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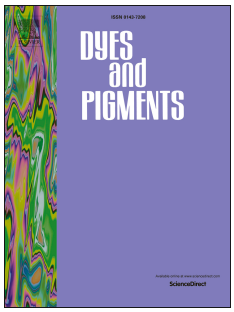

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Synthesis of bis-aminosubstituted indocyanine dyes for their use in polymeric compositions

Sergey Miltsov[a,*], Vladimir Karavan[a], Mikhail Goikhman[a, b], Irina Podeshvo[b], Sara Gómez-de Pedro[c], Mar Puyol[c] and Julian Alonso-Chamarro[c]

[a] St. Petersburg State University, Universitetskii pr. 26, Petrodvorets, St. Petersburg, 198504 Russia
[b] Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31, St. Petersburg, 199004 Russia
[c] Sensors & Biosensors Group, Analytical Chemistry, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
*Corresponding author. Tel.: +7(911)757-35-52; E-mail address: smiltsov2004@mail.ru

Abstract

The synthesis of a set of open-chain bis-aminosubstituted cyanine dyes as well as others with cyclic fragments in the polymethine chain is presented. These dyes are suitable for the development of polymeric compositions with variable optical characteristics as they can be covalently incorporated into the polymer.

Keywords: Cyanine dyes; Diamine dyes; Chromophores; Amino substitution; bis-amino dyes; Chromophore-containing polymeric systems.

1. Introduction

The development of chromophore-containing polymeric systems is an area of growing interest due to their wide applications in optoelectronics [1-3]. Two types of polymeric systems exist depending on the method of incorporating the chromophore into the polymeric matrix; the "guest"-"host" systems, in which chromophore molecules ("guest") are dispersed in the polymeric matrix (the "host") [4], and systems, where chromophore or luminophore groups are covalently incorporated into the main [5] or side chains of the polymer [6]. The latter are of special interest because they do not present some drawbacks [7], which are typical for "guest"-"host" systems, such as (i) limited solubility of the chromophore into the polymeric matrix, (ii) an heterogeneous distribution of the chromophore within the matrix, (iii) poor temperature-time stability of the photophysical properties, and (iv) low optical quality of samples and high level of optical loss due to light scattering from structural heterogeneities.

Cyanine dyes are an important type of chromophores, which have been widely used to modify polymers in order to confer them of valuable photophysical properties. For instance, cyanine dyes have been employed in the design of electroluminescent polymer materials that are based on composites with antracene containing polyimides [8], polyaniline [9] and photorefractive polyimide composites [10]. However, all these approaches are based on the "guest"-"host" systems, the drawbacks of which are intended to be solved.

Recently, we reported the first example of a polymeric system with the cyanine chromophore **1** in the main chain (Fig. 1) and demonstrated its excellent electro-optical and optical properties [11].

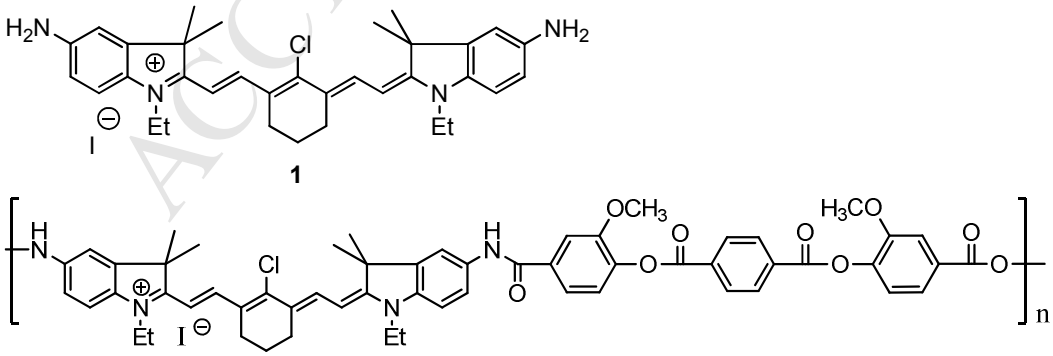


Fig. 1. Structure of cyanine dye **1** and scheme of the previous published polymeric system with a cyanine chromophore in the main chain

In the present study, we have performed the synthesis of a set of structural analogues of diamine **1** and related dyes**,** which could be therefore used as components of polymeric compositions with variable optical characteristics.

2. Experimental

2.1. General (apparatus and procedures)

All starting materials for the dyes syntheses have been purchased form Aldrich Chemical Co. MS-ES measurements have been made in a Bruker micrOTOF. ^{1}H NMR spectra have been measured in a Bruker DPX-300 at 300 MHz. Reproducibility problems have been found in the elemental analysis due to the hard combustion of this kind of compounds. Spectrophotometric studies have been performed in a UV-VIS-NIR Scanning Spectrophotometer Shimadzu UV-3101PC. The absorption spectra have been recorded between 1000 and 400 nm. The concentration of dye solutions used was of 1×10^{-5} mol L^{-1} (unless otherwise indicated) in ethanol 99.8 %.

2.2. Preparation of intermediate compounds

5-Acetylamino-2,3,3-trimethylindoleninium iodide **2** was obtained by reduction of 5-nitro-2,3,3-trimethylindolenine [12] followed by acetylation of the resulted amine by acetic anhydride and quaternization of the latter acetamide with ethyl iodide [11]. The penthamethinecyanine salt **3** was obtained by formylation of cyclohexanone [13]. The synthesis of dye **4** and hemicyanine dye **11** were described in recent articles of our research group [11, 14, 15]. The synthesis of trimethine salts **17a,b** was described elsewhere [16,17]. Sodium nitromalonaldehyde monohydrate **20** was obtained according to [18]. Pentamethine salt **24** was prepared as described in [19].

*2.3. Synthesis of meso-substituted bis-acetylamino dyes (**5a-e, 8, 9, 12, 13, 15, 18a-b, 21, 24**)*

*2.3.1. 3H-Indolium, 5-acetylamino-2-[2-[3-[2-(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-methoxy-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**5a**)*
Dye **4** (753 mg, 1mmol) was dissolved in 10 mL of dry DMF, where a 30 % solution of sodium methylate in methanol (2.3 mL, 10 mmol) was added. The mixture was kept at room temperature overnight. The mixture was neutralized with 2 N HCl in methanol (5 mL) and the volatiles were evaporated *in vacuo* (t < 40 ^{0}C). The residue was recrystallized from methanol, containing sodium iodide (500 mg in 10 mL of methanol). The resulted crystals were washed with ether, water and ether again, and dried on air. Yield 389 mg (52 %). ^{1}H NMR (DMSO-d^{6}) δ (ppm) 1.28 (br. t, J = 7.2 Hz, 6H), 1.62 (s, 12H), 1.79 (br. s, 2H), 2.06 (s, 6H), 2.58 (br. s, 4H), 3.92 (s, 3H), 4.16 (q, J = 7.2 Hz, 4H), 6.11 (d, J = 14 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.86 (s, 2H), 8.45 (d, J =14 Hz, 2H), 10.38 (s, 2H). λ_{max} (EtOH) = 748 nm (ε = $2.70\text{x}10^{5}$ L mol^{-1} cm^{-1}). ES-MS^{+} 621.3696 (cal. 621.3788 for $C_{39}H_{49}N_4O_3$).

