivatives **14** and **18** were prepared through propargyl alkylation of *N*-methyl-(phenylamino)ethanol and *N*,*N*-bis-(2-hydroxyethyl)aniline, respectively. Azide derivative **3** was coupled with propargyl derivatives **14** and **18** *via* click reaction to afford triazole-linked sulfonates **15** and **19**, respectively. Azo-cored dipolar chromophores (**16a-c** and **20a-c**) were prepared by a diazonium coupling reaction.[17] The coupled chromophores were hydrolyzed using tetrabutylammonium hydroxide to give tetrabutylammonium salts of sulfonates as shown in Scheme 4. The use of several diazonium salts with cyano, nitro, and dinitro groups similarly formed final hydrophilic chromophores (**17a-c** and **21 a-c**) with moderate yields.

Characterizations

Hydrophilicity of the Prepared Chromophores. We measured solubility of the hydrophilic chromophores in organic solvents such as chloroform, THF, and methanol as well as water. Sodium salt of **9** showed higher water solubility than tetrabutylammonium salt. Sodium ion as a counter cation was better for the water solubility than tetrabutylammonium ion which resulted inversely for the organic solubility as shown in Table 1. The observed solubility of **9** was very low in both organic and water-media, showing less than 5 mg/mL. The sole hydrophilic sulfonate on the structure of **9** was insufficient to provide water solubility of DANS chromophore. The solubility was improved with dendrons carrying several sulfonates. Four sulfonates increased the water solubility of the dipolar chromophores **13** up to 22 mg/mL. The enhanced solubility was similarly observed with azo-cored dipolar chromophores (**17a-c** and **21a-c**) carrying multi sulfonates. We observed pH dependency of the water solubility of two DANS derivatives. The water solubility of sodium salts (**11**, **13**) was measured with varying from pH = 1.0 to pH = 12.0. The solubility was gently enhanced with pH increment as graphed in Figure 1. The solubility of **13** at pH = 10.0 above was understood with high ionic strength arisen from buffer solution. The effect of ionic strength was proved by using an aqueous NaCl solution with same ionic strength, which gave similar solubility result to pH = 10.0. Protonated triazole groups as reasonable spices in pH media were considered to improve the water solubility although protonation and deprotonation processes are complex in pH change.

Table 1. Solubility results of hydrophilic chromophores in various solvents

Compounds	Solubility (mg/mL)[a]			
	$CHCl_3$	THF	CH_3OH	H_2O
9	5.1	3.2	3.2	×[b]
9[c]	×	×	0.02	0.2
11[c]	×	×	0.5	12.1
13[c]	×	×	×	22.4
17a	3.0	3.0	3.0	×
17b	3.1	3.1	0.02	×
21a	×	×	×	2.4
21b	3.3	3.5	2.1	4.4
21c	×	×	2.1	7.1

[a]The solubility was measured with tetrabutylammonium salt unless otherwise. Excess compound was treated with each solvent (20 mL) for 24 hr (20 °C) and insoluble one was filtered out followed by evaporation of solvent to leave a weight of dissolved compound. [b]The X in the table means undetectable amount of a soluble compound. [c]With sodium salt.

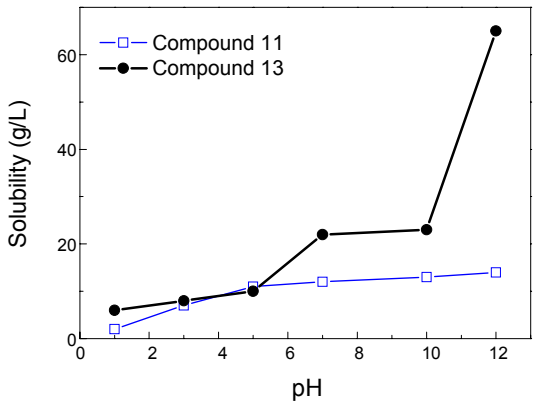


Figure 1. pH dependence of water solubility of **11**-Na and **13**-Na in buffered solutions.

UV-vis Absorption Spectra

As the prepared sulfonate salts of chromophores were slightly soluble in organic solvents as well as water, optical properties

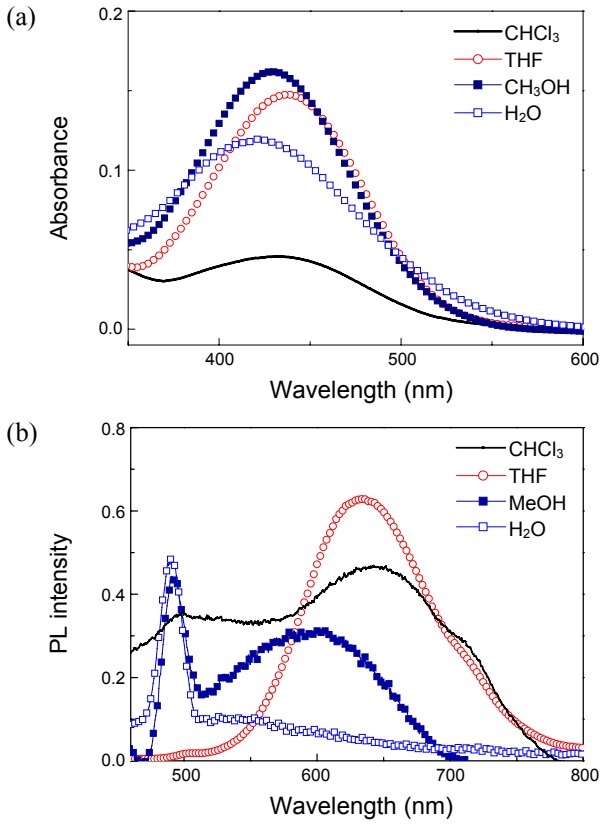


Figure 2. (a) UV-vis absorption (1.0×10^{-5} M) and (b) emission spectra of DANS chromophores **9**-Na irradiated at max. absorption wavelength.

