Reactions of resorcinarene with *N,N*-dimethylcarbamoyl and *N,N*-dimethylthiocarbamoyl chlorides: factors affecting the process performance

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Abstract
Carbamoylation and thiocarbamoylation of resorcinarenes in the presence of alkali metal carbonates were studied. The effects of the pre-organization of the resorcinarene molecule, the base used, and the nature of the acylating reagent on the reaction outcome were demonstrated. It was shown that octacarbamoylated resorcinarenes in the *boat* conformation show high absorption properties and selectivity towards cesium cations.

Keywords: Resorcinarenes, pre-organization, carbamoylation, thiocarbamoylation, alkali metal cations, complexation

Introduction

Resorcinarenes, polyhydroxyaromatic compounds having a molecular cavity, form a convenient basis for the design of receptor systems, because of the ease of modification of these compounds and the possibility of immobilization of the macrocycle in a definite conformation.[1-4] O-Acylation[5-9] and O-alkylation of resorcinarenes[10-15] are used most often to introduce ionophoric groups. Using these reactions, a broad range of polyfunctionalized derivatives of resorcinarenes have been synthesized; many of these compounds exhibit acceptor properties towards metal cations.[16-21] It is noteworthy that the receptor properties of the synthesized compounds and their selectivity are determined by pre-organization of the macrocyclic core of resorcinarene and the nature of the immobilized ionophoric groups.

In order to create new receptor systems with functional groups containing various sets of electron-donating atoms and located in space in a definite way, we studied carbamoylation and thiocarbamoylation of resorcinarenes with a specific pre-organization of the macrocyclic core.

In agreement with this goal, as macrocyclic substrates, we chose resorcinarenes **1** with *rccc* configuration of alkyl (**a-d**), alkylaryl (**e**) and phenyl (**f**) substituents in the methylidene bridges, for which *crown* is the major conformation, and tetranaphthylresorcinarene **2**, which occurs in the *chair* conformation with the *rctt* configuration of the naphthyl moieties (Fig. 1). *N*,*N*-Dimethylcarbamoyl and *N*,*N*-dimethylthiocarbamoyl chlorides served as the acylating reagents.

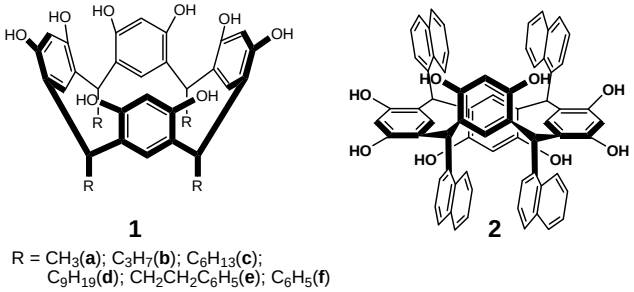


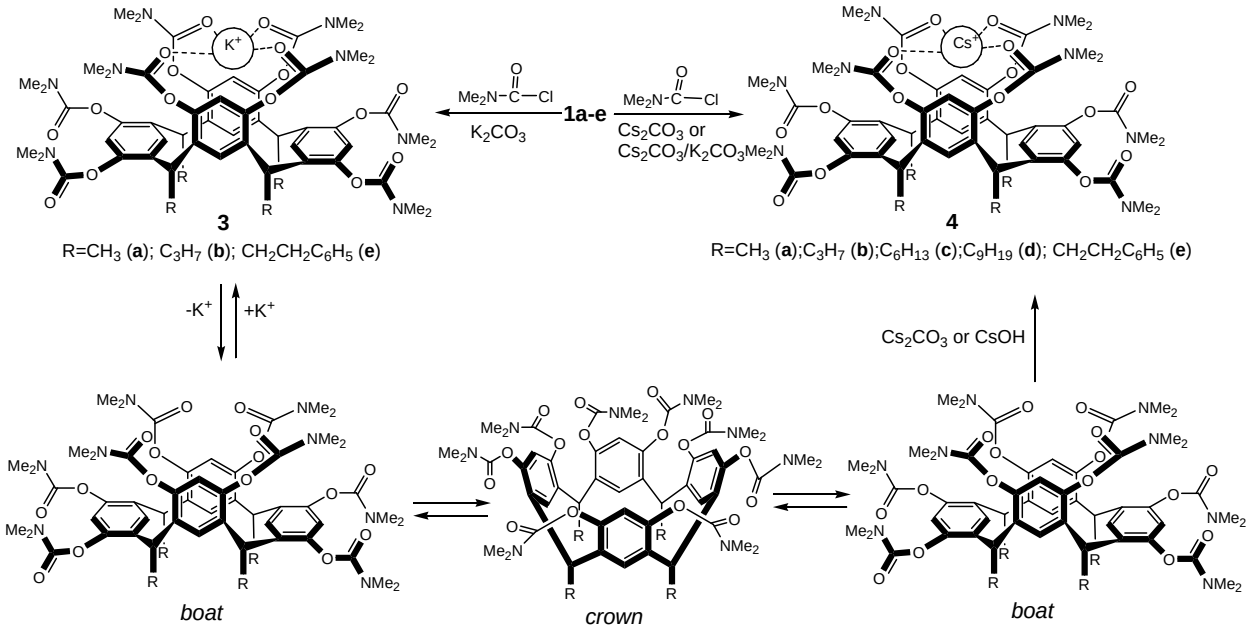
Figure 1. Structure of resorcinarenes **1,2**.

Results and Discussion

Carbamoylation of resorcinarenes **1** and **2** with *N*,*N*-dimethylcarbamoyl chloride was carried out in acetone at 55-60 °C. Alkali metal carbonates (Na_2CO_3, K_2CO_3, Cs_2CO_3) were used as bases. The resorcinarene : carbamoyl chloride : carbonate reactant ratio was 1:12:12.

In the presence of Na_2CO_3, the reaction was in all cases slow and non-selective. Even long-term heating (for more than 40 h) of the reaction mixtures did not result in the formation of percarbamoylated resorcinares, as indicated by MALDI data for the obtained products.

The results of carbamoylation of resorcinarenes **1** and **2** in the presence of potassium and cesium carbonate depended on the pre-organization of the macrocyclic substrate and the nature of the carbonate. When *rccc* resorcinarenes **1a,b,e** reacted with carbamoyl chloride in the presence of K_2CO_3, the reaction was complete in 10-12 h to give octacarbamoylated products **3a,b,e** (Scheme 1, Table 1).



Scheme 1. N,N-Dimethylcarbamoylation of resorcinarenes **1**.

