

Short Note

1,1'-{[3,5-Bis(dodecyloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)}bis{4-[(E)-2-(naphthalen-2-yl)vinyl]pyridin-1-ium}dibromide

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Abstract: Synthesis of a double-charged cationic amphiphilic 1,4-dihydropyridine derivative with dodecyl ester groups at positions 3 and 5 of the 1,4-DHP ring was performed starting from Hantzsch type cyclization of dodecyl acetoacetate, 2-naphthaldehyde and ammonium acetate. Bromination of this compound followed by nucleophilic substitution of bromine with (E)-4-(2-(naphthalen-2-yl)vinyl)pyridine gave the desired cationic amphiphilic 1,1'-{[3,5-bis(dodecyloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)}bis{4-[(E)-2-(naphthalen-2-yl)vinyl]pyridin-1-ium}dibromide. The obtained target compound was fully characterized by IR, UV, ¹H-NMR, ¹³C-NMR, HRMS and microanalysis. The characterization of the cationic 1,4-DHP nanoparticles in an aqueous solution was performed by DLS measurements. The obtained results showed that the compound formed nanoparticles with an average diameter of around 300 nm, a PDI value of around 490 and a zeta-potential of around 20 mV for freshly prepared samples. However, after one week of storage at room temperature, an aggregation of nanoparticles was detected.

Keywords: 1,4-dihydropyridines; styrylpyridinium dyes; DLS; nanoparticles; self-assembling properties; synthetic lipids



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1. Introduction

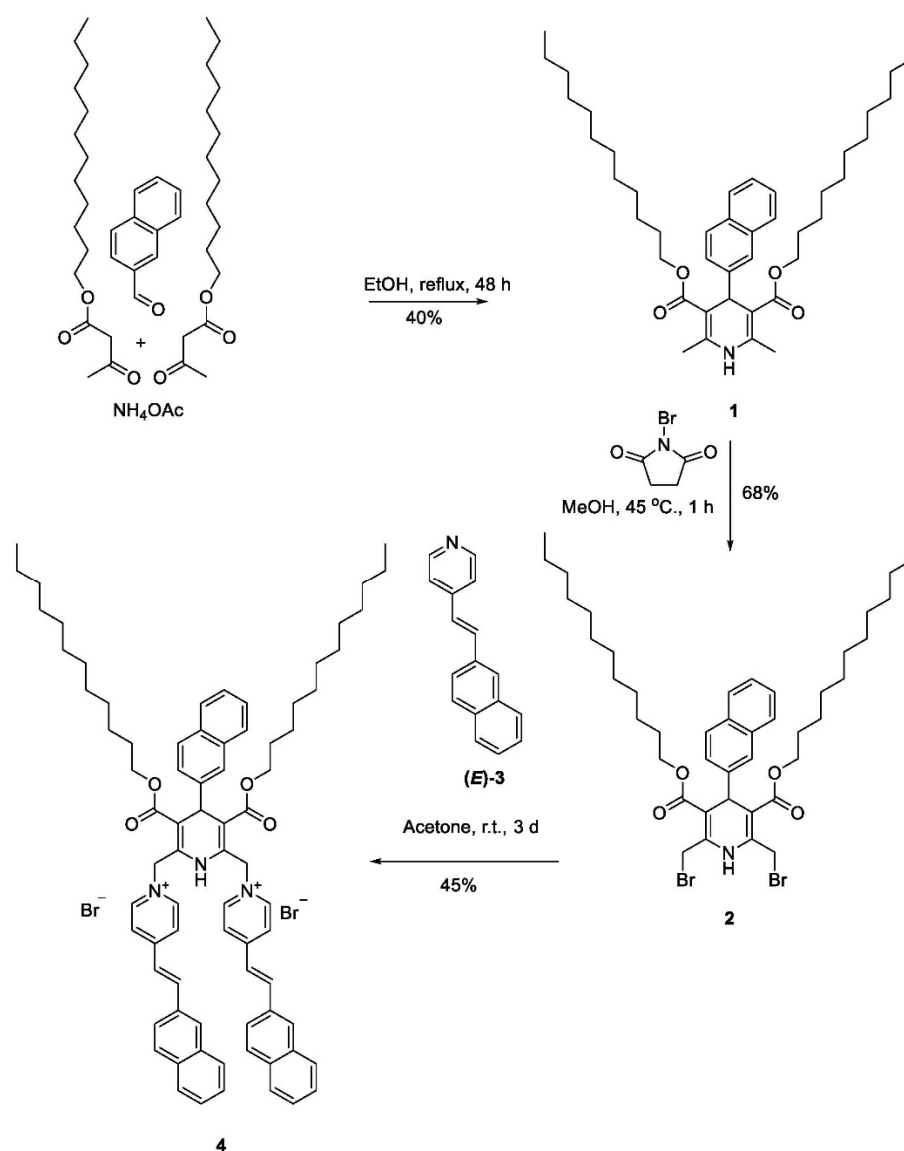
1,4-Dihydropyridines (1,4-DHP) are nitrogen-containing heterocycles widely used for the treatment of hypertension, angina pectoris, cardiac arrhythmias, and other disorders [1,2]. 1,4-DHP derivatives were reported to possess numerous other biological activities including anticancer and antimicrobial agents. Derivatives of 1,4-DHPs were also studied as gene and drug delivery systems [3–6]. Polyfunctional pyridinium amphiphiles based on the 1,4-DHP core may form liposomes and were found to be active in DNA delivery [7]. Change of the 1,4-DHP core to a pyridine [4] and modification of the cationic head-group of the 1,4-DHP molecule [7] strongly affect the ability of compounds to bind pDNA and transfer it into the cells. Insertion of a spacer between the cationic moieties and linker groups changes the delivery activity of cationic 1,4-DHPs [3]. Liposomes formed by amphiphilic 1,4-DHP derivatives and filled with magnetic nanoparticles were proposed for use in biomedical applications [8]. Furthermore, the antiproliferative activity of amphiphilic 1,4-DHP was described in cancer cell lines HT-1080 and MH-22A together with low cytotoxicity in noncancerous NIH3T3 cells [5,9]. Propargyl group-derived cationic amphiphilic 4-(N-alkylpyridinium)-1,4-DHPs also exhibited toxicity towards Gram-positive and Gram-negative bacteria species and eukaryotic microorganisms [5].