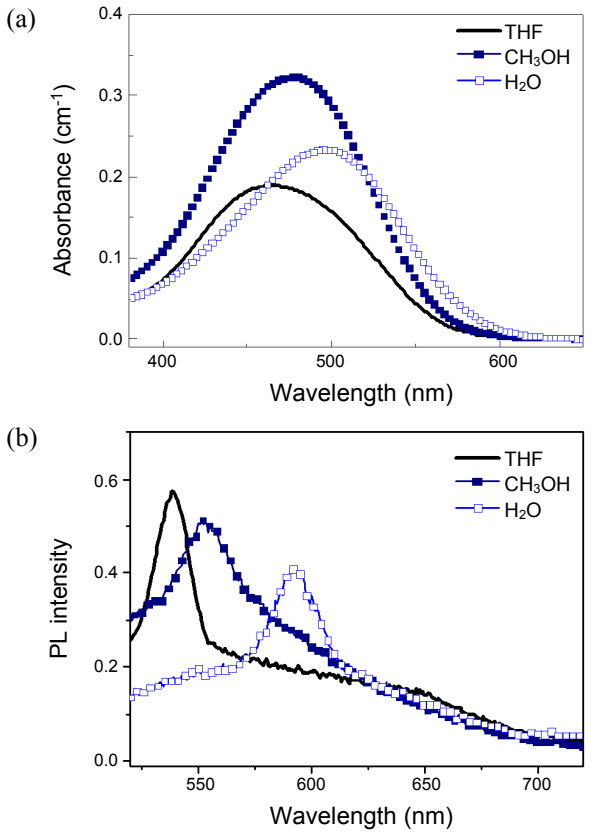


Figure 3. (a) UV-vis absorption (1.0×10^{-5} M) and (b) emission spectra of azo-chromophore **21a** irradiated at max. absorption wavelength.

were examined and compared using various polar solvents. The maximum absorption wavelength shifted with rising solvent polarity through polar interaction of dipolar chromophore. Stilbene-derived dipolar chromophores such as DANS has been reported to exhibit intense π-π* transition and typical negative solvatochromism (hypsochromic shift) in protic solvents.[18] Maximum band at 430 nm of molecule **9** in methanol shifted to 420 nm in water as shown in Figure 2. On the other hand, azo benzene-derived dipolar chromophore such as disperse red (DR) shows typical positive solvatochromism (bathochromic shift) caused by stabilized π* orbital.[19] Figure 3 exhibits a peak wavelength moving toward long wavelength as solvent alters from methanol to water. The negative and positive solvatochromism were similarly observed with other chromophores and summarized in Table 2. DANS derivatives (**11**, **13**) and azobenzene derivatives (**17a-c**, **21b-c**) presented the band shift reversely each other to the solvent polarity. CN attached DR analogues (**17b**, **21b**) afforded a big shift of *ca*. 30 nm and dinitro DR analogues (**17c**, **21c**) also viewed the positive solvatochromism. These spectral shifts were clearly appeared with emission spectrum in Figure 3(b). Maximum emission band of **21a** was moved toward long wavelength as solvent polarity increased. Blue-shifted emission maximum was observed with DANS derivative (**11**) and red-shifted one was observed with azo benzene derivatives (**17a-c**, **21a-c**) listed in Table 2.

Table 2. UV-vis analysis of hydrophilic chromophores in various solvents

Compound	solvent[a]	λ_{max} (nm)	$\lambda_{cut\text{-}off}$ (nm)	$^{c}\varepsilon \times 10^4$	$\lambda_{em\text{-}max}$ (nm)[d]	ϕ_F (%)[e]
11[b]	$CHCl_3$	433	648	1.0	650	1.11
	THF	438	606	1.9	634	0.80
	CH_3OH	432	581	2.9	595	0.01
	H_2O	429	604	1.6	566	0.08
13[b]	CH_3OH	436	576	0.6	594	0.01
	H_2O	428	591	1.6	-	-
17a	THF	483	603	3.7	537	0.01
	CH_3OH	476	603	3.3	542	0.02
	H_2O	499	632	2.1	598	0.03
17b	THF	452	579	0.2	519	0.30
	CH_3OH	449	579	2.9	519	0.01
	H_2O	480	579	0.9	567	0.08
17c	THF	503	635	0.9	521	0.06
	CH_3OH	493	641	0.7	572	0.10
	H_2O	508	659	0.2	607	0.30
21b	THF	449	579	1.5	517	0.20
	CH_3OH	448	579	2.6	517	0.01
	H_2O	480	585	1.5	565	0.10
21c	THF	502	620	1.0	520	0.04
	CH_3OH	492	614	0.9	569	0.02
	H_2O	506	644	0.3	606	0.02

[a]Measured with a concentration of 1.0×10^{-5} M. [b]Sodium salt. [c]Molar absorption coefficient. [d]Emission maximum irradiated at max. absorption wavelength. [e]Quantum efficiency.

Summary

We have demonstrated simple and elegant synthesis of hydrophilic chromophores based on click chemistry. The synthesis contains the generation of hydrophilic sulfonate attached to chromophores. The click triazole formation bound organic chromophores and water-solubilizing groups. Trichloroethyl group to protect a sulfonate ion was useful during the synthetic pathways due to the chemical durability and easy removal. The water solubility was enhanced with the number of dendritic sulfonates. Thus, distinct negative and positive solvatochromism could be observed with two types of dipolar chromophore of stilbene- and azobenzene-derived structures, respectively.

Experimental Section

General. All reagents were purchased from Sigma-Aldrich Chemical Co. and the reagent-grade solvents were dried when necessary and purified by vacuum distillation. Column chromatography was performed using silica gel (Merck, 250 - 430 mesh). ^{1}H-NMR spectroscopy experiments (Bruker AM-300 spectrometer) using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. A MAGNA-IR 750 spectrometer (Nicolet Instrument Co., USA) recorded the FT-IR spectra. The mass spectra were recorded on an Agilent 1200LC/1100 MSD SL mass spectrometer.