Table 1. Yields, melting points and MALDI data of carbamoylation products **3-5**

No	R	Yield, %	Mp, °C	*m/z*
3a	CH_3	42	260-261*	1113.5 [M^+] 1151.1 [M^++K^+]
3b	C_3H_7	68	210-212	1226 [M^+] 1263.9 [M^++K^+]
3e	$CH_2CH_2C_6H_5$	40	212-214	1473 [M^+] 1511.8 [M^++K^+]
4a	CH_3	54	230-232*	1245.8 [M^++Cs^+]
4b	C_3H_7	72	238-240*	1357.7 [M^++Cs^+]
4c	C_6H_{13}	60	198-200	1525 [M^++Cs^+]
4d	C_9H_{19}	57	223-224	1594 [M^++Cs^+]
4e	$CH_2CH_2C_6H_5$	70	245-247*	1606 [M^++Cs^+]
5	$C_{10}H_7$	77(a); 83(b)[a]	290-305*	1561 [M^+]

*melting with decomposition; [a]the synthesis was carried out in the presence of K_2CO_3 (a) or Cs_2CO_3(b)

The mass spectra (Table 1) of **3a,b,e** exhibited peaks corresponding to the octacarbamoylated resorcinarenes **3a,b,e** and their complexes with the potassium cation. The ^1H and ^{13}C NMR spectra of **3a,b,e** were found to exhibit broadened proton and carbon signals of the resorcinarene core and carbamate groups. This spectral pattern is possible in the case of coexistence of both potassium-coordinated and uncoordinated resorcinarene molecules,

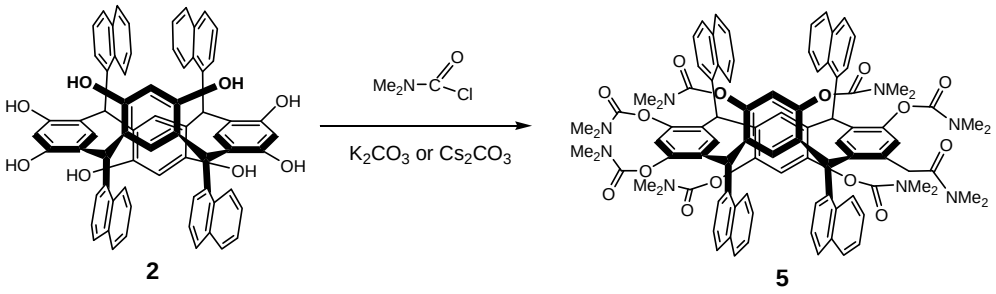
occurring in various conformations owing to retarded *boat-crown-boat* interconversion (Scheme 1). According to elemental analysis and NMR spectroscopy data, the isolated products **3a,b,e** were complexes of the following composition: **3a**•$2C_6H_{14}$, **3b**•C_6H_{14}, **3e**•C_6H_{14}.

In the presence of Cs_2CO_3, percarbamoylation of resorcinarenes **1a-e** with *N*,*N*-dimethylcarbamoyl chloride was complete in 8 h, and the yields of products **4** were higher than those of **3** (Table 1). The difference between the melting/decomposition points of compounds **3a,b,e** and **4a,b,e** is 20-30 °C (Table 1). The mass spectra of **4a-e** exhibited only intense peaks, the spectral parameters corresponding to a 1:1 resorcinarene complex with the cesium cation (Table 1). According to elemental analysis and NMR spectroscopy data, as in the previous case, solvent molecules were incorporated in octacarbamates **4a-e**, apart from CsCl, to form complexes **4a**•$CHCl_3$•C_6H_{14}, **4b**•$2C_6H_{14}$, **4c**•C_6H_{14}, **4d**•C_6H_{14}, and **4e**•C_6H_{14}. The ^{1}H NMR spectra exhibited two singlets for the *ortho*- and *meta*-protons of the benzene rings, one signal for protons of the methylidene bridge, and four singlets corresponding to the methylamide protons. This spectral pattern is characteristic of *rccc* resorcinarenes existing in the *flattened boat* conformation[22]. With this spatial arrangement of the octacarbamoylated resorcinarene molecule, the carbamate groups located on the vertically arranged benzene rings are spatially proximate and provide stable ion–dipole interaction with the cesium cation (Scheme 1).

As shown by additional experiments, octacarbamoylated resorcinarenes exhibit selectivity towards cesium cations. The addition of cesium carbonate or hydroxide to a solution of the potassium complex of tetra(phenethyl)resorcinarene **3e** (*m/z* 1511.8 $[M^+ + K^+]$) induces displacement of the potassium cation to give complex **4e** with a cesium cation (Scheme 1). The mass spectrum of the isolated product exhibited a peak with a mass number of 1606 corresponding to the complex of octacarbamoylated resorcinarene with cesium. The melting point and spectral data of the isolated product fully coincided with the data obtained previously for complex **4e**.

A similar result was obtained when resorcinarene **1e** was carbamoylated with *N*,*N*-dimethylcarbamoyl chloride in the presence of a mixture of equal amounts of potassium and cesium carbonate (Scheme 1). The reactant ratio was as follows: resorcinarene : carbamoyl chloride : K_2CO_3: Cs_2CO_3 = 1:12:6:6. The physicochemical and spectral characteristics of the isolated product fully corresponded to complex **4e**.

In the carbamoylation of *rctt* tetranaphthylresorcinarene **2**, unlike that of *rccc* resorcinarene **1**, the reaction outcome did not depend substantially on the base chosen (either K_2CO_3 or Cs_2CO_3). In both cases, the reaction ended in the formation of an individual compound: octacarbamoylated derivative **5**, as indicated by elemental analysis and mass spectrometry data (Scheme 2, Table 1).

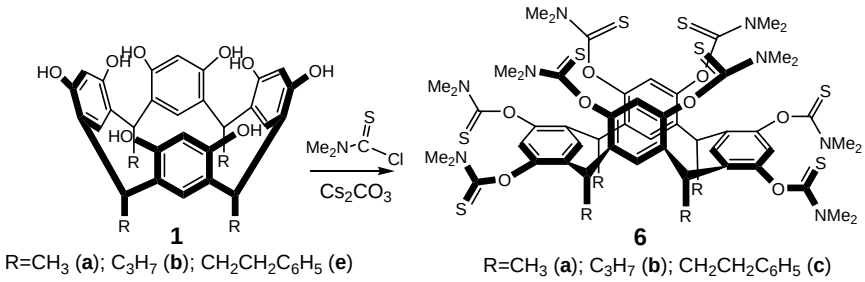


Scheme 2. N,N-Dimethylcarbamoylation of tetranaphthylresorcinarene **2**.

