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Synthesis and Extraction Studies of Some New Anionic Dye Extractors

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A new series of dodecyl derivatives of non-cyclic and cyclic ethers, as the extractors have been synthesized by imination, reduction of imines and cyclization steps, and the structures were identified by FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy. The extractions abilities of these ligands with some anionic dyes [4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (NaPAR), and sodium picrate (NaPIC), and potassium picrate (KPIC)] were determined by UV-VIS spectrophotometry using liquid-liquid extraction method. In this study, all of the synthesized ligands were generally showed higher extraction ability for Na-dyes.

INTRODUCTION

Macrocyclic polyethers, which are commonly called crown ethers, have been utilized as neutral extracting reagent.[1–3] The complexation of crown ethers with alkali and alkaline earth metal ions has been well documented. Also, these types of ligands have been synthesized to enhance the stability of the cation–ligand complex and better selectivity. Diaza crown ethers are interesting compounds because of complexation ability with an alkali and transition metal cations which structures between crown ethers containing oxygen atoms and cyclams containing nitrogen atoms.[4–12] Diaza crown ethers for solvent extraction are highly potent complexing reagents since their affinity is high for cations and hydrophobic properties and they can be optimized with suitable substituents on the nitrogen atoms.[13–17]

The determination of complexation constant of organic ligand-metal ion complexes in water can be examined with different methods by following the extraction of metals to the various organic solvents.[18–22] Complexation constants can be easily determined by spectrophotometric methods using metal cation containing dye-ligands.[23–25]

The extractive-spectrophotometric determination of sodium and potassium ions as ion-pairs using non-cyclic and cyclic ethers as complexing agent and anionic dyes as colored counter ions is used in this study (Figure 1). The effects of the chain length of non-cyclic and cyclic ethers and two different functional groups of anionic dyes, 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (NaPAR), and sodium picrate (NaPIC), and potassium picrate (KPIC) have been studied.[24,26,29]
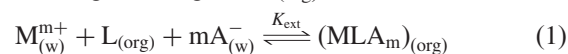
RESULTS AND DISCUSSION

Synthesis

Starting dialdehyde compounds, **1a–1b** were synthesized according to literature.[30] Dodecyl unit containing Schiff bases **2a–2b** have been prepared from **1a–1b** reacting with **1c** in ethanol, respectively. The diamine compounds **3a–3b** have been obtained by reduction of **2a–2b** with NaBH$_4$ in methanol. The aza crown ethers **4a–4d** have been obtained by the cyclic condensation of the diamines **3a–3b** with bischloride and bistosylate of polyglycols. Accordingly, **3a** has reacted with **1d**, **1e** to afford the aza crown ethers **4a** and **4b**. Compound **3b** has reacted with **1d**, **1e** to afford the aza crown ethers **4c** and **4d**, in presence of Na$_2$CO$_3$ in acetonitrile (Scheme 1).

The characterization of novel lariat ethers (see Experimental Section) were made by using FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy.

Extraction Equilibria

In this paper, we used a common formalism of Equations (1–3).[27–29] The equilibrium processes during the extraction between an aqueous solution containing the alkali metal cation, M$^+_{(w)}$, and organic anion, A$^-_{(w)}$, and an organic solution containing diaza ligands L$_{(org)}$, can be written as:

$$M^{m+}_{(w)} + L_{(org)} + mA^-_{(w)} \xrightleftharpoons{K_{ext}} (MLA_m)_{(org)} \quad (1)$$

$$K_{ext} = \frac{[MLA_m]_{(org)}}{[M^{m+}]_{(w)}[L]_{(org)}[A^-]^m_{(w)}} \quad (2)$$