Synthesis of Stilbene Cored Chromophores.

Compound 1: To a solution of toluenesulfonyl chloride (20.0 mmol), 2,2,2-trichloroehtanol (22.0 mmol), were dissolved in CH_2Cl_2 (50 mL), and Et_3N (30.0 mmol) were added. The mixture was stirred at room temperature for 12 h. The progress of the reaction was monitored by TLC and upon completion the reaction mixture was extracted with dichloromethane and washed with water (30 mL), brine (20 mL) and dried over anhydrous $MgSO_4$. The solution was concentrated to afford a crude product and purified by column chromatography on silica gel using ethyl acetate and hexane (1/2, v/v) as eluent to give **1**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57 (s, 3H, CH_3), 4.64 (s, 2H, CH_2CCl_3), 7.36 (d, $J = 6.3$ Hz, 2H, ArH), 7.82 (d, $J = 6.3$ Hz, 2H, ArH).

Compound 2: Compound **1** (18.00 mmol) was dissolved in benzene (55 mL) and NBS (18.00 mmol) and a catalytic amount of AIBN (0.90 mmol) were added. The reaction mixture was reflux at 150 ^{o}C for 12 h. After complete disappearance of starting material as indicated by TLC, the resulting mixture was diluted with ethyl acetate. The organic layer was washed with water (30 mL) and brine (20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. The crude product was re-crystallized with dichloromethane (3 mL), and then poured into methanol (30 mL). After standing overnight, the resulting solid product was filtered to afford corresponding product **2**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.52 (s, 2H, CH_2Br), 4.60 (s, 2H, CH_2CCl_3), 7.61 (d, $J = 6.1$ Hz, 2H, ArH), 7.94 (d, $J = 6.1$ Hz, 2H, ArH).

Compound 3: Compound **2** (19 mmol) was dissolved in dimethylformamide (59 mL) and sodium azide (21.00 mmol) was added. The mixture was stirred at room temperature for 12 h. The progress of the reaction was monitored by TLC. Upon completion the reaction mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL), and then dried over anhydrous $MgSO_4$. The solution was concentrated to afford a crude product and purified by column chromatography on silica gel using ethyl acetate and hexane (1/2, v/v) as eluent to give **3**. IR (KBr) ν_{max} 2140 (N_3) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.52 (s, 2H, CH_2N_3), 4.59 (s, 2H, CH_2CCl_3), 7.54 (d, $J = 6.1$ Hz, 2H, ArH), 7.98 (d, $J = 6.1$ Hz, 2H, ArH).

Compound 4: A methane sulfonate (0.54 mmol) of an alcohol prepared from 3,5-dihydroxybenzaldehyde and sodium azide (1.60 mmol) were dissolved in dimethylformamide (1.5 mL). The mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with dichloromethane and washed with water (30 mL) and dried over anhydrous $MgSO_4$. The solution was concentrated to afford a crude product and purified by column chromatography on silica gel using ethyl acetate and hexane (1/4, v/v) as eluent to give **4**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (s, 2H, CH_2-N_3), 4.60 (s, 4H, CH_2CCl_3), 5.18 (s, 4H, CH_2-Ar), 6.57 (s, 3H, ArH), 7.64 (d, $J = 6.3$ Hz, 4H, ArH), 7.95 (d, $J = 6.3$ Hz, 4H, ArH).

Compound 6: To a flask containing sodium hydride (3.00 mmol) in dimethylformamide (6 mL), compound **5a** (2.00 mmol) and propargyl bromide (3.00 mmol) were successively added. The reaction mixture was stirred at room temperature for 72 h under nitrogen. The progress of the reaction was monitored by TLC and upon completion the reaction mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL), and dried over anhydrous $MgSO_4$. The solution was concentrated to afford a crude product and purified by column chromatography on silica gel using ethyl acetate and hexane (1/2, v/v) as eluent to give **6**. IR (KBr) ν_{max} 3201 (HC≡C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 1H, CH), 3.07 (s, 3H, N-CH_3), 3.62 (t, $J = 6.0$ Hz, 2H, N-CH_2), 3.72 (d, $J = 6.0$ Hz, 2H, NCH_2-CH_2), 4.18 (s, 2H, CH_2-CCH), 6.73 (d, $J = 6.3$ Hz, 2H, ArH), 6.91 (d, $J = 6.3$ Hz, 1H, CH), 7.19 (d, $J = 6.1$ Hz, 1H, CH), 7.44 (d, $J = 6.1$ Hz, 2H , ArH), 7.56 (d, $J = 6.0$ Hz, 2H, ArH), 8.18 (d, $J = 6.0$ Hz, 2H, ArH).

Compound 7: Compound **5b** (10.00 mmol) and sodium hydride (30.00 mmol) were dissolved in dimethylformmaide (20 mL) and propargyl bromide (40.00 mmol) was added. The mixture was stirred at room temperature for 72 h under nitrogen. The progress of the reaction was monitored by TLC and upon completion the reaction mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL), and dried over anhydrous $MgSO_4$. The solution was concentrated to afford a crude product and purified by column chromatography on silica gel using ethyl acetate and hexane (1/1, v/v) as eluent to give **7**. IR (KBr) ν_{max} 3202 (HC≡C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 2H, C-CH), 3.67 (t, $J = 6.0$ Hz, 4H, N-CH_2), 3.72 (d, $J = 6.2$ Hz, 4H, NCH_2-CH_2), 4.18 (s, 4H, CH_2O-CH_2), 6.73 (d, $J = 6.0$ Hz, 2H, ArH), 6.91 (d, $J = 6.0$ Hz, 1H, CH), 7.19 (d, $J = 6.2$ Hz, 1H, CH), 7.42 (d, $J = 6.2$ Hz, 2H, ArH), 7.56 (d, $J = 6.0$ Hz, 2H, ArH), 8.17 (d, $J = 6.0$ Hz, 2H, ArH).