Doubling of the proton and carbon signals of the benzene ring and carbamate groups in the ^{1}H and ^{13}C NMR spectra of compound **5** and the upfield shift (δ_H 5.25 ppm) of the H^{3h} protons of the benzene rings in the ^{1}H NMR spectrum attested to retention of the initial *chair* conformation with C_{2h} symmetry.[23, 24]

The thiocarbamoylation of resorcinarenes **1** and **2** with *N,N*-dimethylthiocarbamoyl chloride was carried out, like carbamoylation, upon refluxing in acetone in the presence of potassium and cesium carbonate. Replacement of the acylating reagent resulted in a sharp increase in the process duration. Completion of the reaction required 48-57 h.

With *rccc* resorcinarenes **1a,b,e** as substrates in the presence of Cs_2CO_3, the reaction was selective giving only the fully acylated resorcinarenes **6a-c** (Scheme 3)**.** The elemental analysis and mass spectrometry data for **6a-c** correspond to single octathiocarbamoylated derivatives containing no species in the cavity (Table 2). The ^{1}H and ^{13}C NMR spectra of compounds **6a-c** exhibited proton and carbon signals for the resorcinarene core and the carbamate groups, the integrated intensities of the signals being in line with calculated values, and the IR spectra showed strong C=S absorption bands (1170 cm^{-1}).



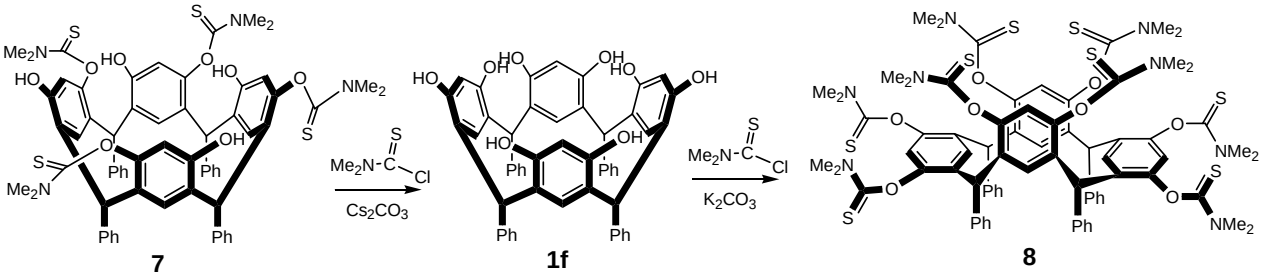
Scheme 3. N,N-Dimethylthiocarbamoylation of resorcinarenes **1a,b,e**.

Table 2. Yields, melting points, and MALDI data of compounds **6-9**

No.	R	Yield, %	M.p., °C	*m/z*
6a	CH_3	45	312-314*	1241 [M^+]
6b	C_3H_7	31	308-310*	1352 [M^+]
6c	$CH_2CH_2C_6H_5$	66	196-198	1601 [M^+].
7	C_6H_5	58	309-310*	1140 [M^+]
8	C_6H_5	54	178-180*	1432 [M^+-4CH_3]
9	$C_{10}H_7$	54	248-250*	1690 [M^+]

* melting with decomposition

Resorcinarenes **1f, 2** with aryl substituents R in the lower rim of the macrocycle behaved in a different way. In the case of tetraphenylresorcinarene **1f**, the use of Cs_2CO_3 as the base resulted in tetracarbamoylated product **7** isolated in a 58% yield (Scheme 4). The formation of the tetraacylated derivative was indicated by elemental analysis and mass spectrometry data (Table 2). In the IR spectrum of **7**, C=S absorption band at 1170 cm^{-1} and OH band at 3228 cm^{-1} were detected.



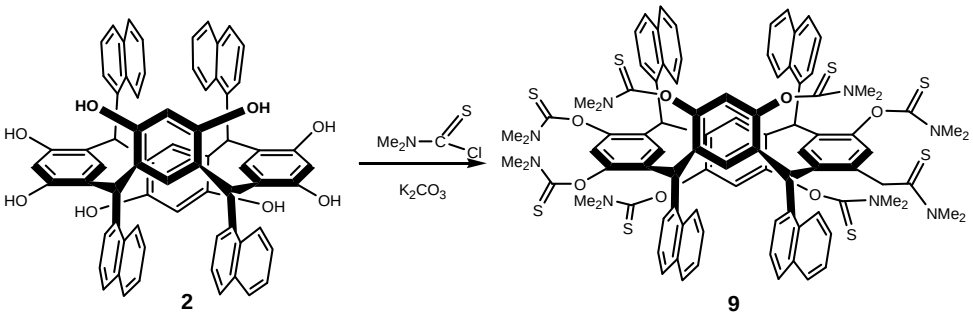
Scheme 4. Reaction of tetraphenylresorcinarene **1f** with *N,N*-dimethylthiocarbamoyl chloride.

The NMR data for resorcinarene **7** correspond to a C_{4v}-symmetric molecular structure, which is possible only in the case of a uniform order of immobilization of hydroxyl and thiocarbamoyl groups on all four benzene rings of the macrocycle. The ^{1}H NMR spectrum of **7** exhibited a singlet for hydrogen atoms of four hydroxyl groups, degenerate proton signals of the benzene rings of the macrocyclic core, and the methylamide proton signals with a 24-proton total integrated intensity. The ^{13}C NMR spectrum exhibited a singlet for the thione carbon, two singlets of the carbon atoms of aminomethyl groups, and four singlets for the resorcinol-ring carbon atoms.

By replacing Cs_2CO_3 and K_2CO_3 and increasing the thiocarbamoylation time to 57 h, we obtained perflunctionalized product **8** in the *boat* conformation in 54% yield (Scheme 4). The elemental analysis and mass spectrometry data (Table 2) confirmed the formation of totally acylated resorcinarene **8**. The IR spectrum of **8** exhibited an intense C=S absorption band at 1170

cm^{-1}, and the ^1H NMR spectrum showed no signals for hydroxyl protons. The ^1H and ^{13}C NMR spectra had a more complicated pattern with signal broadening owing to retardation of the *boat-crown-boat* interconversion (Scheme 1) as a result of steric crowding of molecule **8** created by eight bulky functional groups.