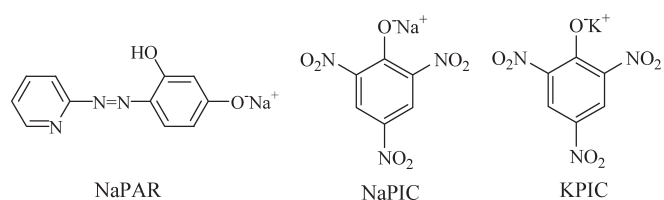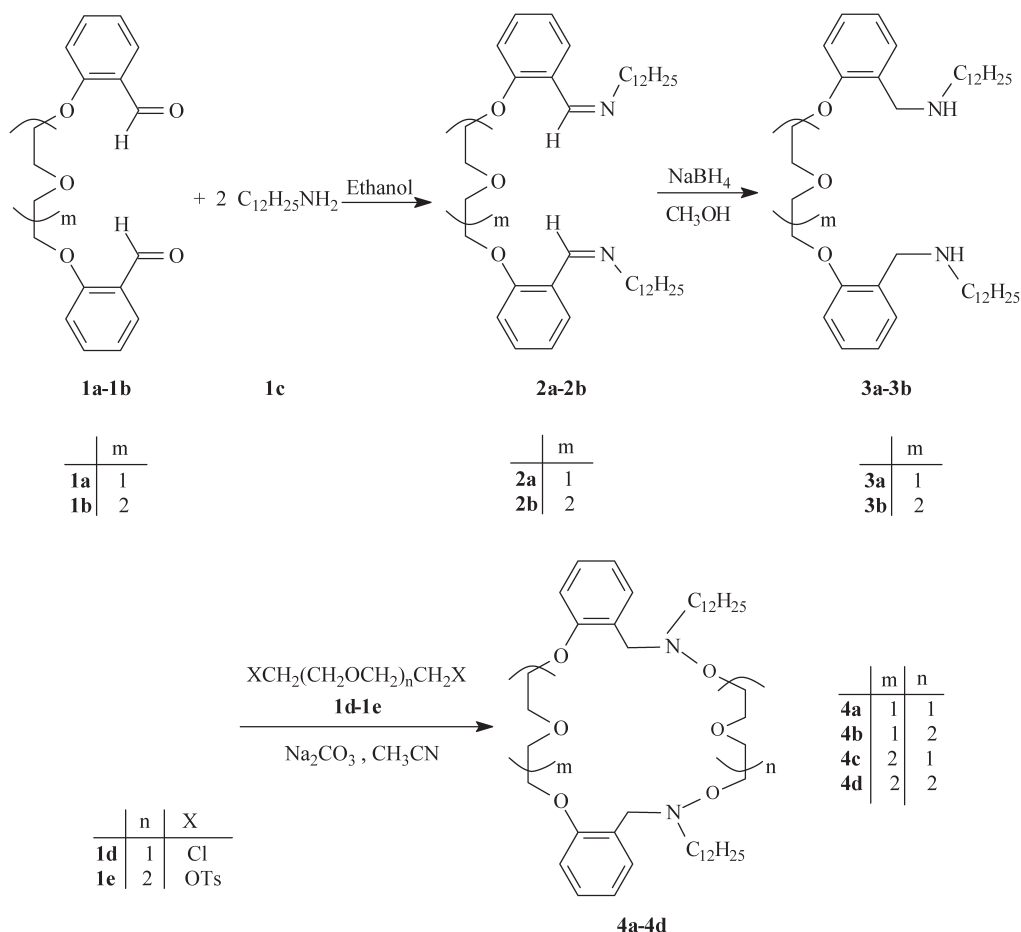$$K_{DL} = [MLA]_{(org)}/[M^+]_{(w)} \quad (3)$$

FIG. 1.

K_{ext} is extraction equilibrium constant; $[M^{m+}]$ and $[MLA_m]$ are the concentration of metal cation in aqueous phase and organic phase, respectively. K_{DL} denotes a distribution constant of ligand between organic solvent and water.[27–29]

The stability constants of metal complexes of the non-cyclic and cyclic ligands as N-pivot side-armed podands and lariat ethers, i.e., **2a–4d**, are listed in Table 1, as the interactions of these ligands with the alkali metal ions in CH_2Cl_2 media. Assuming that formation of 1:1 complexes the alkali metal cations between our ligands extracted at the natural pH of the aqueous metal salt solutions.

The Ln K_{ext} values of the ligands have been decreased with increasing metal ion size (0.095 and 0.133 nm for Na^+ and K^+, respectively,[31,32]) i.e., $Na^+ > K^+$.

Among the new ligands examined, all podands exhibit low extraction of K^+. For K^+ ion, relatively high extraction percentage are observed with **4d** ligand and amine forms of podands, i.e., **3a** and **3b**.