Styrylpyridinium compounds were used in a range of biological applications as fluorescent dyes [10–13]. The development of novel derivatives of fluorescent dyes using such motifs as building blocks remains a priority area [12,13]. Recently naphthylvinyl-pyridinium dyes were proposed as structurally compact, blue–green–red fluorescence trackers which selectively localized on the outer cell membrane [14]. Furthermore, styrylpyridinium

derivatives possess antimicrobial properties against bacteria and are able to inhibit the growth of *C. albicans* cells [15,16].

Taking into account the fact that the introduction of a styrylpyridinium group in a 1,4-DHP scaffold may form hybrid structures possessing more pronounced biological properties, synthesis of cationic amphiphilic 1,4-DHP **4** was performed. The construction of double-charged cationic 1,4-DHPs is a multistep synthesis, where the first step is the preparation of the 1,4-DHP core by Hantzsch synthesis or its variations [17,18]. Insertion of cationic groups at positions 2 and 6 of the 1,4-DHP ring is usually performed via bromination of methyl groups at these positions followed by nucleophilic substitution of bromide with an appropriate heterocyclic or aliphatic amine [4,7]. Previously we reported that the methyl groups of 1,4-DHPs were brominated with NBS in methanol at room temperature giving 2,6-di(bromomethyl)-1,4-DHP derivatives [19]. It was also reported that polycyclic analogues-2-methyl-4-aryl-5-oxo-5H-indeno[1,2-b]pyridine carboxylate derivatives were oxidized with NBS in methanol at room temperature [20]. The variation of the temperature range is also limited due to the lactonization of 2,6-di(bromomethyl) substituted 1,4-DHP-3,5-dicarboxylates into 8-phenyl-5,8-dihydro-1H,3H-difuro[3,4-b:3',4'-e]pyridine-1,7(4H)-dione derivatives at temperatures above 50 °C [21].