Compound 8: Azide compound **3** (0.27 mmol) and propargyl compound **6** (0.27 mmol) were dissolved in THF (2 mL) and mixed with $CuSO_4 \cdot 5H_2O$ (0.027 mmol) and sodium ascorbate (0.054 mmol) in H_2O (1 mL). The mixture was stirred at room temperature for 24 h. The progress of the reaction was monitored by TLC and upon completion the reaction mixture

was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL), and then dried over anhydrous $MgSO_4$. The solution was concentrated to afford a crude product and purified by column chromatography on silica gel using ethyl acetate and hexane (1/1, v/v) as eluent to give **8**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.03 (s, 3H, N-CH_3), 3.61 (t, J = 6.0 Hz, 2H, N-CH_2), 3.72 (t, J = 6.0 Hz, 2H, NCH_2-CH_2), 4.58 (s, 2H, CH_2-Ar), 4.66 (s, 2H, CH_2CCl_3), 5.58 (s, 2H, CH_2O-CH_2), 6.68 (d, J = 9.0 Hz, 2H, ArH), 6.89 (d, J = 12.5 Hz, 1H, CH), 7.18 (d, J = 12.5 Hz, 1H, CH), 7.38 (t, J = 6.3 Hz, 4H, ArH & 1H, CH), 7.56 (d, J = 6.1 Hz, 2H, ArH), 7.94 (d, J = 9.0 Hz, 2H, ArH), 8.18 (d, J = 9.0 Hz, 2H, ArH); LC-MS: m/z 680 $[M+1]^+$.

Compound 9: Compound **8** (0.06 mmol) was dissolved in dry THF (1.5 mL) and treated with tetrabutylammonium hydroxide (0.12 mmol) at room temperature for 1.5 h. The progress of the reaction was monitored by TLC and the solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica gel using methanol and ethyl acetate (1/2, v/v) as eluent to give **9**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, J =14.7 Hz, 12H, $N(CH_2)_3$-CH_3), 1.35-1.43 (m, 8H, NCH_2CH_2-CH_2), 1.59-1.62 (m, 8H, NCH_2-CH_2), 2.96 (s, 3H, N-CH_3), 3.23 (t, J = 12.5 Hz, 8H, N-CH_2-$CH_2CH_2CH_3$), 3.52 (t, J = 9.0 Hz, 2H, N-CH_2), 3.64 (t, J = 9.0 Hz, 2H, NCH_2-CH_2), 4.56 (s, 2H, CH_2-Ar), 5.43 (s, 2H, CH_2-CCH), 6.64 (d, J = 9.0 Hz, 2H, ArH), 6.88 (d, J = 15.0 Hz, 1H, CH), 7.15 (t, J = 15.0 Hz, 2H, ArH & 1H, CH), 7.36 (d, J = 9.0 Hz, 2H, ArH), 7.54 (d, J = 9.0 Hz, 2H, ArH), 7.88 (d, J = 9.0 Hz, 2H, ArH), 8.12 (d, J = 8.7 Hz, 2H, ArH).

Compound **8** (0.06 mmol) was dissolved in THF/H_2O (4/1, v/v) and sodium hydroxide (0.09 mmol) was added and then stirred at room temperature for 48 h. The solution was concentrated and purified by column chromatography on silica gel using methanol and ethyl acetate (1/1, v/v) as eluent to give **9**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.04 (s, 3H, N-CH_3), 3.60 (t, J = 9.0 Hz, 2H, N-CH_2), 3.68 (t, J = 9.0 Hz, 2H, NCH_2-CH_2), 4.58 (s, 2H, CH_2-Ar), 5.39 (s, 2H, CH_2O-CH_2), 6.67 (d, J = 9.0 Hz, 2H, ArH), 7.06 (d, J = 9.0 Hz, 2H, ArH), 7.17 (d, J = 9.0 Hz, 1H, CH), 7.22 (d, J = 9.0 Hz, 1H, CH), 7.40 (d, J = 9.0 Hz, 1H, CH), 7.56 (d, J = 9.0 Hz, 2H, ArH), 7.67 (d, J = 9.0 Hz 2H, ArH), 7.74 (d, J = 8.9 Hz, 2H, ArH), 8.15 (d, J = 8.7 Hz, 2H, ArH).

Compound 10: Compound **4** (0.30 mmol) and compound **6** (0.30 mmol) were dissolved in THF (1 mL) and mixed with $CuSO_4 \cdot 5H_2O$ (0.03 mmol) and sodium ascorbate (0.06 mmol) in H_2O (0.5 mL). The mixture was stirred at room temperature for 19 h. The reaction mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated to afford a crude product and purified by column chromatography on silica gel using ethyl acetate and hexane (1/2, v/v) as eluent to give **10**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02 (s, 3H, N-CH_3), 3.61 (t, J = 9.0 Hz, 2H, N-CH_2), 3.72 (t, J = 9.0 Hz, 2H, NCH_2-CH_2), 4.61 (s, 4H, CH_2CCl_3), 4.65 (s, 2H, CH_2-Ar), 5.11 (s, 4H, CH_2-Ar), 5.42 (s, 2H, CH_2O-CH_2), 6.49 (d, J = 9.0 Hz 3H, ArH), 6.69 (d, J = 9.0 Hz 2H, ArH), 6.88 (d, J = 9.0 Hz 1H, CH), 7.18 (d, J = 9.0 Hz, 1H, CH), 7.38 (t, J = 9.0 Hz, 2H, ArH & 1H, CH), 7.54 (d, J = 9.0 Hz, 2H, ArH), 7.61 (d, J = 9.0 Hz, 4H, ArH), 7.98 (d, J = 9.0 Hz, 4H, ArH), 8.16 (d, J = 9.0 Hz, 2H, ArH); LC-MS: m/z 1126 $[M+2Na]^+$.