The Na^+ ion is wrapped with all of the new ligands better than the larger K^+ ion. The Ln K_{ext} values well display to extraction selectivity of the ligands for Na-organic salt over for K-organic salt. NaPAR is more strongly complexed with imin forms of the podands in the order of **2b** > **4b** > **2a** > **4d** > **3b** > **4a** > **4c** > **3a**. On the other hand, NaPIC is selectively wrapped arround by the amine forms of the podands in sequence of **4d** > **4c** > **3a** > **3b** > **4a** > **2b** > **4b** > **2a** (see Table 1). The lariat crown ethers and podands displayed different extraction characteristics, comparing with an alkali metal cation. For the podands, the complexation constants of sodium metal change by several orders of magnitude depend on the anion of Na-organic salt, namely, $[PAR]^- > [PIC]^-$ and $[PIC]^- > [PAR]^-$ in case of imin and amin forms,

	m
1a	1
1b	2

	m
2a	1
2b	2

	m
3a	1
3b	2

	n	X
1d	1	Cl
1e	2	OTs

	m	n
4a	1	1
4b	1	2
4c	2	1
4d	2	2

SCH. 1.

TABLE 1
K_{DL}, % Ext and Ln K_{ext} values for extraction of **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **4c**, and **4d** ligands in CH_2Cl_2 with NaPAR, NaPIC and KPIC at 25°C

Dyes	Value	Ligands							
		2a	**2b**	**3a**	**3b**	**4a**	**4b**	**4c**	**4d**
NaPAR	K_{DL}	10.09	35.80	1.69	4.11	3.67	21.80	3.42	9.37
	% Ext	90.99	97.28	62.88	80.43	78.58	95.61	77.39	90.35
	Ln K_{ext}	27.38	31.04	22.76	24.93	24.64	29.59	24.46	27.17
NaPIC	K_{DL}	0.79	1.32	15.37	7.61	3.18	1.28	15.49	43.53
	% Ext	44.13	56.96	93.89	88.39	76.06	56.13	93.93	97.75
	Ln K_{ext}	21.18	22.22	28.58	26.59	24.27	22.15	28.60	31.62
KPIC	K_{DL}	0.004	1.00	9.52	4.79	2.57	0.72	2.22	19.21
	% Ext	0.37	50.05	90.49	82.72	71.97	41.71	68.91	95.05
	Ln K_{ext}	14.67	21.64	27.21	25.33	23.74	21.00	23.39	29.22

respectively. This fact can explain the different effect anions exhibit on the complexation of organic sodium salts with the synthesized ligands.[33] We have observed that the Na^+ complexes of podands were generally found more stable than the complex of its macrocyclic analog of coronands. And this shows the strongest hydrogen bonding of the ether oxygen and nitrogen atoms of podands with Na-organic salts compared with the synthesized coronands. Although not always, open-chain ligands form more stable complexes than do the corresponding macrocycles, this phenomenon was observed with the podands as the open-chain ligands in this study. This difference may explain that podands typically exhibit higher overall basicity than the synthesized coronands.[34,35] Naturally, this effect of the nitrogens in podands should make coordination bounds stronger in Na^+ complexation and more strong hydrogen bonding with counter ion. Thus, in the complexation of podands with the Na-organic salts, the hydrogen bonding causes the Ln K_{ext} values to be higher than of the coronands.

On the other hand, the magnitude sequence of complexation effect of both coronands and podands sometimes showed the changing. The differences between alkali metal salt extracting capabilities of **2a**, **2b**, **3a** and **3b** podands and their corresponding model diaza crown ethers, i.e., **4a**, **4b**, **4c**, and **4d**, except for **2a** in case of K^+ ion, weren't relatively high.

The above assumption is clearly confirmed by the study of the structural and chemical aspects of complexation in metal salt-macrocyclic polyether systems.[36]

In general, the Ln K_{ext} values for K^+ ion complexation are found relatively smaller than Na^+ ion complexation of the new lariat crown ethers.

Consequently, the Ln K_{ext} values of Na^+ complexes are found slightly larger than of K^+ complexes. The results are show that the higher extractability of Na^+ organic salts is more attributable to the greater Ln K_{ext} value of

Na^+-complexation than to the relatively lower Ln K_{ext} value of K^+-complexation.