2.3.2. *3H-Indolium, 5-acetylamino-2-[2-[3-[2-(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(1-piperidinyl)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**5b**)*
Dye **4** (753 mg, 1mmol) was dissolved in 10 mL of methanol and after addition of piperidine (850 mg, 10 mmol) the mixture was kept at room temperature overnight. The volatiles were evaporated *in vacuo* and resulted crystals were washed with ether, water and ether again. Yield 690 mg (86 %). ^{1}H NMR (DMSO-d^{6}) δ (ppm) 1.23 (br. t, J = 7 Hz, 6H), 1.60 (s, 12H), 1.74 (br. s, 2H), 1.82 (br. s, 6H), 2.06 (s, 6H), 2.48 (br. s, 4H), 3.66 (br. s, 4H), 4.03 (br. q, J = 7.2 Hz, 4H), 5.87 (d, J = 14 Hz, 2H), 7.16 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 7.57 (d, J =14 Hz, 2H), 7.71 (s, 2H), 10.02 (s, 2H). λ_{max} (EtOH) = 708 nm (ε = 6.34 x 10^{4} L mol^{-1} cm^{-1}). ES-MS^{+} 674.4174 (cal. 674.4334 for $C_{43}H_{56}N_5O_2$).

2.3.3. *3H-Indolium, 5-acetylamino-2-[2-[3-[2-(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-methylphenoxy)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**5c**)*
Dye **4** (753 mg, 1mmol) was dissolved in 10 mL of dry DMF, where a solution of sodium 4-methylphenolate (10 mmol) in 10 mL of dry DMF (freshly prepared from 1.240 g (10 mmol) of 4-methylphenol and 400 mg (10 mmol) of 60 % NaH in mineral oil) was added. The mixture was stirred at 60 ^{0}C for 6 hours. After acidification and evaporation of solvents, the residue was triturated with water. The solids were filtered out and purified on silica (1-5 % MeOH in CH_2Cl_2). Yield 479 mg (58

%). ^{1}H NMR (DMSO-d^6) δ (ppm) 1.24 (t, J = 7 Hz, 6H), 1.26 (s, 12H), 1.91 (br.s, 2H), 2.05 (s, 6H), 2.23 (s, 3H), 2.69 (br. s, 4H), 4.13 (q, J = 7 Hz, 4H), 6.12 (d, J = 14 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.7 Hz), 7.71 (s, 2H), 7.77 (d, J = 14 Hz, 2H), 10.20 (s, 2H). λ_{max} (EtOH) = 797 nm (ε = 3.76 x 10^5 L mol^{-1} cm^{-1}). ES-MS$^+$ 697.4150 (cal. 697.4117 for $C_{45}H_{53}N_4O_3$).

2.3.4. *3H-Indolium, 5-acetylamino-2-[2-[3-[2-(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-methylphenylmercapto)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**5d**)*

From dye **4** and sodium 4-methylthiophenolate.The followed procedure was the same as for **5c.** Yield 379 mg (45 %). ^{1}H NMR (DMSO-d^6) δ (ppm) 1.28 (t, J = 7 Hz, 6H), 1.42 (s, 12H), 1.92 (br.s, 2H), 2.05 (s, 6H), 2.20 (s, 3H), 2.73 (br. s, 4H), 4.17 (br.q, J = 7 Hz, 4H), 6.26 (d, J = 14 Hz, 2H), 7.15 (m, 4H), 7.33 (d, J = 8.5 Hz, 2H), 7.52(d, J = 8.5 Hz), 7.74 (s, 2H), 8.57 (d, J =14 Hz, 2H), 10.06 (s, 2H). λ_{max} (EtOH) = 825 nm (ε = 3.75 x 10^5 L mol^{-1} cm^{-1}). ES-MS$^+$ 713.3864 (cal. 713.3889 for $C_{45}H_{53}N_4O_2S$).

2.3.5. *3H-Indolium, 5-acetylamino-2-[2-[3-[2-(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-chlorophenyl)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**5e**)*

Dye **4** (722 mg, 1 mmol), 4-chlorophenylboronic acid (189 mg, 1.2 mmol) and anhydrous potassium carbonate (207 mg, 1.5 mmol) were mixed with 10 mL of 85% aqueous i-propanol. 0.5 mL of stock solution of Pd[C(NHNHC$_6$H$_4$NO$_2$)-NCyclohexyl](CNCyclohexyl)[Cl$_2$ in $CHCl_3$ (10^{-6} mol mL^{-1}) were added, and the mixture was kept at reflux for one hour. After cooling, the mixture was neutralized with 2 N HCl in methanol and kept at -15 ^{0}C overnight. The solid was filtered out and recrystallized from methanol. The resulted crystals were washed with ether, water and ether again, and dried on air. Yield 654 mg (79%). ^{1}H NMR (DMSO-d6) δ (ppm) 1.13 (s, 12H), 1.22 (br. t, J = 7,2 Hz, 6H), 1.93 (br. s, 2H), 2.04 (s, 6H), 2.67 (br. s, 4H), 4.12 (q, J = 7.2 Hz, 4H), 6.16 (d, J = 14 Hz, 2H), 7.00 (d, J = 14 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.67-7.75 (m, 4H), 8.43 (d, J =13.0 Hz, 2H), 10.14 (s, 2H). λ_{max} (EtOH) = 793 nm (ε = 3.16 x 10^5 L mol^{-1} cm^{-1}). ES-MS$^+$ 701.3578 (cal. 701.3622 for $C_{44}H_{50}N_4ClO_2$)

*2.3.6. 3H-Indolium, 5-acetylamino-2-[2-[3-[2-(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-chloro-1-cyclopenten-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**8**)*

A solution of pentamethine salt **7** (482.5 mg, 1 mmol), 5-acetylamino-2,3,3-trimethyliondoleninium iodide **2** (744 mg, 2 mmol) and anhydrous sodium acetate (200 mg, 2.5 mmol) in absolute EtOH was refluxed for 30 min. After cooling the precipitated solid was recrystallized from methanol. The resulted crystals were washed with ether, water and ether again and dried on air. Yield 620 mg (84%). 1H NMR (DMSO-d6) δ (ppm) 1.29 (m, 6H), 1.62 (s, 12H), 2.06 (s, 6H), 2.92 (s, 4H), 4.18 (m, 4H), 6.09 (d, J = 14.5 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 14.5 Hz, 2H), 7.82 (br.s, 2H), 10.13(s, 2H). λ_{max} (EtOH) 837 nm (ε =7.70x10^4 l/mol cm). ES-MS$^+$ 611,3163 (cal. 611,3153 for $C_{37}H_{44}ClN_4O_2$).