Compound 11: Compound **10** (0.05 mmol) and tetrabutylammonium hydroxide (0.22 mmol) were dissolved in THF (1 mL). The mixture was stirred at room temperature for 1.5 h. Concentrated mixture was purified by column chromatography on silica gel using methanol and ethyl acetate (1/2, v/v) as eluent to give **11**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 12.0 Hz, 24H, $N(CH_2)_3$-CH_3), 1.32-1.44 (m, 16H, NCH_2CH_2-CH_2), 1.54-1.64 (m, 26H, NCH_2-CH_2), 2.98 (s, 3H, N-CH_3), 3.21 (t, J = 9.0 Hz, 16H, N-CH_2), 3.52 (t, J = 9.0 Hz 2H, N-CH_2), 3.68 (t, J = 9.0 Hz, 2H, NCH_2-CH_2), 4.60 (s, 2H, CH_2-Ar), 4.95 (s, 4H, CH_2-Ar), 5.38 (s, 2H, CH_2O-CH_2), 6.38 (s, 1H, ArH), 6.43 (s, 2H, ArH), 6.65 (d, J = 9.0 Hz, 2H, ArH), 6.85 (d, J = 9.0 Hz, 1H, CH), 7.16 (d, J = 9.0 Hz, 1H, CH), 7.28 (d, J = 9.0 Hz, 4H, ArH), 7.38 (d, J = 9.0 Hz, 2H, ArH), 7.44 (s, 1H, CH), 7.52 (d, J = 6.0 Hz, 2H, ArH), 7.84 (d, J = 6.0 Hz, 4H, ArH), 8.12 (d, J = 6.0 Hz, 2H, ArH).

Compound **10** (0.08 mmol) and sodium hydroxide (0.18 mmol) were dissolved in THF/ H_2O (2/1 mL, v/v). The mixture was stirred at room temperature for 72 h. The solvent was concentrated under vacuum. The residue was purified by column chromatography on silica gel using methanol and ethyl acetate (2/1, v/v) as eluent to give **11**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.95 (s, 3H, N-CH_3), 3.57 (t, J = 9.0 Hz, 2H, N-CH_2), 3.69 (t, J = 9.0 Hz, 2H, NCH_2-CH_2), 4.60 (s, 2H, CH_2-Ar), 5.05 (s, 4H, CH_2-Ar), 5.44 (s, 2H, CH_2O-CH_2), 6.48 (d, J = 9.0 Hz, 2H, ArH), 6.62 (d, J = 9.0 Hz, 1H, ArH), 6.68 (d, J = 9.0 Hz 2H, ArH), 6.97 (d, J = 9.0 Hz, 1H, CH), 7.27 (d, J = 9.0 Hz, 1H, CH), 7.40 (d, J = 9.0 Hz, 2H, ArH), 7.46 (d, J = 9.0 Hz, 4H, ArH), 7.66 (d, J = 8.9 Hz, 4H, ArH), 7.83 (d, J = 8.9 Hz, 4H, ArH), 8.16 (d, J = 8.7 Hz, 2H, ArH).

Compound 12: Compound **7** (0.15 mmol) and compound **4** (0.30 mmol) were dissolved in THF (2 mL) and mixed with $CuSO_4 \cdot 5H_2O$ (0.03 mmol) and sodium ascorbate (0.06 mmol) in H_2O (0.5 mL). The mixture was stirred at room temperature for 96 h. The reaction mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. The concentrated crude mixture was purified by column chromatography on silica gel using ethyl acetate and hexane (2/1, v/v) as eluent to give **12**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (d, J = 9.0 Hz, 4H, N-CH_2), 3.71 (d, J = 9.0 Hz 4H, NCH_2-CH_2), 4.60 (s, 8H, CH_2-Ar & CH_2-CCl_3), 5.91 (s, 8H, CH_2-Ar), 5.42 (s, 4H, CH_2O-CH_2), 6.41 (d, J = 9.0 Hz, 6H, ArH), 6.56 (d, J = 9.0 Hz, 2H, ArH), 6.87 (d, J = 12.0 Hz, 1H, CH), 7.16 (d, J = 12.0 Hz, 1H, CH), 7.37 (d, J = 6.3 Hz, 2H, ArH), 7.45 (s, 2H, CH), 7.54 (d, J = 6.3 Hz, 2H, ArH), 7.61 (d, J = 9.0 Hz, 8H, ArH), 7.98 (d, J = 9.0 Hz, 8H, ArH), 8.16 (d, J =9.0 Hz, ArH); LC-MS: m/z 1933 $[M+1]^+$.

Compound 13: Compound **12** (0.046 mmol) and sodium hydroxide (0.23 mmol) were dissolved in THF/ H_2O (4/1 mL, v/v). The reaction mixture was stirred at room temperature for 20 h. The solvent was concentrated under vacuum. The residue was purified by column chromatography on silica gel using methanol and ethyl acetate (2/1, v/v) as eluent to give **13**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (d, J = 9.0 Hz, 4H, N-CH_2), 3.59 (t, J = 9.0 Hz,4H, NCH_2-CH_2), 4.52 (s, 4H, CH_2-Ar), 5.01 (s, 8H, CH_2-Ar), 5.43 (s, 4H, CH_2O-CH_2), 6.51 (s, 4H, ArH), 6.58 (d, J = 6.0 Hz, 2H, ArH), 6.64 (s, 2H, ArH), 6.91 (d, J = 12.0 Hz,1H, CH), 7.20 (d, J = 12.0 Hz, 1H, CH), 7.32 (d, J =

9.0 Hz, 2H, ArH), 7.42 (d, J = 9.0 Hz, 8H, ArH), 7.61 (d, J = 9.0 Hz, 2H, ArH), 7.76 (s, 2H, CH), 7.80 (d, J = 9.0 Hz, 8H, ArH), 8.14 (d, J = 9.0 Hz, , ArH).