Herein, we report the synthesis and full characterization of a new 1,1'-{[3,5-bis(dodecylloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)}bis{4-[(*E*)-2-(naphthalen-2-yl)vinyl]pyridin-1-ium} dibromide **4** via the multistep procedure starting from Hantzsch type cyclization of dodecyl acetoacetate, 2-naphthaldehyde and ammonium acetate. Bromination of 2- and 6-methyl groups of didodecyl 2,6-dimethyl-4-(naphthalen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **1** followed by nucleophilic substitution of bromine with (*E*)-4-(2-(naphthalen-2-yl)vinyl)pyridine **3** gave the desired cationic amphiphilic 1,4-DHP **4** (Scheme 1). The dynamic light scattering (DLS) measurements of nanoparticles formed by the cationic 1,4-DHP **4** in an aqueous solution were performed. The nanoparticles were prepared by the ethanol injection method [22].



Scheme 1. Synthesis of 1,1'-[3,5-bis(dodecyloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)}bis{4-[(*E*)-2-(naphthalen-2-yl)viny]pyridin-1-ium} dibromide 4.

2. Discussion

The desired target product 1,1'-[3,5-bis(dodecyloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)}bis{4-[(*E*)-2-(naphthalen-2-yl)viny]pyridin-1-ium} dibromide 4 was synthesized via a multistep procedure. Firstly, three component Hantzsch-type reactions of dodecyl acetoacetate, 2-naphthaldehyde and ammonium acetate in ethanol under reflux for 48 h gave didodecyl 2,6-dimethyl-4-(naphthalen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate 1 with a 40% yield. Bromination of 2- and 6-methyl groups at the 1,4-DHP 1 was performed by N-bromosuccinimide (NBS) similarly to the previously described procedure [23]. To a solution of 2,6-dimethyl-1,4-DHP 1 in methanol was added NBS in a single portion with the reaction then stirred at 45 °C for 1h. The desired 2,6-bis(bromomethyl)-1,4-DHP 2 was obtained with a 68% yield. The last step—nucleophilic substitution of bromine with (*E*)-4-(2-(naphthalen-2-yl)viny)pyridine (3)—was performed in acetone for 3 days giving the target 1,1'-[3,5-bis(dodecyloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)}bis{4-[(*E*)-2-(naphthalen-2-yl)viny]pyridin-1-ium} dibromide 4 with a 45% yield. Synthesis of 4-(1-naphthylviny)pyridine 3 was performed according to the reported method [24,25]. According to the literature, the reaction of 4-methylpyridine

with 2-naphthaldehyde leads to the formation of *E*-isomer of compound **3** almost exclusively [25].

The obtained target amphiphilic 1,4-DHP derivative **4** and new intermediates—parent 1,4-DHP **1** and 2,6-bis(bromomethyl)-1,4-DHP **2**—were fully characterized by IR, ¹H-NMR, ¹³C-NMR, UV spectra and microanalysis (Supplementary Materials).

¹H-NMR spectra of 1,4-DHP derivatives **1**, **2** and **4** showed characteristic signals for 1,4-DHP 4-H and NH protons at 5.17 and 5.68 ppm, 5.20 and 6.50, 5.34 and 10.85, respectively. Characteristic AB-system signals of 2,6-methylene protons were observed in the ¹H-NMR spectra of didodecyl 2,6-bis(bromomethyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**2**) and target 1,1'-[3,5-bis(dodecyloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)}bis{4-[(*E*)-2-(naphthalen-2-yl)vinyl]pyridin-1-ium} dibromide (**4**) at 4.94/4.67 and 6.46/5.44 ppm, respectively.