2.3.7. 3H-Indolium, 5-acetylamino-2-[2-[3-[2-(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(3-trifluoromethylphenylamino)-1-cyclopenten-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**9**)

A solution of dye **8** (369 mg, 0.5 mmol) and 3-trifluoromethylaniline (805 mg, 5 mmol) in absolute EtOH was refluxed for 6 h. After evaporation of methanol in *vacuo* the residue was washed with ether and recrystallized from methanol. The resulted crystals were washed with ether and dried on air. Yield 328 mg (76%). 1H NMR (DMSO-d6) δ (ppm) 1.30 (s, 12H), 2.03 (s, 6H), 2.80 (s, 4H), 4.01 (m, 4H), 5.72 (br.s, 2H), 7.18 (br.s, 2H), 7.41 (d, J = 8 Hz, 2H), 7.53 - 7.78 (m, 8H), 9.90 (br.s, 1H), 9.98 (s, 2H). λ_{max} (EtOH) 757 nm (ε =1.57·10^5 l/mol cm). ES-MS$^+$ 736,3861 (cal. 736,3838 for $C_{44}H_{49}F_3N_5O_2$).

2.3.8. *3H-Indolium, 5-acetylamino-2-[2-[3-[2-(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-chloro-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**12**)*

A mixture of 392 mg (0.76 mmol) of dye **11**, 282 mg (0.76 mmol) of quaternary salt **2** and 60 mg of sodium acetate were refluxed in 15 mL of methanol for 10 min. The crude product remained after evaporation of all volatiles, which was purified on silica (0-5% MeOH in CH_2Cl_2) resulting in 347 mg

of dye **12** (yield 68 %). (DMSO-d6) δ (ppm) 1.22 - 1.37 (m, 6H), 1.66 (s, 12H), 1.85 (br. s, 2H), 2.07 (s, 3H), 2.71 (br. s, 4H), 4.19 (m, 2H), 4.29 (m, 2H), 6.21 (d, J = 13.5 Hz, 1H), 6.41 (d, J = 14.0 Hz, 1H), 7.23 (m, 1H), 7.32 -7.45 (m, 7.56, 1H), 7.48 (d, J = 9.0 Hz, 1H), 7.53 - 7.67 (m, 2H), 7.90 (s, 2H), 8.18 (d, J =13.5 Hz, 1H), 8.28 (d, J =14.0 Hz, 1H), 10.20 (s, 1H). λ_{max} (EtOH) = 797 nm (ε = 2.53 x 10^5 L mol^{-1} cm^{-1}).ES-MS^+ 568.3094 (cal. 568.3094 for $C_{36}H_{43}ClN_3O$). ES-MS^- 98.9440 (cal. 98.9485 for ClO_4^-).

2.3.9. *3H-Indolium, 5-acetylamino-2-[2-[3-[2-(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-acetylaminophenoxy)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**13**)*

Yield 503 mg (62 %) from dye **12** and sodium 4-acetylaminophenolate, using the procedure for **5c**. (DMSO-d6) δ (ppm) 1.24(m, 3H), 1.27(m, 3H), 1.29 (s, 6H), 1.30 (s, 6H), 1.94 (m, 2H), 1.98 (s, 3H), 2.00 (s, 3H), 2.71 (m, 4H), 4.11 (m, 2H), 4.19 (m, 2H), 6.09 (d, J = 14 Hz, 1H), 6.23 (d, J = 14.5 Hz, 1H), 7.09 (d, J = 9.0 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.27- 7.36 (m, 2H), 7.38(d, J = 8.5 Hz, 2H), 7.47 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 9.0 Hz, 2H), 7.73 (br.s, 1H), 7.77 (d, J = 14 Hz, 1H), 7.85 (d, J = 14.5 Hz, 1H), 9.86 (s, 1H), 10.10 (s, 1H). λ_{max} (EtOH) = 782 nm (ε = 2.65 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 683.3948 (cal. 683.3961 for $C_{44}H_{51}N_4O_3$).

2.3.10. *3H-Indolium, 5-acetylamino-2-[[3-[(5-acetylamino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-1-ethyl-3,3-dimethyl-, inner salt (**15**)*

A mixture of squaric acid (114 mg, 1 mmol), 5-acetylamino-2,3,3-trimethyliondoleninium iodide **2** (744 mg, 2 mmol) and quinoline (516 mg, 8 mmol) were refluxed in 30 mL of a 1:1 mixture of *n*-butanol and benzene with Dean-Stark trap for 6 hours. After cooling the volatiles *in vacuo* the residue was recrystallized from methanol, yielding 475 mg (84 %) of **16**. ^{1}H NMR (DMSO-d6) δ (ppm) 1.23 (br. t, 6H), 1.66 (s, 12H), 2.05 (s, 6H), 4.09 (br.s, 4H), 5.73 (s, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8 Hz, 2H), 7.69 (s, 2H), 10.0 (s, 2H). λ_{max} (EtOH) = 655 nm (ε = 3.72 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 566.2930 (cal. 566.2893 for $C_{34}H_{38}N_4O_4$).

2.3.11. *3H-Indolium, 2-[5-(1-ethyl-1,3-dihydro-5-acetylamino-3,3-dimethyl-2H-indol-2-ylidene)-1,3-pentadien-1-yl]-1-ethyl-5-acetylamino-3,3-dimethyl-, iodide (**18a**)*

Acetic anhydride (200 mg, 2 mmol) was added dropwise to a solution of N-(3-anilino-3-propenylidene)aniline perchlorate **17a** (323 mg, 1 mmol) and diisopropylethylamine (DIEA, 0.38 mL, 2 mmol) in 7 mL of CH_2Cl_2. The mixture was kept at room temperature for 3 hours and added to the solution of salt **2** (746 mg, 2 mmol) and anhydrous sodium acetate (430 mg, 5.2 mmol) in 25 mL of methanol. Methylene chloride was distilled off and the remaining methanol solution was heated at reflux for 8 hours. After reducing to 10 mL the solution was kept at -15 ^{0}C overnight. The resulted crystals were washed with ether, water and ether again, and dried on air. Yield 469 mg (72 %). ^{1}H NMR (DMSO-d6) δ (ppm) 1.26 (m, 6H), 1.65 (s, 12H), 2.06 (s, 6H), 4.10 (m, 4H), 6.25 (d, J = 13 Hz, 2H), 6.52 (t, J = 13 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 9.0 Hz, 2H), 7.88 (br.s, 2H), 8.26 (t, J = 13 Hz, 1H), 10.08 (s, 2H). λ_{max} (EtOH) = 674 nm (ε = 2.26 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 525.3229 (cal. 525.3229 for $C_{33}H_{41}N_4O_2$).

2.3.12. *3H-Indolium, 2-[3-chloro-5-(1-ethyl-1,3-dihydro-5-acetylamino-3,3-dimethyl-2H-indol-2-ylidene)-1,3-pentadien-1-yl]-1-ethyl-5-acetylamino-3,3-dimethyl-, iodide (**18b**)*

A solution of N-(3-anilino-2-chloro-2-propenylidene)aniline hydrochloride **17b** (293 mg, 1 mmol), 5-acetylamino-2,3,3-trimethyliondoleninium iodide **2** (746 mg, 2 mmol) and anhydrous sodium acetate (200 mg, 2.5 mmol) in absolute EtOH was refluxed for 2 hours. After cooling, the precipitated solid was recrystallized from methanol. The resulted crystals were washed with ether, water and ether again, and dried on air. Yield 370 mg (62 %). ^{1}H NMR (DMSO-d6) δ (ppm) 1.31 (t, J = 7 Hz, 6H), 1.68 (s, 12H), 2.06 (s, 6H), 4.18 (br.t, 4H), 6.24 (d, J = 13.5 Hz, 2H), 7.34 - 7.54 (m, 4H), 7.94 (br.s, 2H), 8.39 (d, J = 13.5 Hz, 2H), 10.14 (s, 2H). λ_{max} (EtOH) = 676 nm (ε = 2.30 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 559.2729 (cal. 559.2840 for $C_{33}H_{40}ClN_4O_2$).