EXPERIMENTAL

All the used chemicals were purchased from Aldrich or Merck unless otherwise cited. FT-IR spectra have taken a KBr pellet with a Perkin Elmer Spectrum spectrometer, model BX-II, high resolution EI mass spectra have been obtained with Agilent 1100 LC/MSD, NMR spectra have been obtained with a Bruker-Spectrospin AvanceDPX-400 Ultra-Shield ^{1}H: 400 MHz ^{13}C: 100 MHz. CPX and TMS was the internal standard. All melting points reported are uncorrected.

Sodium dye, 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (NaPAR), was commercial products from Aldrich dried over P_2O_5 for 48 h at 0.1 torr. Sodium and potassium picrates were prepared by adding an alkali metal hydroxyde solution to an aqueous solution of picric acid; the resulting precipitate of sodium picrate monohydrate and potassium picrate were recrystallized from a water ethanol (1:3) mixture and water, respectively. The picrate salts were dried at 100°C for 24 h. The dichloromethane used was of analytical-reagent grade.

Extraction Procedure and Determination of Organic Anions

The overall extraction equilibrium constants for the 1:1 complexes of the above diaza crown ethers and podands with sodium and potassium ions, between the organic solvent and water, have been determined at 25°C. They were conducted in CH_2Cl_2-water systems maintaining an identical initial cation concentration in water, $[M_0^+]_w$, and a macrocyclic ligand concentration in the organic phase, $[L_0]_{org}$, so that in all extractions $[M_0^+]_w:[L_0]_{org}$ ratios were 1:1. An ion association complex formed between the alkali-crown ether complex ion

and a metal anion was extracted into the CH_2Cl_2 organic solvent, and then the metal concentration of the separated aqueous phase was measured with an ultravioletvisible spectrophotometer.

The extraction measurements were done in 100 mL glass thermostated cell compartment with a mechanical stirrer where a 25 mL solution of an aqueous salt (4×10^{-5} M) and ligand in CH_2Cl_2 organic solvent in appropriate concentration were placed and stirred for 120 min at $25 \pm 0.1°C$ and subsequently allowed to stand for 60 min to complete the phase separation. The optimum concentrations of the ligands were determined by extracting the alkali salts with 10 mL of various concentrations of the ligands (4×10^{-5} M).

After extraction, the Na^+ and K^+ concentrations in the aqueous phase were determined using UV-visible (Varian Cary 1E) spectrophotometer. Each value was the average of three subsequent measurements. Complexation and distribution constants summarized in Table 1.

General Procedure for the Synthesis of Dodecyl Unit Containing Schiff Bases (2a–2b)

In a typical reaction, 95.00 mmol of dialdehyde compound was dissolved in 150 mL of ethanol under reflux. Then, 191.00 mmol of dodecylamine (**1c**) was dissolved in 50 mL of ethanol and added to initial solution at reflux temperature in 1 hour it was cooled. Then a part of ethanol was evaporated. The remaining solution was waited for 24 hours at 0°C. The precipitated product was obtained as a white solid by suction and crystalized from methanol.

Synthesis of 1,15-N,N′-Didodecyl-3,4;12,13-dibenzo-5,8,11-trioxa-1,14-pentadecadiene (2a: C₄₂H₆₈N₂O₃)

1a was used as the dialdehyde compound. Reactions were done as described above. Yield 89%. mp: 37–38°C (methanol).

FT-IR (γ cm^{-1}, KBr): 2916, 2847 (C-H); 1641 (Ar-C=N-); 1599 (C=C); 1488, 1448 (C-H); 1244, 1137, (C-O-C); 748 (Ar-H).

^{1}H NMR (δ ppm, CDCl$_3$/TMS): 0.8 (6H, t, -CH$_3$), 1.2 (36H, m, -(CH$_2$)$_9$-), 1.6 (4H, m, -N-CH$_2$CH$_2$-), 3.5 (4H, t, -N-CH$_2$-), 3.9 (4H, t, Ar-OCH$_2$-), 4.2 (4H, t, CH$_2$-O-CH$_2$-), 6.8 (2H, d, Ar), 6.9 (2H, m, Ar), 7.3 (2H, m, Ar), 7.9 (2H, dd, Ar), 8.6 (2H, s, C=NH).