Synthesis of Azo-cored Chromophore.

Compound 14: *N*-Methyl-(phenyl-amino)ethanol (5.00 mmol) was dissolved in dimethylsulfoxide (5 mL) and stirred with potassium hydroxide (7.00 mmol) and propargyl bromide (7.50 mmol) at room temperature for 72 h. The reaction mixture was diluted with dichloromethane and washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. A concentrated crude product was purified by column chromatography on silica gel using ethyl acetate and hexane (1/20, v/v) as eluent to give **14**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 3H, N-CH_3), 3.49 (t, J = 9.0 Hz, 2H, N-CH_2), 3.66 (t, J = 9.0 Hz, 2H, NCH_2-CH_2), 4.20 (s, 2H, CH_2-CCH), 6.79 (t, J = 6.0 Hz, 3H, ArH), 7.30 (t, J = 6.0 Hz, 2H, ArH).

Compound 15: Compound **14** (1.30 mmol) and compound **3** (1.6 mmol) were dissolved in THF (3 mL) and mixed with $CuSO_4$·$5H_2O$ (0.13 mmol) and sodium ascorbate (0.26 mmol) in H_2O (0.5 mL) at room temperature for 19 h. The mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (2/1, v/v) as eluent to give **15**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 3H, N-CH_3), 3.49 (t, J = 9.0 Hz, 2H, N-CH_2), 3.66 (t, J = 9.0 Hz, 2H, NCH_2-CH_2), 4.55 (s, 2H, CH_2-Ar), 4.61 (s, 2H, CH_2-CCl_3), 5.52 (s, 2H, CH_2O-CH_2), 6.62 (t, J = 9.0 Hz, 3H,ArH), 7.14 (t, J = 9.0 Hz, 2H, ArH), 7.34 (d, J = 9.0 Hz, 2H, ArH), 7.88 (d, J = 9.0 Hz, 2H, ArH).

Compound 16a: *p*-Nitroaniline (0.38 mmol) was dissolved in acetic acid (0.14 mL) and tetrafluoroboric acid (0.07 mL) and mixed with sodium nitrite (0.42 mmol) in water (0.1 mL) for appropriate time at 0 °C. After complete disappearance of starting material as indicated by TLC, compound **15** (0.19 mmol) in acetonitrile was added dropwise at room temperature. Upon completion of starting material on TLC, the reaction mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (1/1, v/v) as eluent to give **16a**. Yield 62%.;^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10 (s, 3H, N-CH_3), 3.66 (t, J = 6.3 Hz, 2H, N-CH_2), 3.75 (t, J = 6.3 Hz, 2H, NCH_2-CH_2), 4.57 (s, 2H, CH_2-Ar), 4.65 (s, 2H, CH_2-CCl_3), 5.56 (s, 2H, CH_2O-CH_2), 6.77 (d, J = 9.0 Hz, 2H, ArH), 7.37 (d, J = 9.0 Hz, 2H, ArH), 7.56 (s, 1H, CH), 7.87-7.97 (m, 4H, ArH), 8.29 (d, J = 9.0 Hz, 2H, ArH). LC-MS: m/z 682 $[M+1]^+$.

Compound 16b: 4-Aminobenzonitrile (0.38 mmol) was dissolved in acetic acid (0.14 mL) and tetrafluoroboric acid (0.07 mL) and mixed with sodium nitrite (0.42 mmol) in water (0.1 mL) at 0 °C. After complete disappearance of starting material, compound **15** (0.19 mmol) in acetonitrile was added dropwise at room temperature. The reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The mixture was concentrated and purified by column chromatography on silica gel with ethyl acetate/hexane (2/1, v/v) as eluent to give **16b**. Yield 37.%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.11 (s, 3H, N-CH_3), 3.66 (t, J = 6.0 Hz, N-CH_2), 3.76 (t, J = 6.0 Hz, 2H, NCH_2-CH_2), 4.55 (s, 2H, CH_2-Ar), 4.63 (s, 2H, CH_2-CCl_3), 5.54 (s, 2H, CH_2O-CH_2), 6.76 (d, J = 9.0 Hz, 2H, ArH), 7.36 (t, J = 6.0 Hz, 2H, ArH & 1H, CH), 7.70 (d, J = 9.0 Hz, 2H, ArH), 7.86-7.96 (m, 8H, ArH). LC-MS: m/z 662 $[M+1]^+$.

Compound 16c: 2,4-Dinitroanline (0.20 mmol) was dissolved in acetic acid (0.14 mL) and hydrochloric acid (0.09 mL) and mixed with sodium nitrite (0.42 mmol) in water (0.5 mL) at 0 °C and then stirred at room temperature. After complete disappearance of starting material on TLC, compound **15** (0.19 mmol) in THF was added dropwise at room temperature. Upon completion of the reaction, the mixture was diluted with ethyl acetate and washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (1/1, v/v) as eluent to give **16c**. Yield 40%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.11 (s, 3H, N-CH_3), 3.68 (t, J = 12.0 Hz, N-CH_2), 3.78 (t, J = 15.0 Hz, 2H, NCH_2-CH_2), 4.57 (s, 2H, CH_2-Ar), 4.66 (s, 2H, CH_2-CCl_3), 5.56 (s, 2H, CH_2O-CH_2), 6.78 (d, J = 9.0 Hz, 2H, ArH), 7.41 (t, J = 15.0 Hz, 2H, ArH & 1H, CH), 7.77 (d, J = 9.0 Hz, 2H, ArH), 7.86-7.96 (m, 8H, ArH).