2.3.13. *3H-Indolium, 2-[3-nitro-5-(1-ethyl-1,3-dihydro-5-acetylamino-3,3-dimethyl-2H-indol-2-ylidene)-1,3-pentadien-1-yl]-1-ethyl-5-acetylamino-3,3-dimethyl-, iodide (**21**)*

A solution of 2-nitromalonic dialdehyde sodium salt monohydrate **20** (139 mg, 1 mmol), 5-acetylamino-2,3,3-trimethyliondoleninium iodide **2** (746 mg, 2 mmol) and anhydrous sodium acetate (200 mg, 2.5 mmol) in absolute EtOH was refluxed for 1 hour. After cooling, the precipitated solid

was recrystallized from methanol. The resulted crystals were washed with ether, water and ether again, and dried on air. Yield 432 mg (62 %). ^{1}H NMR (DMSO-d6) δ (ppm) 1.40 (m, 6H), 1.74 (s, 12H), 2.09 (s, 6H), 4.37(m, 4H), 6.96 (d, J = 15 Hz, 2H), 7.50 - 7.69(m, 4H), 8.00 (s, 2H), 8.37 (d, J = 15 Hz, 2H), 10.27(s, 2H). λ_{max} (EtOH) = 610 nm (ε = 7.10 x 10^4 L mol^{-1} cm^{-1}). ES-MS$^+$ 570.3058 (cal. 570.3080 for $C_{33}H_{40}N_5O_4$).

2.3.14. *3H-Indolium, 2-[5-(1-ethyl-1,3-dihydro-5-acetylamino-3,3-dimethyl-2H-indol-2-ylidene)-1,3,5-heptatrien-1-yl]-1-ethyl-5-acetylamino-3,3-dimethyl-, Iodide (**24**)*
From 2 mmol of salt **2** and 1 mmol of N-(5-anilino-2,4-pentadienylidene)aniline hydrochloride **23.** The followed procedure was the same as for **18a**. Yield 515 mg (76 %). ^{1}H NMR (DMSO-d6) δ (ppm) 1.27 (m, 6H), 1.61 (s, 12H), 2.06 (s, 6H), 4.09 (m, 4H), 6.32 (d, J = 13 Hz, 2H), 6.51 (t, J = 13 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.61 -7.92 (m, 3H), 7.81 (br.s, 2H), 10.05 (s, 2H). λ_{max} (EtOH) = 776 nm (ε = 2.30 x 10^5 L mol^{-1} cm^{-1}). ES-MS$^+$ 551.3377 (cal. 551.3386 for $C_{35}H_{43}N_4O_2$).

*2.4. Syntheses of bis-amino dyes (**6a-e**, **14**, **16**, **19a**-**b**, **22**, **25**).*

2.4.1. *General procedure for deprotection of bis-acetylamino dyes.*

1 eq of *bis*-acetylamino dye and 12 eq (1.05 mL / 1 mmol of dye) of boron trifluoride - methanol complex 50 % in methanol (20 mL / 1 mmol of dye) were heated under reflux for 4-6 hours (VIS control). After cooling, 15 eq (2.2 mL / 1mmol of dye) of triethylamine were added, and all volatiles were evaporated *in vacuo*. The residue was stirred with 50 mL of water for an hour. The filtered solid was washed with ether and dried on air.

2.4.1.1. *3H-Indolium, 5-amino-2-[2-[3-[2-(5-amino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-methoxy-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**6a**)*
Yield 85%. ^{1}H NMR (DMSO-d6) δ (ppm) 1.25 (br.t, 6H), 1.51 (s,12H), 1.77 (br.s, 2H), 2.54 (br.s, 4H), 3.88 (s, 3H), 4.08 (br.s, 4H), 5.98 (d, J = 13.5 Hz, 2H), 6.58 (d, J = 7 Hz, 2H), 6.72 (s, 2H), 7.06 (d, J = 7 Hz, 2H), 7.84 (d, J = 13.5 Hz, 2H). ^{1}H NMR (DMSO-d6 + CF_3COOH) δ (ppm) 1.28 (m, 6H), 1.63 (s, 12H), 1.79 (br.s, 2H), 2.57 (br.s, 4H), 3.89 (s, 3H), 4.15 (br.s, 4H), 6.15 (d, J = 14Hz, 2H), 7.06 (d, J = 8 Hz, 2H), 7.19 (s, 2H), 7.31 (d, J = 8 Hz, 2H), 7.87 (d, J = 14 Hz, 2H). λ_{max} (EtOH) = 806 nm (ε = 1.63 x 10^5 L mol^{-1} cm^{-1}). ES-MS$^+$ 537.3499 (cal. 537.3576 for $C_{35}H_{45}N_4O$).

2.4.1.2. *3H-Indolium, 5-amino-2-[2-[3-[2-(5-amino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(1-piperidinyl)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**6b**)*
Yield 78 %. ^{1}H NMR (DMSO-d6) δ (ppm) 1.22 (m, 6H), 1.59 (s, 12H), 1.74 (br.s, 8H), 2.48 (br.s, 4H), 3.30 (br.s, 4H), 4.01 (br.s, 4H), 5.20 (br.s, 4H), 5.73 (d, J = 12.5 Hz, 2H), 6.56 (m, 2H), 6.70 (s, 2H), 6.99 (d, J = 8 Hz, 2H), 7.74 (d, J = 12.5 Hz, 2H). ^{1}H NMR (DMSO-d6 + CF_3COOH) δ (ppm) 1.22 (m, 6H), 1.60 (s, 12H), 1.80 (br.s, 8H), 2.48 (br.s, 4H), 3.63 (br.s, 4H), 4.03 (br.s, 4H), 5.86 (d, J = 13 Hz, 2H), 7.00 - 7.30 (m, 6H), 7.52 (d, J = 13 Hz, 2H). λ_{max} (EtOH) = 760 nm (ε = 3.25 x 10^4 L mol^{-1} cm^{-1}). ES-MS$^+$ 590.4123 (cal. 590.4210 for $C_{39}H_{52}N_5$).

2.4.1.3. *3H-Indolium, 5-amino-2-[2-[3-[2-(5-amino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-methylphenoxy)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**6c)***
Yield 73 %. ^{1}H NMR (DMSO-d6 + CF_3COOH) δ (ppm) 1.23 (br.t, 6H), 1.27 (s,12H), 1.92 (br.s, 2H), 2.22 (s, 3H), 2.69 (br.s, 4H), 4.12 (br.q, 4H), 6.18 (d, J = 14 Hz, 2H), 7.01 (d, J = 8 Hz, 2H), 7.09 (d, J =8 Hz, 2H), 7.13 - 7.24 (m, 4H), 7.31 (d, J = 8 Hz, 2H), 7.70 (d, J = 14 Hz, 2H). λ_{max} (EtOH) = 825 nm (ε = 1.56 x 10^5 L mol^{-1} cm^{-1}). ES-MS$^+$ 613.3930 (cal. 613.3906 for $C_{41}H_{49}N_4O$).