^{13}C NMR: δ ppm 14.52, 21.67, 23.09, 27.83, 29.77, 29.93, 30.06, 30.09, 31.49, 32.33, 34.56, 62.55, 68.64, 70.36, 112.87, 121.70, 125.75, 127.82, 131.94, 156.92, 163.2.

Synthesis of 1,18-N,N′-Didodecyl-3,4;15,16-dibenzo-5,8,11,14-tetraoxa-1,17-octadeca diene (2b: C₄₄H₇₂N₂O₄)

1b was used as the dialdehyde compound. Reaction were done as described above. Yield 92%. mp: 47–49°C (methanol).

FT-IR (γ cm^{-1}, KBr): 2920, 2849 (C-H); 1638 (Ar-C=N-); 1599 (C=C); 1460 (C-H); 1246, 1135, (C-O-C); 751 (Ar-H).

^{1}H NMR (CDCl$_3$/TMS): 0.8 (6H, t, -CH$_3$), 1.2 (36H, m, -(CH$_2$)$_9$-), 1.6 (4H, m, -N-CH$_2$CH$_2$-), 3.5 (4H, t, -N-CH$_2$-), 3,7 (4H, s, CH$_2$-O-CH$_2$), 3.9 (4H, t, Ar-OCH$_2$-), 4.2 (4H, t, -CH$_2$-O-CH$_2$-), 6.9 (4H, m, Ar), 7.3 (2H, m, Ar), 7.9 (2H, m, Ar), 8.6 (2H, s, C=NH).

^{13}C NMR: δ ppm 14.52, 23.08, 27.84, 29.76, 29.94, 30.05, 30.09, 31.50, 32.32, 34.11, 62.53, 68.47, 70.20, 71.37, 112.81, 121.58, 125.67, 127.74, 131.92, 156.75, 162.20.

General Procedure for the Synthesis of Dodecyl Unit Containing Diamines (3a–3b)

In a typical reduction reaction, 28.00 mmol Schiff base **2a–2b** was stirred to dissolve in 200 mL methanol. 158.70 mmol of NaBH$_4$ with small portion was added to this solution and stirred for 12 hours. Then the solvent was evaporated under reduced pressure. The obtained solid was dissolved in chloroform and extracted with 50 mL 0.1 M NaOH. The separated organic phase was washed with water and then the dried on Na$_2$SO$_4$. The solvent was rmoved under reduced pressure. The oily product was purified with silica column using hexane/methanol as a solvent. The obtained compound was as a yellow solid at room temperature.

Synthesis of N,N′-Didodecyl-1,15-diamino-3,4;12,13-dibenzo-5,8,11-trioxa-pentadecane (3a: C₄₂H₇₂N₂O₃)

2a was used as Schiff base and reaction were done as described above. Yield 30%.

FT-IR (γ cm^{-1}, KBr): 2923, 2853 (C-H); 1600 (C=C); 1491, 1453 (C-H); 1241, 1134, (C-O-C); 751 (Ar-H).

^{1}H NMR (CDCl$_3$/TMS): 0.8 (6H, t, -CH$_3$), 1.2 (36H, m, -(CH$_2$)$_9$-), 1.5 (4H, m, -HN-CH$_2$CH$_2$-), 2.5 (4H, m, -HN-CH$_2$-), 2.6 (2H, broad, -HN), 3.7 (4H, s, Ar-CH$_2$), 3.9 (4H, t, Ar-O-CH$_2$-), 4.2 (4H, t, -CH$_2$-O-CH$_2$-), 6.7 (2H, d, Ar), 6.9 (2H, m, Ar), 7.2 (4H, m, Ar).

^{13}C NMR: δ ppm 14.51, 21.67, 23.09, 27.81, 29.76, 29.99, 30.05, 30.08, 30.35, 32.32, 34.42, 49.41, 49.67, 67.99, 70.42, 111.81, 121.15, 128.63, 128.84, 130.53, 157.23.

Synthesis of N,N′-Didodecyl-1,18-diamino-3,4;15,16-dibenzo-5,8,11,14-tetraoxa-octa decane (3b: C₄₄H₇₆N₂O₄)

2b was used as Schiff base and reaction were done as described above. Yield 30%. mp: 33–35°C.