The thiocarbamoylation of tetranaphthylresorcinarene **2** in the presence of Cs_2CO_3 afforded a mixture of compounds with different degrees of functionalization, which proved to be inseparable. A success was achieved when K_2CO_3 was used, octa(thiocarbamate) **9** was isolated from the reaction mixture in 54% yield (Scheme 5).



Scheme 5. N,N-Dimethylthiocarbamoylation of resorcinarene **2**.

The introduction of eight functional groups into *rctt*-resorcinarene **2** with remote benzene rings did no affect the conformation of the macrocyclic core. The elemental analysis, mass spectrometry (Table 2), and IR and NMR spectroscopy fully corresponded to the octa(thiocarbamoyl)resorcinarene **9**.

Thus, we synthesized a new family of oligofunctionalized resorcinarenes with a specific orientation of the carbamate and thiocarbamate groups immobilized on a macrocyclic matrix. It was found that octacarbamoylated *rccc* resorcinarenes in the *boat* conformation exhibit a high capacity for recognition, binding, and recovery of cesium cations. In addition, resorcinarenes containing carbamate and thiocarbamate groups are of interest as potential receptors for organic amines and alcohols.

Experimental Section

General. ^1H and ^{13}C NMR spectra (TMS as an internal standard) were recorded on a Jeol ECX-400 spectrometer operating at 400 MHz for ^1H, 100.5 MHz for ^{13}C. The signals of **3-9** were assigned using H-H homonuclear double resonance (proton spin decoupling). The full assignment of the signals of compounds **3-9** was based on $^1H/^{13}C$ 2D correlation. Elemental analysis was performed on Thermo Flash EA112 CHN Elemental analyzer. IR spectra were measured on a NICOLETE 380 Thermo spectrometer in reflection mode in the 4000–500 cm^{-1} range for samples as Nujol mulls. Resorcinarenes **1** and **2** were synthesized by procedures

reported in [25] and [7], respectively.

General procedure of N,N-Dimethylcarbamoylation of resorcinarenes 1 and 2. N,N-Dimethylcarbamoyl chloride (2.65 mmol) was added to a suspension of resorcinarene (0.221 mmol) and metal carbonate (2.65 mmol) in acetone (10 mL). The reaction mixture was stirred at reflux for 40 h (Na_2CO_3), 10-12 h (K_2CO_3), or 8 h (Cs_2CO_3). After that, acetone was fully evaporated, and 10 mL of 5% sulfuric acid was added. The insoluble precipitate was filtered off and washed with 60 mL of water and 20 mL of hexane. The product was kept for 5 h at 80 °C/1 mmHg.

Complex 3a $2C_6H_{14}$. Beige powder; yield 0.125 g (42%). decomp. p 260-261 °C. ^{1}H NMR ($CDCl_3$): δ 0.87 (t, *J* 7.0 Hz, 12H, CH_3-hexane), 1.29 (m, 16H, CH_2-hexane), 1.46 (d, *J* 6.9 Hz, 12H, CH_3), 2.52 (s, 12H, NCH_3), 2.82 (s, 12H, NCH_3), 3.01 (s, 12H, NCH_3), 3.13 (s, 12H, NCH_3); 4.37 (q, *J* 6.8 Hz, 4H, H^1), 6.01 (s, 2H, H^{3h}), 6.60 (s, 2H, H^{5h}), 6.95 (s, 2H, H^{5v}), 7.32 (s, 2H, H^{3v}). ^{13}C NMR ($CDCl_3$): δ 14.13 (CH_3-hexane), 20.31 (CH_3), 22.72 (CH_2-hexane), 31.60 (CH_2-hexane), 32.26 (C^1), 35.99 (NCH_3), 36.48 (NCH_3), 36.83 (NCH_3), 115.87 (C^{5h}), 116.90 (C^{5v}), 125.26 (C^{3h}), 125.68 (C^{3v}), 131.97 (C^{2v}); 135.68 (C^{2h}), 146.22 (C^{4h}), 148.22 (C^{4v}), 153.89 (C=O), 154.43 (C=O). IR, λ, cm^{-1}: 1701.3 (C=O). MS, *m/z*: 1113.5 [M^+], 1151.1 [M^++K^+]. Calculated for $C_{56}H_{72}N_8O_{16}$ KCl $2C_6H_{14}$.(%): C 60.05, H 7.41, N 8.24. Found (%): C 60.37, H 7.71, N 8.13.

Complex 3b C_6H_{14}. Beige powder; yield 0.208 g (68%); mp 220-212 °C. ^{1}H NMR (d_6-DMSO, 25ºC): δ 0.83 (t, *J* 7.3 Hz, 12H, $CH_2CH_2C\underline{H}_3$. 6H, CH_3-hexane), 1.14 (m, *J* 7.4 Hz, 8H, $CH_2C\underline{H}_2CH_3$), 1.28 (m, 8H, CH_2-hexane), 2.03 (m, 8H, $C\underline{H}_2CH_2CH_3$), 2.46 (s, 24H, NCH_3), 2.64 (s, 24H, NCH_3), 4.16 (t, *J* 7.4 Hz, 4H, H^1), 6.10 (s, 4H, H^3), 7.19 (s, 4H, H^5). ^{13}C NMR (d_6-DMSO, 25 ºC): δ 14.14 (CH_3-hexane), 14.39 (CH_3), 20.90 (CH_2), 21.19 (CH_2), 22.70 (CH_2-hexane), 31.63 (CH_2-hexane), 33.09 (C^1), 36.10 (NCH_3), 36.75 (NCH_3), 38.77 (NCH_3), 40.01 (NCH_3), 102.92 (C^5), 123.78 (C^3), 125.48 (C^2); 152.11 (C^4); 154.02 (C=O). MS, *m/z*: 1226 [M^+], 1263.9 [M^++K^+]. Calculated for $C_{64}H_{88}N_8O_{16}$ KCl C_6H_{14} (%): C 60.65, H 7.42, N 8.08. Found (%): C 60.91, H 7.26, N 8.27.