2.4.1.4. *3H-Indolium, 5-amino-2-[2-[3-[2-(5-amino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-methylphenylmercapto)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**6d**)*
Yield 67 %. ^{1}H NMR (DMSO-d6 + CF_3COOH) δ (ppm) 1.25 (br.t, 6H), 1.42 (s,12H), 1.88 (br.s, 2H), 2.20 (s, 3H), 2.73 (br.s, 4H), 4.15 (br.q, 4H), 6.28 (d, J = 14 Hz, 2H), 6.98 (d, J = 8 Hz, 2H), 7.14 (br. s, 6H), 7.31 (d, J = 8 Hz, 2H), 8.47 (d, J = 14 Hz, 2H). λ_{max} (EtOH) = 850 nm (ε = 1.19 x 10^5 L mol^{-1} cm^{-1}). ES-MS$^+$ 629.3700 (cal. 629.3678 for $C_{41}H_{49}N_4S$).

2.4.1.5. *3H-Indolium, 5-amino-2-[2-[3-[2-(5-amino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-chlorophenyl)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**6e**)*

Yield 82 %. ^{1}H NMR (DMSO-d6) δ (ppm) 1.09 (s,12H), 1.19 (br.t, 6H), 1.91 (br.s, 2H), 2.61 (br.s, 4H), 4.03 (br.q, 4H), 5.28 (br.s, 4H), 6.00 (br.s, 2H), 6.54 (br. s, 2H), 6.61 (s, 2H). 6.88 (br.s, 2H). 7.01 (br.s, 2H), 7.23 (d, J = 8 Hz, 2H), 7.67 (d, J = 8 Hz, 2H). λmax (EtOH) = 822 nm (ε = 1.63 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 617.3400 (cal. 617.3400 for $C_{40}H_{46}N_4Cl$).

2.4.1.6. *3H-Indolium, 5-amino-2-[2-[3-[2-(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-2-(4-aminophenoxy)-1-cyclohexen-1-yl]ethenyl]-1-ethyl-3,3-dimethyl-, iodide (**14**)*
Yield 76 %. ^{1}H NMR (DMSO-d^6) δ (ppm) 1.17 (br.t, 6H), 1.27 (s,8H), 1.30 (s,6H),1.88(m, 2H), 2.65(br.s, 4H), 3.92 (m, 2H), 4.25 (m, 2H), 5.17 - 6.17(br.s, 4H), 5.78(d, J = 13 Hz, 1H), 6.35 (d, J = 15 Hz, 1H), 6.56 - 6.77 (m, 4H), 6.80 - 6.93(m, 2H), 6.93 - 7.15(m, 2H), 7.15 - 7.45 (m, 3H), 7.52 (d, J = 13 Hz, 1H), 7.89 (d, J = 15 Hz, 1H) λ_{max} (EtOH) = 788 nm (ε = 7.91 x 10^4 L mol^{-1} cm^{-1}). ES-MS^+ 599.3731 (cal. 599.3750 for $C_{40}H_{47}N_4O$).

2.4.1.7. *3H-Indolium, 5-amino-2-[[3-[(5-amino-1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-1-ethyl-3,3-dimethyl-, inner salt (**16**).*
Yield 79 %. ^{1}H NMR (DMSO-d6 + CF_3COOH) δ (ppm) 1.28 (br.t, 6H), 1.70 (s,12H), 4.13 (br.q, 4H), 5.85 (s, 2H), 7.34 (br,d, J = 8.7 Hz, 2H), 7.43 (d, J = 8 Hz, 2H), 7.49 (br.s, 2H). λ_{max} (EtOH) = 669 nm (ε = 1.42 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 482.2662 (cal. 482.2682).

2.4.1.8. *3H-Indolium, 2-[5-(1-ethyl-1,3-dihydro-5-amino-3,3-dimethyl-2H-indol-2-ylidene)- 1,3-pentadien -1-yl]-1-ethyl-5-amino-3,3-dimethyl-, iodide (**19a**)*
Yield 72 %. ^{1}H NMR (DMSO-d_6) δ (ppm) 1.23 (m, 6H), 1.60 (s, 12H), 4.02(m, 4H), 5.57(br. s, 4H), 6.09 (d, J = 13 Hz, 2H), 6,38 (br.t, 1H), 6.60 (d, J = 7.5 Hz, 2H), 6.76 (s, 2H), 7.08 (d, J = 7.5 Hz, 2H), 8.07 (br.t, 2H). λ_{max} (EtOH) = 700 nm (ε = 9.64 x 10^4 L mol^{-1} cm^{-1}). ES-MS^+ 441.2977 (cal. 441.3018 for $C_{29}H_{36}ClN_4$).

2.4.1.9. *3H-Indolium, 2-[3-chloro-5-(1-ethyl-1,3-dihydro-5-amino-3,3-dimethyl-2H-indol-2-ylidene)-1,3-pentadien-1-yl]-1-ethyl-5-amino-3,3-dimethyl-, iodide (**19b**)*
Yield 94 %. ^{1}H NMR δ (ppm) 1.29 (m, 6H), 1.64 (s, 12H), 4.09(m, 4H), 5.40 (br.s, 4H), 6.13 (d, J = 13 Hz, 2H), 6.61 (m, 2H), 6.79 (s, 2H), 7.16 (d, J = 8.5 Hz, 2H) 8.38 (d, J = 13 Hz, 2H). λ_{max} (EtOH) = 688 nm (ε = 1.10 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 475.2640 (cal. 475.2628 for $C_{29}H_{36}ClN_4$).

2.4.1.10. *3H-Indolium, 2-[3-nitro-5-(1-ethyl-1,3-dihydro-5-amino-3,3-dimethyl-2H-indol-2-ylidene)-1,3-pentadien-1-yl]-1-ethyl-5-amino-3,3-dimethyl-, iodide(**22**)*
Yield (92 %). ^{1}H NMR (DMSO-d_6 +CF_3COOH) δ (ppm) 1.38 (m, 6H), 1.70 (s, 12H), 4.31(overlapped with water), 6.77-6.97 (m, 4H), 7.05 (s, 2H), 7.46 (d, J = 9 Hz, 2H), 8.31 (d, J = 15 Hz, 2H). λ_{max} (EtOH) = 638 nm (ε = 4.70 x 10^4 L mol^{-1} cm^{-1}). ES-MS^+ 428.2846 (cal. 486.2868 for $C_{29}H_{36}N_5O_2$).