FT-IR (γ cm^{-1}, KBr): 2920, 2852 (C-H); 1595 (C=C); 1457 (C-H); 1240, 1124, (C-O-C); 749 (Ar-H).

^{1}H NMR (CDCl$_3$/TMS): 0.8 (6H, t, -CH$_3$), 1.2 (36H, m, -(CH$_2$)$_9$-), 1.4 (4H, m, -HN-CH$_2$CH$_2$-), 1.9 (2H, broad, -HN), 2.4 (4H, t, -HN-CH$_2$-), 3.6 (4H, s, Ar-CH$_2$), 3.7 (4H, s, CH$_2$-O-CH$_2$), 3.8 (4H, t, Ar-OCH$_2$-), 4.1 (4H, t, -CH$_2$-O-CH$_2$-), 6.7 (2H, d, Ar), 6.8 (2H, m, Ar), 7.1 (4H, m, Ar).

^{13}C NMR: δ ppm 14.52, 22.01, 23.09, 27.85, 29.76, 30.06, 30.09, 30.61, 32.32, 33.59, 34.63, 49.62, 49.88, 67.87, 70.31, 71.37, 111.78, 121.03, 128.43, 129.33, 130.33, 157.26.

General Procedure for the Synthesis of Dodecyl Unit Containing Azacrown Ethers (4a–4d)

The typical reaction procedure for the cyclization reaction leading to macrocyclic ethers (4a–4d) is as follows. A mixture of diamines 3a–3b (3.30 mmol), polyethylene glycol dichloride or polyethylene glycol ditosylate 1d–1e (3.30 mmol), 6.60 mmol Na_2CO_3 and 6.60 mmol NaI was dissolved 80 mL of CH_3CN. The mixture was heated for 35–40 h at 80–85°C. The solvent was evaporated in vacuo. The obtained solid product was extracted with $CHCl_3$/water (2 × 50 mL). The combined organic phases was dried over Na_2SO_4 and evaporated in vacuo. Chromotograph of the crude products (Al_2O_3, Merck) with hexane/ethanol gave pure azacrown ethers.

Synthesis of N,N′-Didodecyl-1,15-diaza-3,4;12,13-dibenzo-5,8,11,18-tetraoxa-cyclo eicosane (4a: $C_{46}H_{78}N_2O_6$)

Compounds 3a and 1d and other reagents reacted as described above. Yellow oily product. Yield 35%.

FT-IR (γ cm^{-1}, KBr): 3161 (C-H); 2923, 2853 (C-H); 1603 (C=C); 1495, 1453 (C-H); 1256 (C-O-C); 1122 (C-N-C); 757 (Ar-H).

^{1}H NMR ($CDCl_3$/TMS): 0.8 (6H, t, -CH_3), 1.2 (36H, m, -$(CH_2)_9$-), 1.4 (4H, m, -N-CH_2CH_2-), 2.2 (4H, t, -N-CH_2-), 2.3 (4H, m, -NCH_2CH_2O-), 3,1 (4H, s, Ar-CH_2), 3.9 (12H, m, O-CH_2-), 6.8 (2H, m, Ar), 6.9 (2H, m, Ar), 7.3 (2H, m, Ar), 7.7 (2H, m, Ar).

^{13}C NMR: δ ppm 14.49, 19.15, 27.70, 30.12, 31.05, 31.59, 32.55, 33.85, 34.20, 34.33, 34.36, 47.71, 58.84, 64.28, 70.94, 72.18, 116.17, 122.22, 126.89, 136.55, 138.24, 157.12.

MS: (m/z) M$^+$: 722.4 (5%).

Synthesis of N,N′-Didodecyl-1,15diaza-3,4;12,13-dibenzo-5,8,11,18,21-pentaoxa-cyclo trieicosane (4b: $C_{48}H_{82}N_2O_7$)

Compounds 3a and 1e and other reagents reacted as described above. Yellow solid product at room temperature. Yield 38.5%.

FT-IR (γ cm^{-1}, KBr): 2924, 2854 (C-H); 1601 (C=C); 1493, 1455 (C-H); 1251 (C-O-C); 1123 (C-N-C-); 756 (Ar-H).