Complex 3e C_6H_{14}. Beige powder; yield 0.143 g (40%). decomp.p 212-214 °C. ^{1}H NMR (d_6-DMSO, 25 ºC): δ 0.85 (t, *J* 6.9 Hz, 12H, CH_3-hexane), 1.27 (m, 16H, CH_2-hexane), 2.23 (m, 8H, $C\underline{H}_2CH_2Ph$), 2.55 (br.m, 8H, $CH_2C\underline{H}_2Ph$), 2.78 (s, 24H, NCH_3) 2.85 (s, 24H, NCH_3), 4.33 (t, *J* 7.3Hz, 4H, H^1,), 7.04 (m, 12H, H^3, *o*-Ph), 7.16 (m, 16H, H^5, *p, m*-Ph). ^{13}C NMR (d_6-DMSO, 25ºC): δ 14.13 (CH_3-hexane), 22.70 (CH_2-hexane), 31.67 (CH_2-hexane), 33.92 ($CH_2\underline{C}H_2Ph$), 35.47 ($\underline{C}H_2CH_2Ph$), 35.88 (NCH_3), 36.03 (C^1), 36.19 (NCH_3), 116.41 (C^5), 125.66 (C^2), 126.08 (C^3), 128.10 (Ph), 128.14 (Ph), 141.39 (C^4), 153.35 (C=O). IR, λ, cm^{-1}: 1703.6 (C=O). MS, *m/z*: 1473 [M^+], 1511.8 [M^++K^+]. Calculated for $C_{84}H_{96}N_8O_{16}$ KCl C_6H_{14}.(%): C 66.14, H 6.78, N 6.86. Found (%): C 66.52, H 6.39, N 6.48.

Complex 4a $CHCl_3$ C_6H_{14}. Beige powder; yield 0.177 g (54%). decomp.p 230-323 °C. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, *J* 7.3 Hz, 12H, CH_3-hexane), 1.26 (m, 16H, CH_2-hexane), 1.46 (d, *J* 6.9 Hz,

12H, CH_3,); 2.61 (s, 12H, NCH_3), 2.82 (s, 12H, NCH_3), 3.01 (s, 12H, NCH_3), 3.09 (s, 12H, NCH_3). 4.40 (q, *J* 6.8 Hz, 4H, H^1), 6.01 (s, 2H, H^{3h}), 6.77 (s, 2H, H^{5h}), 7.16 (s, 2H, H^{5v}), 7.37 (s, 2H, H^{3v}). ^{13}C NMR ($CDCl_3$): δ 14.14 (CH_3-hexane), 20.31 (CH_3), 22.72 (CH_2-hexane), 31.61 (CH_2-hexane), 32.26 (C^1); 35.99(NCH_3). 36.48 (NCH_3); 36.83 (NCH_3); 115.87 (C^{5h}), 116.90 (C^{5v}), 125.26 (C^{3h}), 125.68 (C^{3v}), 131.97 (C^{2v}); 135.68 (C^{2h}), 146.22 (C^{4h}), 148.22 (C^{4v}), 153.89 (C=O), 154.43 (C=O). IR, λ, cm^{-1}: 1705.3 (C=O). MS, *m/z*: 1245.8 [M^++Cs^+]. Calculated for $C_{56}H_{72}N_8O_{16}$ CsCl $CHCl_3$ C_6H_{14}.(%): C 50.88, H 5.90, N 7.53. Found(%): C 50.86, H 6.02, N 7.18.

Complex 4b 2C_6H_{14}. Beige powder; yield 0.249 g (72%); decomp.p 238-240 °C. ^{1}H NMR (d_6-DMSO, 25 ºC): δ 0.83 (t, *J* 7.3 Hz, 12H, $CH_2CH_2C\underline{H}_3$, 12H, CH_3-hexane), 1.14 (m, *J* 7.4 Hz, 8H, $CH_2C\underline{H}_2CH_3$), 1.28 (m, 16H, CH_2-hexane), 2.03 (m, 8H, $C\underline{H}_2CH_2CH_3$), 2.46 (s, 24H, NCH_3), 2.64 (s, 24H, NCH_3), 4.16 (t, *J* 7.4 Hz, 4H, H^1), 6.10 (s, 4H, H^3), 7.19 (s, 4H, H^5). ^{13}C NMR (d_6-DMSO, 25 ºC): δ 14.16 (CH_3-hexane), 14.39 (CH_3), 20.90 (CH_2), 21.19 (CH_2), 22.70 (CH_2-hexane), 31.64 (CH_2-hexane), 33.09 (C^1), 36.10 (NCH_3), 36.75 (NCH_3), 38.77 (NCH_3), 40.01 (NCH_3), 102.92 (C^5), 123.78 (C^3), 125.48 (C^2); 152.11 (C^4); 154.02 (C=O). MS, *m/z*: 1357.7 [M^++Cs^+]. Calculated for $C_{64}H_{88}N_8O_{16}$ CsCl 2C_6H_{14}.(%): C 58.28, H 7.47, N 7.15. Found(%): C 58.61, H 7.16, N 6.76.

Complex 4c C_6H_{14}. Beige powder; yield 0.219 g (60%). mp. 198-200 °C. ^{1}H NMR ($CDCl_3$, 25 ºC); δ 0.83 (t, *J* 6.4 Hz, 12H, $CH_2(CH_2)_4C\underline{H}_3$, 6H, CH_3-hexane), 1.22 (m, 32H, $CH_2(C\underline{H}_2)_4CH_3$, 8H, CH_2-hexane), 1.75 (m, 8H, $C\underline{H}_2(CH_2)_4CH_3$), 2.62 (s, 12H, NCH_3), 2.80 (s, 12H, NCH_3), 3.00 (s, 12H, NCH_3), 3.08 (s, 12H, NCH_3), 4.26 (t, *J* 6.8 Hz, 4H, H^1), 6.06 (s, 2H, H^{3h}), 6.69 (s, 2H, H^{5h}), 7.19 (s, 2H, H^{5v}), 7.32 (s, 2H, H^{3v}). ^{13}C NMR ($CDCl_3$, 25ºC): δ 14.11 (CH_3, CH_3-hexane), 22.80 (CH_2, CH_2-hexane), 23.05 (CH_2), 28.20 (CH_2), 29.71 (CH_2), 31.64 (CH_2-hexane), 31.84 (CH_2), 33.09 (C^1), 36.47 (NCH_3), 36.60 (NCH_3), 36.74 (NCH_3), 36.78 (NCH_3), 115.88 (C^5), 117.08 (C^5), 125.94 (C^3), 126.03 (C^3), 130.03 (C^2), 134.62 (C^2), 146.04 (C^4), 148.75 (C^4), 153.93 (C=O), 154.28 (C=O). MS, *m/z*: 1525 [M^++Cs^+]. Calculated for $C_{76}H_{112}N_8O_{16}$ CsCl C_6H_{14}(%): C 59.75, H 7.71, N 6.80. Found(%): C 59.84, H 7.37, N 6.68.