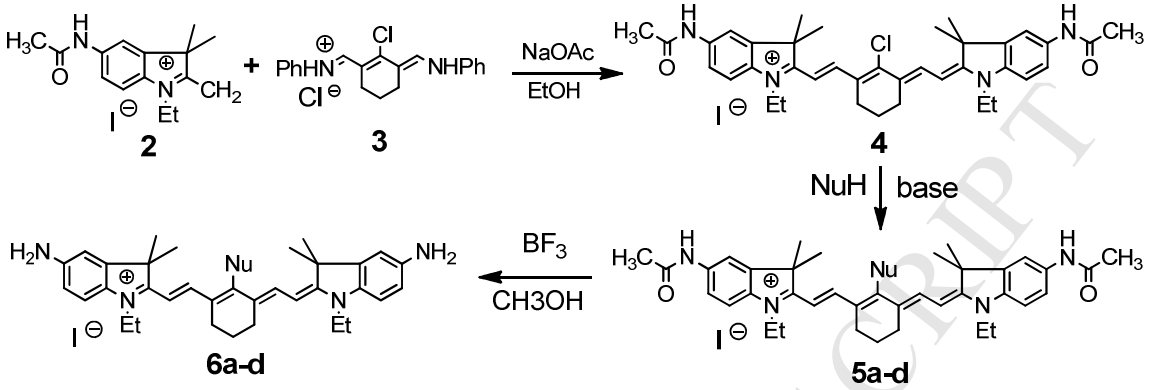
2.4.1.11. *3H-Indolium, 2-[5-(1-ethyl-1,3-dihydro-5-amino-3,3-dimethyl-2H-indol-2-ylidene)- 1,3,5-heptatrien-1-yl]-1-ethyl-5-amino-3,3-dimethyl-, iodide (**25**)*
Yield (74 %). ^{1}H NMR (DMSO-d_6) δ (ppm) 1.24 (m, 6H), 1.56 (s, 12H), 4.11(m, 4H), 5.30(br.s, 4H), 6.16 (d, J = 14 Hz, 2H), 6.37 (t, J = 12.5 Hz, 2H), 6.58 (d, J = 8.5 Hz, 2H), 6.71 (s, 2H), 7.05 (d, J = 8.5 Hz, 2H), 7.51 (t, J = 12.5 Hz, 1H), 7.66 (t, J = 12 Hz, 2H). λ_{max} (EtOH) = 804 nm (ε = 1.45 x 10^5 L mol^{-1} cm^{-1}). ES-MS^+ 467.3155 (cal. 467.3175 for $C_{31}H_{39}N_4$).

3. Results and discussion

Cyanine dyes are usually prepared via condensation of quaternized nitrogen heterocycles containing activated methyl groups with unsaturated dialdehydes or their derivatives (anils, acetals, etc). In order to prepare the starting heterocyclic salts as well as to perform condensation to obtain the aminosubstituted cyanines, amino-groups should be protected. Thus, deprotection only can be undertaken on very last step, being the key step for the whole synthetic route. Since cyanine dyes are rather labile compounds, this deprotection step is likely to proceed in very mild conditions. Recently, we have developed an effective procedure that allows accomplishing the cleavage of acetylated amino dyes in high yields by simple refluxing their methanolic solutions in the presence of

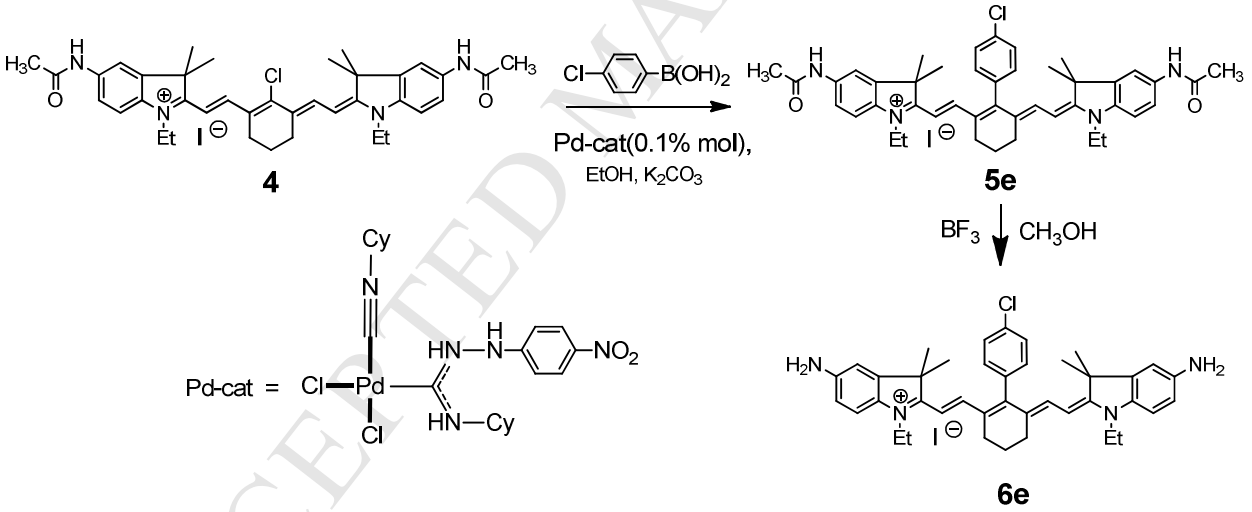
boron trifluoride [20]. In the present work, we have successfully used this method for the liberation of target diamines from their acetylated derivatives.

Dye **1,** used previously in polymer compositions by our research group (Fig. 1), has a vinylic chlorine atom, which exhibits considerable reactivity towards various nucleophiles [14, 21] and can be involved in side reactions in course of polymerization. In order to overcome this drawback, we prepared from dye **4** (protected dye **1**) various *meso*-substituted derivatives **5a-d**, which were further converted into free diaminodyes **6a-d** by the above procedure [20] (Scheme 1):



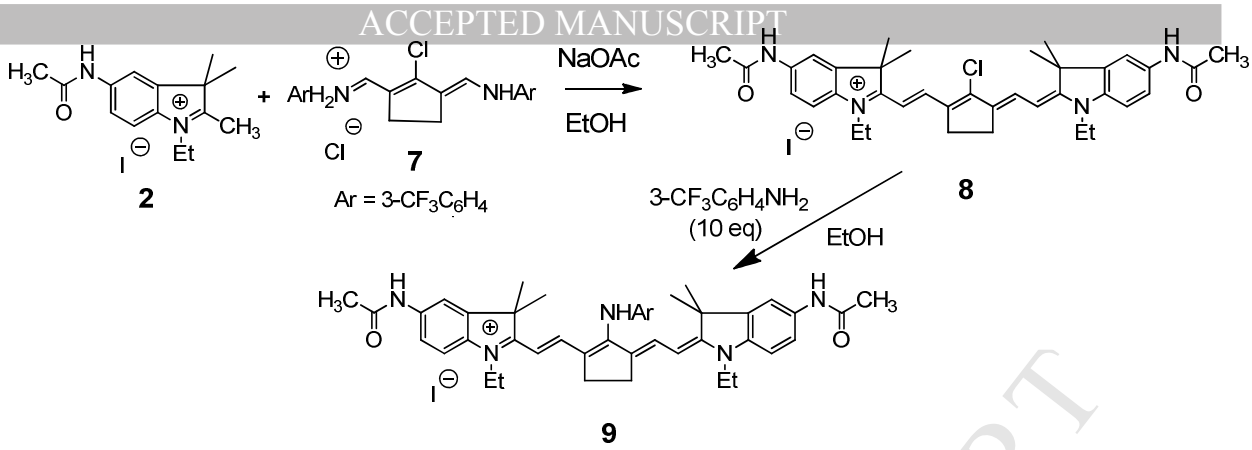
Scheme 1. Preparation of *meso*-substituted derivatives from dye **1** and their deprotection. Nu = a) CH_3O-, b) c-$C_5H_{10}N$-, c) 4-$CH_3C_6H_4O$-, d) 4-$CH_3C_6H_4S$-

It is known that *meso*-chlorosubstituted analogues of **4** can be arylated by means of Suzuki reaction [22]. Thus, we performed this reaction with dye **4** and 4-chlorophenylboronic acid, using the palladium-based catalyst, which was also developed by our research group [23] (Scheme 2):



Scheme 2. Arylation of dye **4** by a palladium-based catalyst and its deprotection.