^{1}H NMR ($CDCl_3$/TMS): 0.8 (6H, t, -CH_3), 1.2 (36H, m, -$(CH_2)_9$-), 1.4 (4H, m, -N-CH_2CH_2-), 2.4 (4H, t, -N-CH_2-), 2.7 (4H, m, -NCH_2CH_2O-), 3,5 (12H, m, -CH_2-O-CH_2- and Ar-CH_2), 3.9 (4H, m, Ar-O-CH_2-), 4.1 (4H, m, -CH_2-O-CH_2-), 6.8 (4H, m, Ar), 7.1 (2H, m, Ar), 7.3 (2H, m, Ar).

^{13}C NMR: δ ppm 14.52, 21.67, 23.08, 27.89, 29.76, 29.92, 30.05, 30.08, 30.89, 32.32, 34.60, 49.53, 49.92, 64.32, 70.40, 70.75, 72.02, 121.24, 121.98, 126.45, 128.85, 139.21, 157.25.

MS: (m/z) M$^+$: 767.9 (10%).

Synthesis of N,N′-Didodecyl-1,18-diaza-3,4;15,16-dibenzo-5,8,11,14,21-pentaoxa-cyclo trieicosane (4c: $C_{48}H_{82}N_2O_7$)

Compounds 3b and 1d and other reagents reacted as described above. Yellow oily product. Yield 26%.

FT-IR (γ cm^{-1}, KBr): 2924, 2854 (C-H); 1601 (C=C); 1493, 1452 (C-H); 1249 (C-O-C); 1120 (C-N-C); 754 (Ar-H).

^{1}H NMR ($CDCl_3$/TMS): 0.8 (6H, t, -CH_3), 1.2 (36H, m, -$(CH_2)_9$-), 1.5 (4H, m, -N-CH_2CH_2-), 2.2 (4H, t, -N-CH_2-), 2.4 (4H, m, -NCH_2CH_2O-), 3.8 (20H, m, O-CH_2 and Ar-CH_2-), 6.7 (2H, m, Ar), 6.9 (2H, m, Ar), 7.2 (2H, m, Ar), 7.7 (2H, m, Ar).

^{13}C NMR: δ ppm 14.53, 19.17, 27.72, 31.53, 31.89, 32.15, 32.34, 32.55, 34.16, 34.30, 34.38, 48.85, 58.35, 64.27, 71.97, 72.75, 72.96, 116.61, 125.92, 126.35, 134.68, 136.01, 157.22.

MS: (m/z) M$^+$: 767.8 (10%).

Synthesis of N,N′-Didodecyl-1,18-diaza-3,4;15,16-dibenzo-5,8,11,14,21,24-hekzaoksa-cyclohexaeicosane (4d: $C_{50}H_{86}N_2O_8$)

Compounds 3b and 1e and other reagents reacted as described above. Yellow solid product at room temperature. Yield 23%. mp: 40–42°C.

FT-IR (γ cm^{-1}, KBr): 2920, 2851 (C-H); 1599 (C=C); 1491,1450 (C-H); 1239 (C-O-C); 1130 (C-N-C-); 752 (Ar-H).

^{1}H NMR ($CDCl_3$/TMS): 0.8 (6H, t, -CH_3), 1.2 (36H, m, -$(CH_2)_9$-), 1.4 (4H, m, -N-CH_2CH_2-), 2.5 (4H, m, -N-CH_2-), 2.7 (4H, m, -NCH_2CH_2O-), 3.4 (4H, s, Ar-CH_2-), 3.5 (4H, t, -OCH_2CH_2N-), 3.7 (8H, m, CH_2-O-CH_2), 3.8 (4H, t, Ar-O-CH_2-), 4.1 (4H, t, -CH_2-O-CH_2-), 6.7 (2H, d, Ar), 6.8 (2H, m, Ar), 7.1 (2H, m, Ar), 7.3 (2H, d, Ar).

^{13}C NMR: δ ppm 14.55, 19.21, 27.78, 31.96, 32.49, 34.45, 34.66, 34.74, 34.77, 37.01, 34.65, 47.95, 58.17, 69.55, 71.11, 73.07, 74.50, 74.99, 116.62, 125.65, 131.11, 133.07, 133.62, 156.98.

MS: (m/z) M$^+$: 811.9 (100%).

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