Complex 4d C_6H_{14}. Beige powder; yield 0.228 g (57%); mp. 223-224 °C. ^{1}H NMR (d_6-DMSO, 25 ºC), δ, ppm: 0.84 (t, *J* 6.9 Hz, 12H, $CH_2(CH_2)_7C\underline{H}_3$, 6H, CH_3-hexane), 1.22 (m, 56H, $CH_2(C\underline{H}_2)_7CH_3$, 8H, CH_2-hexane), 2.00 (m, 8H, $C\underline{H}_2(CH_2)_7CH_3$), 2.88 (br.s, 48H, NCH_3), 4.17 (t, *J* 7.4 Hz, 2H, H^1), 4.22 (t, *J* 7.6 Hz, 2H, H^1), 6.15 (s, 4H, H^3), 7.12 (s, 4H, H^5). ^{13}C NMR (d_6-DMSO, 25 ºC): δ 14.14 (CH_3-hexane), 14.40 (CH_3), 21.18 (CH_2), 22.90 (CH_2, CH_2-hexane), 31.64 (CH_2-hexane), 33.09 (C^1), 36.10 (NCH_3), 36.75 (NCH_3), 102.92 (C^5), 123.72 (C^2), 125.48 (C^3), 152.11 (C^4), 154.28 (C=O). MS, *m/z*: 1594 [M^++Cs^+]. Calculated for $C_{88}H_{136}N_8O_{16}$ CsCl C_6H_{14}(%): C 62.15, H 8.32, N 6.17. Found(%): C 62.55, H 8.27, N 6.57.

Complex 4e C_6H_{14}. *Method 1.* The general procedure of carbamoylation of **1e** was used. *Method 2.* Cesium carbonate (0.06 mmol) was added to a solution of complex **3a** (0.06 mmol) in 5 mL of acetone. The suspension was stirred for 3 h at 20 °C. Then acetone was distilled off and the residue was washed with water (10 mL) and hexane (5 mL) and dried for 5 h at 80 °C/1 mmHg. *Method 3.* Cesium hydroxide (0.06 mmol) was added to a solution of complex **3a** (0.06 mmol) in

5 mL of acetone. The resulting suspension was stirred for 3 h at 20 °C. The precipitate formed was filtered off, washed with water (10 mL) and hexane (5 mL), and dried for 5 h at 80 °C/1 mmHg. *Method 4.* Carbamoyl chloride (2.65 mmol) was added to a suspension of resorcinarene **1e** (0.221 mmol), potassium carbonate (1.3 mmol), and cesium carbonate (1.3 mmol) in 10 mL of acetone. The reaction mixture was stirred at reflux for 8 h. After that, acetone was completely distilled off, and 10 mL of 5% sulfuric acid was added to the reaction mixture. The insoluble precipitate was filtered off and washed with 60 mL of water and 20 mL of hexane. The product was dried for 5 h at 80 °C/1 mmHg. Beige powder; yield 0.267 g (70%) (method 1), 0.08 g (79%, method 2), 0.084 g (83%, method 3), 0.317 g (85%, method 4); decomp.p 245-247 °C. ^{1}H NMR (d_6-DMSO, 25 ºC): δ 0.88 (t, *J* 7.3 Hz, 6H, CH_3-hexane), 1.28 (m, 8H, CH_2-hexane), 2.23 (m, 8H, $C\underline{H}_2CH_2Ph$), 2.55 (br.m,8H, $CH_2C\underline{H}_2Ph$), 2.78 (s, 24H, NCH_3) 2.85 (s, 24H, NCH_3), 4.33 (t, *J* 7.3Hz, 4H, H^1), 7.04 (m, 10H, H^3, *o*-Ph), 7.16 (m, 14H, H^5, *p, m*-Ph). ^{13}C NMR (d_6-DMSO, 25 ºC): δ 14.12 (CH_3-hexane), 22.68 (CH_2-hexane), 31.65 (CH_2-hexane), 33.92 ($CH_2\underline{C}H_2Ph$), 35.47 ($\underline{C}H_2CH_2Ph$), 35.88 (NCH_3), 36.03 (C^1), 36.19 (NCH_3), 116.41 (C^5), 125.66 (C^2), 126.08 (C^3), 128.10 (Ph), 128.14 (Ph), 141.39 (C^4), 153.35 (C=O). IR, λ, cm^{-1}: 1718.7 (C=O). MS, *m/z*: 1606 [M^++Cs^+]. Calculated for $C_{84}H_{96}N_8O_{16}$ CsCl C_6H_{14}(%): C 62.55, H 6.42, N 6.48. Found(%): C 62.84, H 6.27, N 6.68.

Octa(*N,N*-dimethylcarbamoyl)tetranaphthyl-resorcinarene (5). Beige powder; yield 0.265 g (77%, in the presence of K_2CO_3); 0.286 g (83%, in the presence of Cs_2CO_3); mp 290-305 °C. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 2.24 (s, 12H, NCH_3), 2.35 (s, 12H, NCH_3), 2.68 (s, 12H, NCH_3), 2.92 (s, 12H, NCH_3), 5.25 (s, 2H, H^{3h}), 6.20 (s, 2H, H^{3v}) 6.21 (s, 4H, H^1), 6.50 (d, *J* 6.8 Hz, 4H, H^2-Naph), 6.93 (dd, *J* 6.8 Hz, *J* 8.0 Hz,4H, H^7-Naph), 6.95 (dd, *J* 7.3 Hz, *J* 6.8 Hz, 4H, H^3-Naph), 7.03 (dd, *J* 7.1 Hz, *J* 6.8 Hz, 4H, H^6-Naph), 7.14 (s, 2H, H^{5h}), 7.17 (s, 2H, H^{5v}), 7.39 (d, *J* 8.0 Hz, 4H, H^4-Naph), 7.41 (d, *J* 7.8 Hz, 4H, H^5-Naph) , 7.44 (d, *J* 8.2 Hz, 4H, H^8-Naph). ^{13}C NMR ($CDCl_3$, 25 ºC): δ 34.72 (C^1), 35.25 (NCH_3), 36.13 (NCH_3), 36.14 (NCH_3), 36.21 (NCH_3), 116.70 (C^{5h}), 117.50 (C^{5v}), 124.10 (C-Naph), 124.42 (C-Naph), 124.53 (C-Naph), 124.79 (C-Naph), 126.23 (C-Naph), 126.34 (C-Naph), 127.82 (C-Naph), 128.01 (C-Naph), 128.57 (C^{2v}); 128.55 (C^{2h}); 130.62 (C^{3h}), 130.84 (C^{3v}), 147.74 (C^{4h}); 148.50 (C^{4v}), 152.82 (C=O), 153.77 (C=O). IR, λ, cm^{-1}: 1719.4 (C=O). MS, *m/z*: 1561 [M^+]. Calculated for $C_{92}H_{88}N_8O_{16}$(%): C 70.75, H 5.68, N 7.17. Found (%): C 70.77, H 5.65, N 7.15.