Compound 17a-c: Compound **16a-c** (0.07 mmol) and tetrabutylammonium hydroxide (0.12 mmol) were dissolved in THF (1 mL). The reaction mixture was stirred room temperature for 12 h. The solvent was removed by rotary evaporation and the crude residue was purified by column chromatography on silica gel with methanol/ethyl acetate (1/2, v/v) as eluent to give **17a-c**:

Compound 17a: Yield 42%.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 12.0 Hz, 12H, $N(CH_2)_3$-CH_3), 1.24-1.36 (m, 8H, NCH_2CH_2-CH_2), 1.48-1.58 (m, 8H, NCH_2-CH_2), 2.99 (s, 3H, N-CH_3), 3.19 (t, J = 12.0 Hz, 8H, N-CH_2), 3.54 (d, J = 6.0 Hz, 2H, N-CH_2), 3.58 (d, J = 6.0 Hz, 2H, NCH_2-CH_2), 4.46 (s, 2H, CH_2-Ar), 5.36 (s, 2H, CH_2O-CH_2), 6.62 (d, J = 9.0 Hz, 2H, ArH), 7.10 (d, J = 9.0 Hz, 2H, ArH), 7.31 (s, 1H, CH), 7.74-7.82 (m, 6H, ArH), 8.17 (d, J = 9.0 Hz, 2H, ArH).

Compound 17b: Yield 33%.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 15.0 Hz,12H, $N(CH_2)_3$-CH_3), 1.28-1.40 (m, 8H, NCH_2CH_2-CH_2), 1.51-1.62 (m, 8H, NCH_2-CH_2), 3.01 (s, 3H, N-CH_3), 3.21 (t, J = 15.0 Hz, 8H, N-CH_2), 3.57 (d, J = 6.0 Hz, 2H, N-CH_2), 3.62 (d, J = 6.0 Hz, 2H, NCH_2-CH_2), 4.50 (s, 2H, CH_2-Ar), 5.38 (s, 2H, CH_2O-CH_2), 6.70 (d, J = 9.0 Hz, 2H, ArH), 7.16 (d, J = 9.0 Hz, 2H, ArH), 7.29 (s, 1H, CH), 7.69 (d, J = 9.0 Hz, 2H, ArH), 7.78-7.86 (m, 6H, ArH).

Compound 17c: Yield= 36%.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, J = 12.0 Hz, 12H, $N(CH_2)_3$-CH_3), 1.28-1.40 (m, 8H, NCH_2CH_2-CH_2), 1.51-1.62 (m, 8H, NCH_2-CH_2), 3.01 (N-CH_3), 3.27 (t, J = 12.0 Hz, 8H, N-CH_2), 3.58 (d, J = 6.0 Hz, 2H, N-CH_2), 3.67 (d, J = 6.0 Hz, 2H, NCH_2-CH_2), 4.50 (s, 2H, CH_2-Ar), 5.38 (s, 2H, CH_2O-CH_2), 6.70 (d, J = 9.0 Hz, 2H, ArH), 7.17 (d, J = 9.0 Hz, 2H, ArH), 7.29 (s, 1H, CH), 7.74 (d, J = 9.0 Hz, 2H, ArH), 7.78-7.86 (m, 6H, ArH).

Compound 18: *N*,*N*-Bis-(2-hydroxy ethyl)aniline (5 mmol) was dissolved in dimethylsulfoxide (5 mL) and potassium hydoxide (15 mmol) and propargyl bromide (20 mmol) were added. The mixture was stirred at 50 °C for 120 h. The progress of the

reaction was monitored by TLC and upon completion the reaction mixture was extracted with dichloromethane and washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (1/10, v/v) as eluent to give **18**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (s, 2H, C-CH), 3.58 (t, J = 9.0 Hz, 4H, N-CH_2), 3.70 (t, J = 9.0 Hz, 4H, NCH_2-CH_2), 4.15 (s, 4H, CH_2O-CH_2), 6.59 (d, J = 6.0 Hz, 3H, ArH), 7.25 (d, J = 6.0 Hz, 2H, ArH).

Compound 19: Compound **18** (1.20 mmol) and compound **3** (3.00 mmol) were dissolved in THF (3 mL) and mixed with $CuSO_4$·$5H_2O$ (0.12 mmol) and sodium ascorbate (0.24 mmol) in H_2O (0.5 mL). The mixture was stirred at room temperature for 19 h and diluted with ethyl acetate. The solution was washed with water (30 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (2/1, v/v) as eluent to give **19**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (t, J = 9.0 Hz, 4H, N-CH_2), 3.62 (t, J = 9.0 Hz, 4H, NCH_2-CH_2), 4.60 (s, 8H, CH_2-Ar & CH_2-CCl_3), 5.61 (s, 4H, CH_2O-CH_2), 6.53 (d, J = 6.0 Hz, 3H, ArH), 7.20 (d, J = 6.0 Hz, 2H, ArH), 7.27 (s, 2H, CH), 7.41 (d, J = 9.0 Hz, 4H, ArH), 7.94 (d, J = 9.0 Hz, 4H, ArH).

Compound 20a: *p*-Nitroaniline (2.0 mmol) was dissolved in acetic acid (1.4 mL) and hydrochloric acid (0.3 mL) and treated with sodium nitrite (4.2 mmol) in water (1.0 mL) for appropriate time at 0 °C. After complete disappearance of starting material as indicated by TLC, compound **19** (1.0 mmol) in acetonitrile was added dropwise at room temperature. The progress of the reaction was monitored by TLC and upon completion, the reaction mixture was diluted with ethyl acetate and washed with water (30 (60 mL) and brine (40 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (2/1, v/v) as eluent to give **20a**. Yield 65%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (d, J = 9.0 Hz, 4H, N-CH_2), 3.74 (d, J = 9.0 Hz, 4H, NCH_2-CH_2), 4.58 (s, 4H, CH_2-Ar), 4.63 (s, 4H, CH_2-CCl_3), 5.62 (s, 4H, CH_2O-CH_2), 6.75 (d, J = 9.0 Hz, 2H, ArH), 7.41 (d, J = 9.0 Hz, 4H, ArH), 7.51 (s, 2H, CH), 7.84 (d, J = 6.0 Hz, 2H, ArH), 7.94 (d, J = 6.0 Hz, 6H, ArH), 8.32 (d, J = 9.0 Hz, 2H, ArH).