In IR spectra, all the compounds demonstrated characteristic absorption bands above 3300 cm⁻¹ of the NH group and absorptions around 1700 cm⁻¹ of its C=O and C=C groups. UV-Vis spectra of 1,4-DHP derivatives **1**, **2** and **4** showed absorption characteristics for the DHP system in the range of 338–360 nm.

Since the fact that the target amphiphilic 1,4-DHP derivative **4** contained the naphthalen-2-yl)vinyl)pyridinium functional group, which is a fluorophore, photoluminescence quantum yields (PLQY) were measured. The PLQY value for the EtOH solution of the 1,4-DHP derivative **4** is 1%.

Self-assembling properties of cationic moieties containing 1,4-DHPs are their characteristic feature. The hydrodynamic average diameter ($Z_{av} D_H$), polydispersity index (PDI), diameter of all populations (D), zeta-potential (Z_{pot}) and stability of nanoparticles formed by cationic 1,4-DHP **4** with final compound concentration of 0.125 mM in the aqueous medium were determined by the DLS method. Nanoparticles were prepared by the ethanol injection method, which involved the dissolution of the lipid-like compound into organic solvent followed by dispersion of the lipid solution into water. This method is simple, rapid and easy to scale up [22]. The results are summarized in Table 1. The DLS measurements were performed for freshly prepared samples (entry 1, Table 1), after storage for 3 days (entry 2, Table 1) and after storage for 1 week (entry 3, Table 1) at room temperature.

Table 1. Values of polydispersity index (PDI), diameter of populations (D), Z-average diameter (Z_{av}) and zeta-potential (Z_{pot}) of nanoparticles formed by 1,4-DHP amphiphile **4** obtained by DLS measurements. The PDI value describes polydispersity of the sample; diameter of populations shows size of each fraction of nanoparticles, the Z-average diameter represents the average hydrodynamic diameter of all nanoparticles in the sample; the zeta-potential gives information about the surface charge of nanoparticles. The final concentration of the compound was 0.125 mM.

Entry	Conditions	PDI	D, nm (%)	$Z_{av} D_H$, nm	Z_{pot} , mV
1	Fresh prep *	0.491 ± 0.076	417 ± 93 (76) 33 ± 6 (24)	300 ± 24	20 ± 1
2	After 3 days **	0.498 ± 0.057	401 ± 103 (67) 39 ± 8 (33)	203 ± 14	20 ± 1
3	After 1 week ***	0.945 ± 0.032	515 ± 223 (63) 45 ± 12 (34) 5051 ± 583 (3)	119 ± 4	21 ± 2

* Freshly prepared sample ** Sample after storage of 3 days at r. t. *** Sample after storage of 1 week at r. t.

It was demonstrated that cationic 1,4-DHP **4** formed nanoparticles with an average diameter of ~300 nm for the freshly prepared sample, but the diameter decreased after 3 days of storage to ~200 nm and after one week to ~120 nm. Values of PDI confirmed that during storage for one week, the sample became more heterogeneous. Thus, the PDI value for the freshly prepared sample was 0.491, after storage for 3 days-0.498, but after storage for 1 week the PDI value was 0.945. This may be explained by the changes in the nanoparticle

population ratio. Thus, the freshly prepared sample contained mainly 76% of nanoparticles with a diameter of ~400 nm and 24% of nanoparticles with a diameter of around 30 nm. After 3 days of storage, the sample contained mainly 67% nanoparticles with a diameter of around 400 nm and 33% of nanoparticles had a diameter of around 40 nm. However, after one week of storage, the tested sample contained 3% of large nanoaggregates with a diameter of around 5000 nm, 34% of particles with a diameter of around 40 nm and 63% particles with a very broad diameter range from 300 up to 700 nm. Values of the zeta-potential of nanoparticles formed by 1,4-DHP **4** indicated the positive surface charge and values were around 20 mV. According to the literature data, the obtained zeta-potentials over ± 20 mV confirmed that the formed nanoparticle solutions were also relatively electrostatically stable [26]. However, in our case, the formed nanoparticles of cationic 1,4-DHP **4** were not stable after storage for 1 week as an aggregation of them occurred.