General procedure of *N,N*-dimethylthiocarbamoylation of resorcinarenes 1a,b,e,f. *N,N*-Dimethylthiocarbamoyl chloride (3.25 mmol) and cesium carbonate (3.25 mmol) was added to a solution of the specified resorcinarene (0.27 mmol) in 10 mL of acetone. The reaction mixture was stirred for 48 h at 50-55 °C. Then acetone was completely distilled off, and 20 mL of 5% sulfuric acid was added to the residue. The precipitate was filtered off and washed with water (50 mL) and hexane (10 mL). The product was dried for 6 h at 75-80 °C *in vacuo* (1 mmHg).

Octa(*N,N*-dimethylthiocarbamoyl)-tetramethyl-resorcinarene (6a). Beige powder; yield 0.165 g (45%); decomp.p 312-314 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (d, *J* 6.9 Hz, 12H, CH_3), 2.61 (s, 12H, NCH_3), 2.82 (s, 12H, NCH_3), 3.01 (s, 12H, NCH_3), 3.08 (s, 12H, NCH_3), 4.40 (q, *J* 6.8 Hz, 4H, H^1), 6.01 (s, 2H, H^{3h}), 6.77 (s, 2H, H^{5v}), 7.16 (s, 2H, H^{5h}), 7.36 (s, 2H, H^{3v}), ^{13}C NMR (d_6-

DMSO): δ 21.13 (CH_3), 31.99 (C^1), 38.73 (NCH_3), 39.04 (NCH_3), 43.15 (NCH_3), 43.54 (NCH_3), 118.65 (C^{5h}), 119.64 (C^{5v}), 125.81 (C^{3h}), 126.20 (C^{3v}), 133.35 (C^{2v}); 136.54 (C^{2h}); 148.47 (C^{4h}); 150.78 (C^{4v}), 185.70 (C=S), 186.48 (C=S). IR, λ, cm^{-1}: 1125.7 (C=S). MS, *m/z*: 1241 [M^+]. Calculated for $C_{56}H_{72}N_8O_8S_8$ $CHCl_3$(%): C 50.30, H 5.41, N 8.23. Found (%): C 50.68, H 5.46, N 8.38.

Octa(*N,N*-dimethylthiocarbamoyl)-tetrapropyl-resorcinarene (**6b).** Light yellow powder; yield 0.113 g (31%). decomp.p 308-310 °C. ^{1}H NMR (d_6-DMSO, 25 ºC): δ 0.80 (br.s, 12H, $CH_2CH_2C\underline{H}_3$), 1.20 (br.s, 8H, $CH_2C\underline{H}_2CH_3$), 1.83 (br.s, 8H, $C\underline{H}_2CH_2CH_3$), 2.46 (s, 24H, NCH_3), 2.89 (s, 24H, NCH_3), 4.19 (br.t, 4H, H^1), 6.27 (br.s, 2H, H^{3h}), 6.56 (br.s, 2H, H^{5v}), 6.84 (br.s, 2H, H^{5h}), 7.42 (br.s, 2H, H^{3v}). ^{13}C NMR (d_6-DMSO, 25 ºC): δ 14.03 (CH_3), 20.77 ($\underline{C}H_2CH_3$), 20.93 ($CH\underline{C}H_2$), 32.20 (C^1), 38.61 (NCH_3), 39.86 (NCH_3), 40.28 (NCH_3), 40.49 (NCH_3), 118.26 (C^5), 126.49 (C^3), 132.10 (C^2), 153.79 (C^4), 185.90 (C=S), 186.16 (C=S). MS, *m/z*: 1352 [M^+]. Calculated for $C_{64}H_{88}N_8O_8S_8$(%): C 56.77, H 6.55, N 8.28. Found (%): C 57.00, H 6.52, N 8.25.

Octa(*N,N*-dimethylthiocarbamoyl)-tetraphenetyl-resorcinarene (6c). Beige powder; yield 0.285 g (66%). mp 196-198 °C. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 2.31 (m, *J* 6.9 Hz, *J* 7.3 Hz, 8H, $C\underline{H}_2CH_2Ph$), 2.57 (m, *J* 7.8 Hz, 4H, $CH_2C\underline{H}_2Ph$), 2.75 (m, *J* 6.4 Hz, 4H, $CH_2C\underline{H}_2Ph$), 2.92 (s, 12H, NCH_3), 3.05 (s, 12H, NCH_3), 3.18 (s, 12H, NCH_3), 3.31 (s, 12H, NCH_3), 4.24 (t, *J* 6.4 Hz, 4H, H^1), 6.61 (s, 2H, H^{3h}), 6.65 (s, 2H, H^{5v}), 6.80 (s, 2H, H^{5h}), 7.06-7.15 (m, 20H, Ph) 7.59 (s, 2H, H^{3v}). ^{13}C NMR ($CDCl_3$, 25 ºC): δ 34.19 ($CH_2\underline{C}H_2Ph$), 36.27 ($\underline{C}H_2CH_2Ph$), 36.54 (C^1), 38.61 (N-CH_3), 39.36 (NCH_3), 42.92 (NCH_3), 43.42 (NCH_3), 119.47 (C^{5h}), 120.63 (C^{5v}), 125.61 (Ph), 127.32 (C^{3h}), 128.68 (Ph), 129.10 (Ph), 129.82 (C^{3v}), 135.22 (C^{2v}), 141.59 (C^{2h}); 148.63 (C^{4h}), 151.77 (C^{4v}), 186.29 (C=S), 186.67 (C=S). IR), λ, $см^{-1}$: 1161.9 (C=S), 1100.0 (C=S). MS, *m/z*: 1601 [M^+]. Calculated for $C_{84}H_{96}N_8O_8S_8$(%): C 62.97, H 6.04, N 6.99. Found (%): C 62.61, H 6.02, N 6.63.