Compound 20b: 4-Aminobenzonitrile (3.8 mmol) was dissolved in acetic acid (1.4 mL) and tetrafluoroboric acid (0.7 mL) and mixed with sodium nitrite (4.2 mmol) in water (1.0 mL) at 0 °C. After complete disappearance of starting material, compound **19** (1.9 mmol) in acetonitrile was added dropwise at room temperature. The reaction mixture was diluted with ethyl acetate and washed with water (60 mL) and brine (40 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (2/1, v/v) as eluent to give **20b**. Yield 40%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (d, J = 9.0 Hz, 4H, N-CH_2), 3.67 (d, J = 9.0 Hz, 4H, NCH_2-CH_2), 4.60 (s, 8H, Ar-CH_2, CH_2-CCl_3), 5.65 (s, 4H, CH_2O-CH_2), 6.75 (d, J = 9.0 Hz, 2H, ArH), 7.19 (d, J = 9.0 Hz, 4H, ArH), 7.29 (s, 2H, CH), 7.71 (d, J = 9.0 Hz, 4H, ArH), 7.82-7.89 (m, 6H, ArH).

Compound 20c: 2,4-Dinitroaniline (2.0 mmol) was dissolved in acetic acid (1.4 mL) and hydrochloric acid (0.9 mL) and mixed with sodium nitrite (5.0 mmol) in water (5.0 mL) at 0 °C. After complete disappearance of starting material, compound **19** (1.0 mmol) in THF was added dropwise at room temperature. Upon completion, the reaction mixture was diluted with ethyl acetate and washed with water (60 mL) and brine (40 mL) and then dried over anhydrous $MgSO_4$. The solution was concentrated and purified by column chromatography on silica gel using ethyl acetate and hexane (2/1, v/v) as eluent to give **20c**. Yield 48%.; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.31 (t, J = 9.0 Hz, 4H, N-CH_2), 3.54 (t, J = 9.0 Hz, 4H, NCH_2-CH_2), 4.52 (s, 4H, CH_2-Ar), 4.58 (s, 4H, CH_2-CCl_3), 5.64 (s, 4H, CH_2O-CH_2), 7.11 (d, J = 6.0 Hz, 1H, ArH), 7.42 (d, J = 6.0 Hz, 6H, ArH), 7.53 (s, 2H, CH), 7.72 (d, J = 6.0 Hz, 1H, ArH), 7.94 (d, J = 9.0 Hz, 4H, ArH), 8.01 (d, J = 9.0 Hz, 1H, ArH).

Compound 21a-c: Compound **20a-c** (0.70 mmol) and tetrabutylammonium hydroxide (1.2 mmol) were dissolved in THF (5.0 mL). The reaction mixture was stirred room temperature for 12 h. The solvent was removed by rotary evaporation and the crude residue was purified by column chromatography on silica gel with methanol/ethyl acetate (1/2, v/v) as eluent to give **21a-c**:

Compound 21a: Yield 45%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 12.0 Hz, 24H, N$(CH_2)_3$-CH_3), 1.32-1.44 (m, 16H, NCH_2 CH_2-CH_2), 1.56-1.66 (m, 16H, NCH_2-CH_2), 3.20 (t, J = 12.0 Hz, 16H, N-CH_2), 3.60 (d, J = 6.0 Hz, 4H, N-CH_2), 3.66 (d, J = 6.0 Hz, 4H, NCH_2-CH_2), 4.55 (s, 4H, CH_2-Ar), 5.49 (s, 4H, CH_2O-CH_2), 6.80 (d, J = 6.0 Hz, 2H, ArH), 7.18 (d, J = 6.0 Hz, 4H, ArH), 7.47 (s, 2H, CH), 7.86 (d, J = 9.0 Hz, 8H, ArH), 8.35 (d, J = 9.0 Hz, 2H, ArH).

Compound 21b: Yield 35%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 12.0 Hz, 12H, N$(CH_2)_3$-CH_3), 1.31-1.41(m, 8H, NCH_2 CH_2-CH_2), 1.51-1.59 (m, 8H, NCH_2-CH_2), 3.04 (s, 3H, N-CH_3), 3.62 (d, J = 9.0 Hz, 4H, N-CH_2), 3.67 (d, J = 9.0 Hz, 4H, NCH_2-CH_2), 4.60 (s, 4H, Ar-CH_2), 5.45 (s, 4H, CH_2O-CH_2), 6.80 (d, J = 6.0 Hz, 2H, ArH), 7.16 (d, J = 6.0 Hz, 4H, ArH), 7.29 (s, 2H, CH), 7.69 (d, J = 9.0 Hz, 4H, ArH), 7.82-7.89 (m, 6H, ArH).

Compound 21c: Yield 37%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 12.0 Hz, 24H, N$(CH_2)_3$-CH_3), 1.33-1.45 (m, 16H, NCH_2CH_2-CH_2),1.58-1.69 (m, 16H, NCH_2-CH_2), 3.19 (t, J = 9.0 Hz, 16H, N-CH_2), 3.50 (t, J = 6.0 Hz, 4H, N-CH_2), 3.52 (t, J = 6.0 Hz, 4H, NCH_2-CH_2), 4.51 (s, 4H, CH_2-Ar), 5.62 (s, 4H, CH_2O-CH_2), 6.71 (d, J = 9.0 Hz, 2H, ArH), 7.34 (d, J = 9.0 Hz, 4H, ArH), 7.82 (d, J = 6.0 Hz, 4H, ArH), 7.88 (d, J = 6.0 Hz, 2H, ArH), 7.82 (s, 2H, CH), 8.02 (d, J = 6.0 Hz, 1H, ArH), 8.16 (d, J = 6.0 Hz, 1H, ArH), 8.54 (s, 1H, ArH).

Acknowledgments. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (KRF-2008-521-D00200) and supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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