3. Materials and Methods

All reagents were purchased from Acros Organics (Geel, Belgium), Sigma-Aldrich/Merck KGaA (Darmstadt, Germany), or Alfa Aesar (Lancashire, UK) and used without further purification. TLC was performed on silica gel 60 F254 aluminium sheets 20 cm \times 20 cm (Merck KGaA, Darmstadt, Germany). Silica gel of particle size 35–70 μ m (Merck KGaA, Darmstadt, Germany) was used for column chromatography. Melting points were recorded on an OptiMelt digital melting point apparatus (Stanford Research Systems, Sunnyvale, CA, Canada) and are uncorrected. $^1\text{H-NMR}$ spectra were recorded with a Bruker Fourier (300 MHz) or a Bruker Avance Neo (400 MHz) spectrometer and $^{13}\text{C-NMR}$ spectra were recorded with a Bruker Avance Neo (101 MHz) spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany). Chemical shifts of the hydrogen and carbon atoms are presented in parts per million (ppm) and referred to as the residual signals of the non-deuterated CDCl_3 (δ : 7.26) solvent for the $^1\text{H-NMR}$ spectra and CDCl_3 (δ : 77.16) solvent for the $^{13}\text{C-NMR}$, respectively. Coupling constants J were reported in hertz (Hz). Infrared spectra were recorded with a Prestige-21 FTIR spectrometer (Shimadzu, Kyoto, Japan). UV spectra were recorded on UV-Vis Spectrophotometer (501 UV-Vis CamSpec Spectrophotometer; Spectronic CamSpec Ltd., Leeds, UK). Elemental analyses were determined on an Elemental Combustion System ECS 4010 (Costech International S.p.A., Milano, Italy) at Laboratory of Chromatography of Latvian Institute of Organic Synthesis. High-resolution mass spectra (HRMS) were determined on an Acquity UPLC H-Class system (Waters, Milford, MA, USA) connected to a Waters Synapt GII Q-ToF operating in the ESI positive ion mode on a Waters Acquity UPLC[®] BEH C18 column (1.7 μ m, 2.1 mm \times 50 mm, using gradient elution with acetonitrile (0.01% formic acid) in water (0.01% formic acid). The DLS measurements of the nanoparticles in an aqueous solution were carried out on a Zetasizer Nano ZSP (Malvern Panalytical Ltd., Malvern, UK) instrument with Malvern Instruments Ltd. Software 8.01.4906. The luminescence data were collected with Edinburgh Instruments FS5 Spectrofluorometer (Edinburgh Instruments Ltd., Kirkton Campus, UK). Photoluminescence quantum yields (PLQY) were measured using a standard complementary integrating sphere (the measurement module contains a 150 mm inner diameter integrating sphere for the measurement of fluorescence quantum yields by the absolute method and reflection measurements).

Synthesis of didodecyl 2,6-dimethyl-4-(naphthalen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1**). To a stirred solution of dodecyl 3-oxobutanoate (2.50 g, 9.2 mmol) in ethanol (30 mL) 2-naphthaldehyde (0.72 g, 4.6 mmol) and ammonium acetate (0.53 g, 6.9 mmol) were added, after which a resulting mixture was stirred for 48 h under reflux. The reaction course was monitored by TLC. The reaction mixture was concentrated under reduced pressure and the crude product was purified by flash column chromatography with EtOAc/PE, (0:100 to 20:80%) to give the desired product **1** as a yellow solid (1.22 g, 40%) with melting point 42–44 $^\circ\text{C}$. R_f = 0.30 (PE:EtOAc, 5:1). UV-Vis λ_{max} (EtOH): 223 (log ϵ 4.92); 360 (3.75) nm. IR ν_{max} (film) 3342, 3055, 2924, 2853, 1696, 1675, 1615, 1488 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 7.76–7.71 (m, 2H), 7.69 (d, J = 8.5 Hz, 1H), 7.67–7.65 (m, 1H), 7.47 (dd, J = 8.5,