Tetrahydroxy-tetra(*N,N*-dimethylthiocarbamoyl)-tetraphenyl-resorcinarene (7). Beige powder; yield 0.1774 g (58%); decomp.p 309-310 °C. ^{1}H NMR (DMSO, 25 ºC): δ 2.93 (s, 12H, NCH_3), 3.24 (s, 12H, NCH_3), 5.58 (s, 4H, H^1), 6.10 (s, 4H, H^5), 6.10 (s, 4H, H^3), 6.69 (m, 8H, Ph), 6.93 (m, 12H, Ph), 8.56 (s, 4H, OH). ^{13}C NMR (DMSO, 25 ºC): δ 41.90 (C^1), 44.33 (NCH_3), 45.03 (NCH_3), 102.71 (C^5), 120.89 (C^{Ph}), 125.01 (C^{Ph}), 127.66 (C^{Ph}), 127.84 (C^3), 129.09 (C^{Ph}), 146.25 (C^2), 153.06 (C^4), 186.63 (C=S). IR, ν, cm^{-1}: 3402 (OH), 1145 (C=S). MS *m/z*: 1136 [M^+]. Calculated for $C_{64}H_{60}N_4O_8S_4$(%): C, 67.34; H, 5.30; N, 4.91. Found (%): C, 67.43; H, 5.35; N, 4.64.

Octa(*N,N*-dimethylthiocarbamoyl)-tetraphenyl-resorcinarene (**8).** The synthesis was conducted similarly to the synthesis of **6** by stirring resorcinarene **1f** (1.6448 g, 0.207 mmol), *N,N*-dimethylthiocarbamoyl chloride (3.077 g, 24.9 mmol), and potassium carbonate (2.4651 g, 24.9 mmol) in 10 mL of acetone for 57 h at 50-55 °C. Then acetone was completely distilled off, and 20 mL of 5% sulfuric acid was added to the residue. The product was extracted with CH_2Cl_2 (10 mL), the organic layer was separated, CH_2Cl_2 was distilled off, the residue was dissolved at reflux in a minimum amount of methanol, and the solution was refluxed for 5 min. The methanol-insoluble precipitate was filtered off, washed with hot methanol, and dried for 6 h at

75-80 °C *in vacuo* (1 mmHg). Beige powder; yield 0.3138 g (54%); decomp.p 248-250 °C. ^{1}H NMR ($CDCl_3$, 25 ºC):δ 2.74 (s, 12H, NCH_3), 2.94 (s, 12H, NCH_3), 3.29 (s, 12H, NCH_3), 3.36 (s, 12H, NCH_3), 5.61 (s, 4H, H^1), 6.31-6.83 (m, 2H, H^{3h}; 2H, H^{5v}; 2H, H^{5h}; 2H, H^{3v}), 6.90-7.10 (br.s, 20H, Ph). ^{13}C NMR ($CDCl_3$, 25 ºC):δ 36.72 (NCH_3), 39.05 (NCH_3), 43.28 (NCH_3), 45.09 (NCH_3), 46.82 (C^1), 119.01 (C^{3v}), 126.31 (C^{Ph}), 128.05 ($C^{5v,5h}$), 129.53 (C^{Ph}), 131.16 (C^{3h}), 140.61 (C^{2v}), 147.56 (C^{2h}), 150.07 (C^{4h}), 154.53 (C^{4h}), 185.46 (C=S). IR, ν, cm^{-1}: 1163 (C=S). MS *m/z*: 1432 [M^+-4CH_3]. Calculated for $C_{76}H_{80}N_8O_8S_8$(%): C, 61.26; H, 5.41; N, 7.52. Found (%): C, 61.48; H, 5.35; N, 7.34.

Octa(*N,N*-dimethylthiocarbamoyl)-tetranaphthyl-resorcinarene (9). *N,N*-Dimethylthiocarbamoyl chloride (0.932 g, 7.55 mmol) and potassium carbonate (1.057 g, 7.55 mmol) were added to a solution of tetranaphthylresorcinarene **2** (0.3406 g, 0.343 mmol) in acetone (10 mL). The reaction mixture was stirred for 12 h at room temperature and for 48 h at 50-55°C. Acetone was distilled off, and 20 mL of 5% sulfuric acid was added to the residue. The product was extracted with CH_2Cl_2 (10 mL), and the organic layer was separated and washed with 50 mL of distilled water. Then $CHCl_3$ was distilled off, 50 mL of hexane was added to the amorphous residue, and the formed powdered precipitate was filtered off and washed with 15 mL of hexane. The product was dried for 6 h at 75-80°C *in vacuo* (1 mmHg). Beige powder; yield 0.3138 g (54%). decomp.p 248-250 °C. ^{1}H NMR ($CDC1_3$, 25 ºC):δ 2.02 (s, 12H, NCH_3), 2.75 (s, 12H, NCH_3), 3.28 (s, 12H, NCH_3),), 3.58 (s, 6H, NCH_3), 3.62 (s, 6H, NCH_3), 6.22 (s, 4H, H^1), 6.32 (s, 2H, H^{3h}), 6.52 (d, *J* 7.3 Hz, 4H, H^2-Naph), 6.75 (s, 2H, H^{5v}), 6.79 (s, 2H, H^{5h}), 6.93 (dd, *J* 7.8 Hz; *J* 6.9 Hz, 4H, H^6-Naph), 6.96 (s, 2H, H^{3v}), 7.01 (dd, *J* 7.8 Hz; *J* 7.3 Hz, 4H, H^3-Naph), 7.19 (dd, *J* 7.8 Hz; *J* 6.9 Hz, 4H, H^7-Naph), 7.44 (d, *J* 8.3 Hz, 4H, H^4-Naph), 7.61 (d, *J* 8.2 Hz, 4H, H^8-Naph), 7.8 (d, *J* 8.8 Hz, 4H, H^5-Naph). ^{13}C NMR ($CDC1_3$, 25 ºC):δ 37.48 (NCH_3), 39.56 (C^1), 42.17 (NCH_3), 44.11 (NCH_3), 45.06 (NCH_3), 119.53 (C^{5h}), 120.15 (C^{5v}), 123.7 (C^5-Naph), 124.02 (C^7-Naph), 124.99 (C^3-Naph), 125.21 (C^6-Naph), 125.82 (C^{10}-Naph), 126.6 (C^2-Naph), 127.2 (C^4-Naph), 128.03 (C^8-Naph), 130.34 (C^9-Naph), 131.36 (C^{3v}), 132.89 (C^{2v}), 133.37 (C^{3h}), 138.45 (C^{2h}), 149.82 (C^{4h}), 150.48 (C^{4v}), 187.39 (C=S). IR, ν, cm^{-1}: 1160 (C=S), 1125 (C=S). MS *m/z*: 1689 [M^+]. Calculated for $C_{92}H_{88}N_8O_8S_8$(%): C, 65.37; H, 5.25; N, 6.63. Found (%): C, 65.54; H, 5.29; N, 6.59.

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