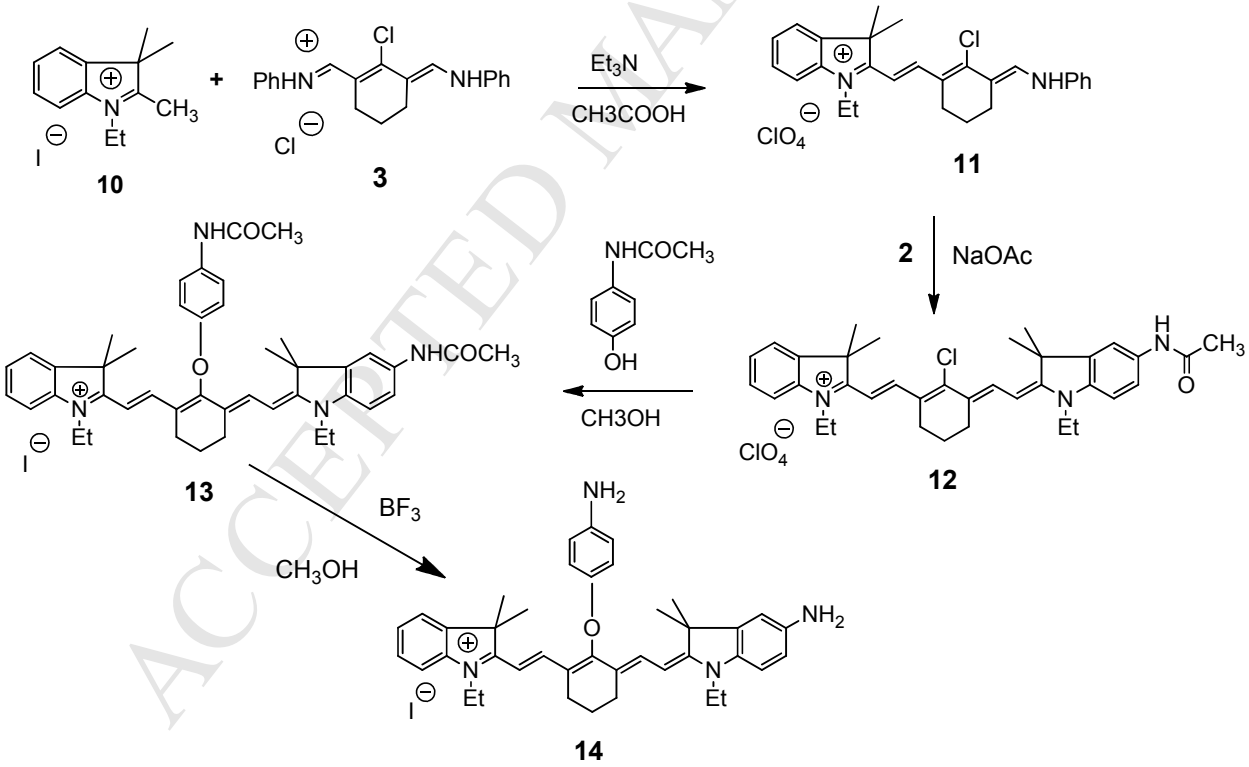
As it has been stated in other works, preparation attempts of dye **4** analogues with five-membered ring in the polimethine chain, according to the Scheme **1,** leads to *meso*-anilinoderivatives. This happens because of the increased reactivity of the corresponding *meso*-chlorinated dyes towards nucleophilic substitution by aniline, which is released in the course of the process [24]. In this sense, we tried to use the 5-membered bis-anil **7,** containing weakly-basic 3-triflurомethylaniline to obtain dye **8** in high yield. Corresponding meso-anilinosubstituted dye **9** was prepared only by 6-hour heating in ethanol with 10-fold excess of 3-triflurомethylaniline (Scheme 3). Unfortunate attempts of deacetylation of dye **8** lead to a complex mixture, probably rising from the substitution of highly reactive *meso*-chlorine by liberated amino groups.



2 **7** **8** **9**

Scheme 3. Scheme of the synthesis of dye **4** analogues with five-membered ring in the polimethine chain (dyes **8** and **9**).

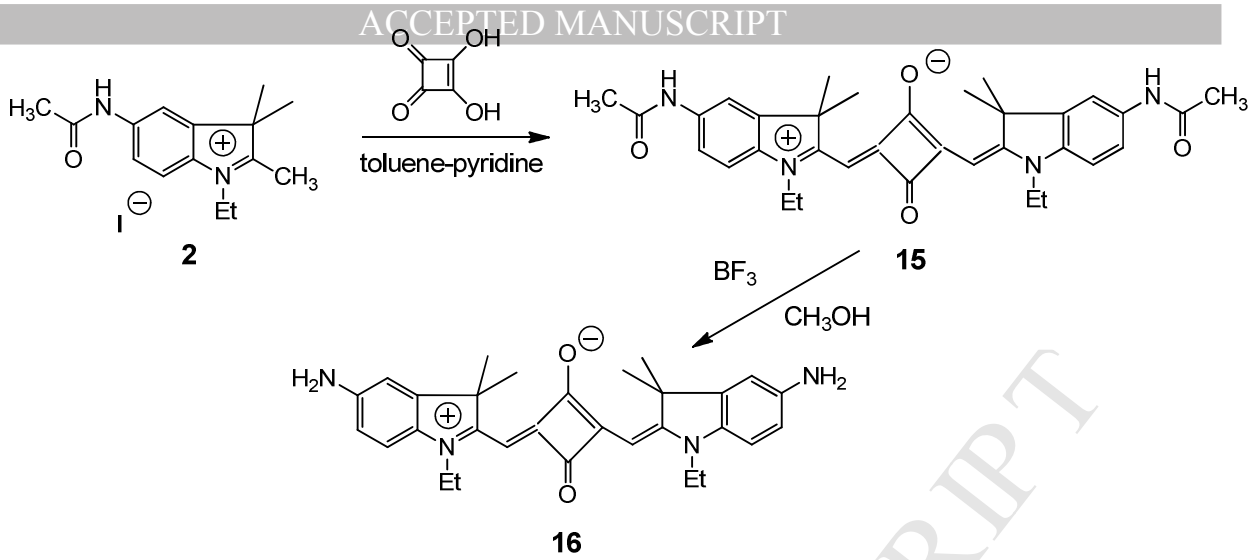
All the above dyes are suitable for their incorporation into the main chain of polyamide polymers. However, it is also of special interest to obtain polymeric compositions with cyanine chromophores in the side chain, which is attached by two points to the polymeric chain. For this reason we have synthesized diaminodye **15** following the route depicted on Scheme 5. From hemicyanine **12** [15] and salt, **2** we prepared unsymmetrical dye **13** containing one acetylamino group. The second one was introduced in the *meso*-position of **13** in the same manner as in the case of dye **5c,** resulting on the diacetylamino dye **13**, which was successfully deprotected in the usual way giving diaminodye **14** in good yield (Scheme 5):



10 **3** **11** **12** **13** **14**

Scheme 4. Syntheses of dyes **12, 13** and **14**.