1.8 Hz, 1H), 7.42–7.35 (m, 2H), 5.68 (s, 1H), 5.17 (s, 1H), 4.07–3.96 (m, 4H), 2.37 (s, 6H), 1.62–1.54 (m, 4H), 1.29–1.17 (m, 36H), 0.93–0.85 (m, 6H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ : 167.8, 145.2, 144.1, 133.5, 132.5, 128.0, 127.6, 127.6, 127.1, 126.3, 125.6, 125.2, 104.3, 64.1, 40.0, 32.1, 29.82, 29.80, 29.78, 29.7, 29.5, 29.5, 28.9, 26.3, 22.8, 19.8, 14.3. Anal. calc. for $\text{C}_{43}\text{H}_{65}\text{NO}_4$: C, 78.25; H, 9.93; N, 2.12 found: C, 77.87; H, 9.88; N, 2.00.

Synthesis of didodecyl 2,6-bis(bromomethyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**2**). To a stirred solution of compound (**1**, 0.50 g, 0.76 mmol) in methanol (50 mL) at 45 °C N-bromosuccinimide (NBS) (0.27 g, 1.52 mmol) was added and the resulting mixture was stirred additionally for 1h at 45 °C. The reaction was monitored by TLC. The reaction mixture was cooled to –10 °C the formed precipitates were filtered off, washed with H_2O (15 mL) and dried under vacuum to give the product **2** as a yellow solid (0.42 g, 68%) with melting point 36–38 °C. $R_f = 0.65$ (PE:EtOAc, 5:1). UV-Vis λ_{max} (EtOH): 222 (log ϵ 4.96); 257 (4.32); 338 (3.70) nm. IR ν_{max} (film) 3393, 3056, 2923, 2852, 1695, 1675, 1616, 1510 cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.79–7.69 (m, 3H), 7.69–7.65 (m, 1H), 7.48–7.36 (m, 3H), 6.50 (s, 1H), 5.20 (s, 1H), 4.94 and 4.67 (AB-system, $J = 11.5$ Hz, 2H and 2H), 4.12–4.02 (m, 4H), 1.66–1.55 (m, 4H), 1.29–1.17 (m, 36H), 0.92–0.85 (m, 6H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ : 166.4, 143.1, 141.8, 133.5, 132.7, 128.1, 128.0, 127.7, 126.7, 126.6, 126.0, 125.7, 106.1, 65.0, 40.4, 32.1, 29.83, 29.80, 29.8, 29.77, 29.5, 29.4, 28.8, 27.5, 26.2, 22.9, 14.3. Anal. calc. for $\text{C}_{43}\text{H}_{63}\text{Br}_2\text{NO}_4$: C, 63.16; H, 7.76; N, 1.71 found: C, 63.54; H, 7.83; N, 1.72.

Synthesis of 1,1'-[[3,5-Bis(dodecyloxycarbonyl)-4-(naphthalen-2-yl)-1,4-dihydropyridine-2,6-diyl]bis(methylene)]bis{4-[(E)-2-(naphthalene-2-yl)vinyl]pyridin-1-ium} dibromide (**4**). To a stirred solution of dibromo derivative (**2**, 0.111 g, 0.14 mmol) in acetone (10 mL) at r. t. (E)-4-(2-(naphthalen-2-yl)vinyl)pyridine (0.066 g, 0.29 mmol) was added and the resulting mixture was stirred at r. t. for 3d. The reaction was monitored by TLC. The precipitates were filtered off washed with cold acetone and dried under vacuum to give product **4** as a yellow powder (0.077 g, 45%) with melting point 155 °C (decomposition). $R_f = 0.40$ (MeOH:DCM: NH_4OH , 3:1:1). UV-Vis λ_{max} (EtOH): 224 (log ϵ 5.14); 359 (3.80) nm. IR ν_{max} (film) 3312, 3057, 2953, 2925, 2853, 1701, 1624, 1505 cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 10.85 (s, 1H), 8.69 (d, $J = 6.8$ Hz, 4H), 8.37–8.30 (m, 6H), 7.94–7.91 (m, 2H), 7.84–7.77 (m, 4H), 7.60–7.56 (m, 2H), 7.53 (dd, $J = 8.5, 1.9$ Hz, 1H), 7.51–7.43 (m, 2H), 7.39–7.32 (m, 6H), 7.31–7.27 (m, 2H), 7.19 (d, $J = 16.1$ Hz, 2H), 7.09 (d, $J = 8.6$ Hz, 2H), 6.46 and 5.44 (AB-system, $J = 13.7$ Hz, 2H and 2H), 5.34 (s, 1H), 4.24–4.06 (m, 4H), 1.75–1.66 (m, 4H), 1.38–1.22 (m, 36H), 0.90–0.86 (m, 6H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ : 166.3, 155.0, 144.9, 143.3, 142.1, 139.4, 134.3, 133.4, 133.0, 132.9, 132.0, 131.7, 128.8, 128.6, 128.5, 128.1, 127.7, 127.6, 127.5, 126.9, 126.5, 126.4, 126.3, 126.1, 124.5, 122.9, 121.6, 110.5, 66.0, 55.7, 39.9, 32.1, 29.9, 29.8, 29.7, 29.5, 28.7, 26.3, 22.8, 14.3. Anal. calc. for $\text{C}_{77}\text{H}_{89}\text{Br}_2\text{N}_3\text{O}_4$ with 3.4% of H_2O : C, 69.78; H, 7.15; N, 3.17; found: 69.57; H, 6.97; N, 3.07. HRMS TOF ES^+ of $[\text{C}_{77}\text{H}_{89}\text{Br}_2\text{N}_3\text{O}_4 - 2\text{H} + \text{H}]^+$ (m/z) 1118.6797; calcd: 1118.6775.

Self-Assembling Properties of compound **4** by Dynamic Light Scattering Measurements. Sample for DLS studies was prepared by making stock solution of compound **4** in EtOH at the concentration 0.5 mM. A solution of compound **4** (250 μL , 0.5 mM in EtOH 96%) was injected into 750 μL of deionized water with maximum stirring (IKA Vortex 2 (IKA, Staufen, Germany)) to give a sample with a final concentration of the compound of 0.125 mM. A sample was sonicated for 30 min at 50 °C using a bath-type sonicator (Cole Parmer Ultrasonic Cleaner 8891CPX (Vernon Hills, IL, USA)). The DLS measurements of the nanoparticles in an aqueous solution were carried out using the following specifications—medium: water; refractive index: 1.33; viscosity: 0.8872 cP; temperature: 25 °C; dielectric constant: 78.5; nanoparticles: liposomes; refractive index of materials: 1.60; detection angle: 173°; wavelength: 633 nm. Data were analyzed using the multimodal number distribution software that was included with the instrument. The measurements were performed in triplicate in order to check their reproducibility. Results were expressed as mean standard deviation (SD).

4. Conclusions

Synthesis of the cationic 1,4-DHP **4** was achieved via the multistep procedure. The compound was characterized by IR, UV, ¹H-NMR, ¹³C-NMR, HRMS and microanalysis. DLS measurements confirmed that the cationic 1,4-DHP **4** in an aqueous solution formed nanoparticles with an average diameter of around 300 nm, a PDI value of around 490 and a zeta-potential around 20 mV for freshly prepared samples. However, after one week of storage at room temperature, an aggregation of nanoparticles was detected. The photoluminescence quantum yield (PLQY) value for the EtOH solution of 1,4-DHP derivative **4** is 1%.

Supplementary Materials: The following are available online, ¹H-NMR: ¹³C-NMR spectra of compounds **1**, **2** and **4**.

Author Contributions: Conceptualization was conducted by M.R.; methodology and experimental works were conducted by M.R., M.K., N.P., K.P., A.S. and A.P.; data analysis, writing, and editing of the paper were conducted by A.P., M.R. and A.S.; project administration and supervision were conducted by A.S. and M.R. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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