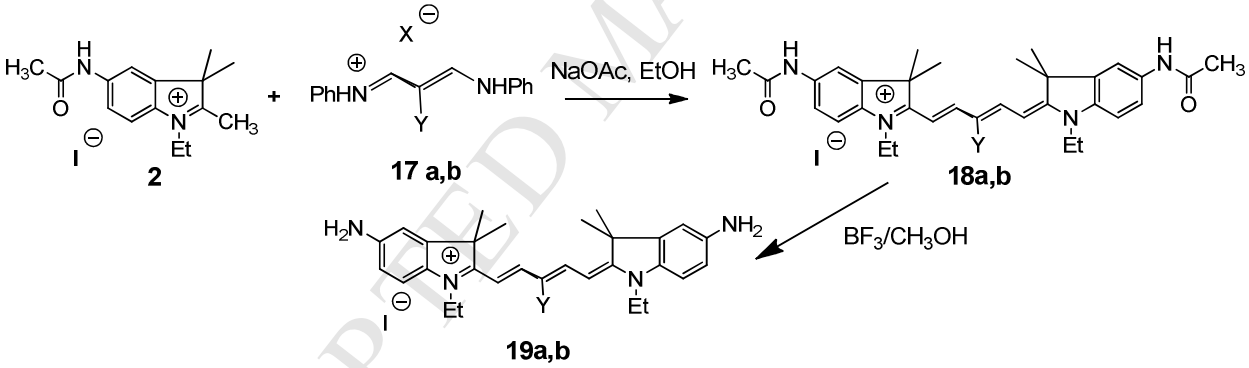
Up to now, all synthesized dyes were containing iodide-anion salts. The presence of these highly oxidizable species in polymer films could decrease its stability as well as change its properties. In order to avoid this problem, we also prepared zwitterionic diaminosquarine **15**. The synthesis of bis-acetylaminosquarine dye **16** was carried out according to reported procedure [25] and its subsequent deprotection was performed in the usual manner (Scheme 5):



2 **15** **16**

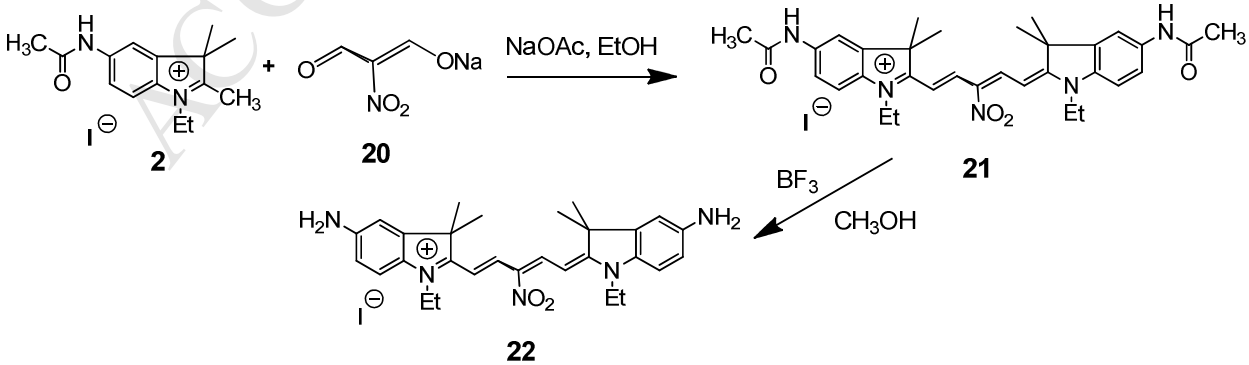
Scheme 5. Synthesis of zwitterionic diaminosquarine **16**.

In order to modify the flexibility of future developed polymers, we have also synthesized three open-chain pentamethine and one heptamethine dyes (Schemes 6-8). Thereby, we have used the conventional procedures for the synthesis of dyes **18b** and **22.** However, we have observed that the absence of substituent in the *meso*-position of trimethine salts **17a** and **23** generated very low reactivity, resulting in a low yield of **24** (<15%) and only traces of **18a** after 10-hour reflux. For the synthesis of these dyes, we have successfully applied the recently disclosed protocol [26], which required preliminary acetylation of salts **17a** and **23**. In the case of **18a-b, 21** and **24**, the further deacetylation resulted on the target diaminodyes **19a-b, 22** and **25** in good yields.



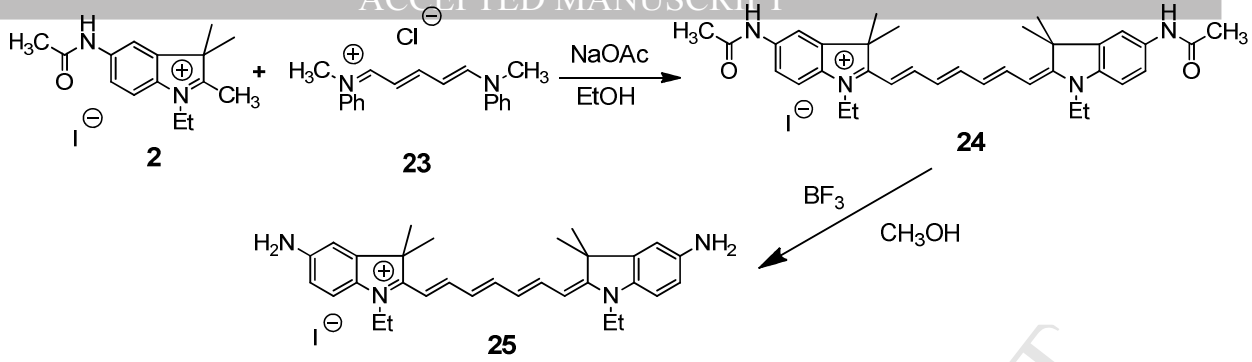
2 **17 a,b** **18a,b** **19a,b**

Scheme 6. Syntheses of open-chain pentamethine dyes **18a,b** and **19a,b**. X = a) ClO_4, b) Cl. Y = a) H-, b) Cl-.



2 **20** **21** **22**

Scheme 7. Syntheses of open-chain pentamethine dyes **21** and **22**.



Scheme 8. Syntheses of open-chain heptamethine dyes **24** and **25**.

4. Conclusions

To sum up, we have synthesized bis-aminosubstituted cyanine dyes with cyclic fragments in the polymethine chain as well as open-chained. All them are potential chromophores to be employed in the development of chromophore-containing polymeric systems by their covalently incorporation into the main or the side chains of the polymer. In this way, problems related to solubility, heterogeneous distribution, stability or low optical quality present in typical "guest"-"host" systems could be avoided.

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- Synthesis of bis-aminosubstituted cyanine dyes with variable optical characteristics.

- Chromophores for the development of polymeric systems with optical properties.

- Chromophore-containing polymeric systems development by covalent incorporation.