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Synthesis and characterization of new mono- and dicarboxyalkylselenacarbocyanines

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Abstract

Novel asymmetric *N*-carboxyalkyl-*N*′-alkylcarbocyanines and symmetric *N*,*N*′-dicarboxyalkylcarbocyanines derived from benzoselenazole have been synthesized and fully characterized by ^{1}H and ^{13}C NMR, FTIR and visible spectroscopy and HR-FAB-MS.

Keywords: Selenacarbocyanines; Carboxyalkyl; Asymmetric carbocyanines; Dyes; Spectroscopic characterization

1. Introduction

Since its introduction in the late 1960s [1], affinity chromatography (AC) has become one of the most powerful tools for the separation and purification of biologically active molecules. It is based on the reversible specific interaction between a biomolecule and a ligand, having recognition capability, coupled to a chromatographic matrix.

Following the growing interest for this technique, the development of materials capable of circumventing the main drawbacks of the conventional natural biological ligands, namely high cost and biological and chemical liabilities, has concentrated a considerable research effort. Synthetic dyes have evolved as one important alternative to natural counterparts for AC and this approach has been intensively investigated, particularly with respect to immobilized textile triazine dyes [2,3].

Notwithstanding, cyanines have found multiple and extensive applications as functional dyes in many different fields [4], their use as biomimetic ligands for AC remains to be explored.

This subject has recently attracted our attention and the encouraging results obtained in a preliminary study [5] regarding the viability of the cyanine–ligand approach prompted us to start a program of design and synthesis of new cyanine dyes possessing terminal benzoazole nuclei and capable of binding to typical chromatographic matrices with hydroxyl reactive groups, envisioning their use as specific ligands for AC.

Following our previous work on the preparation of carbocyanines derived from benzothiazole [6] and benzoxazole [7] for dye–ligand AC, we present herein the synthesis and full spectroscopic characterization of new asymmetric *N*-carboxyalkyl-*N*′-alkylselenacarbocyanines and symmetric *N*,*N*′-dicarboxyalkylselenacarbocyanines.

To the best of our knowledge, the synthesis of selenacarbocyanines bearing pendant carboxyalkyl groups, as well as their applications, has not hitherto been described and, therefore, remains an unexplored field.

The purification of affinity supports carrying the benzoxazole, benzothiazole and benzoselenazole cyanines referred above immobilized on cellulose is currently being evaluated and will show the influence of the sixth raw elements

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polarizability on the interaction between the dye–ligand and the biological molecule to be purified. The results of such study will be reported elsewhere.

2. Results and discussion

Symmetric *N*,*N*′-dicarboxyalkylselenacarbocyanines **5** and asymmetric *N*-carboxyalkyl-*N*′-alkylselenacarbocyanines **7** were synthesized from the same precursor salts **3** (Scheme 1), following a synthetic route previously developed for the corresponding thia- [6] and oxacarbocyanine analogues [7].

The condensation of *N*-carboxyalkylbenzoselenazolium bromides **3a–d**, readily prepared through base catalysed coupling of a suitable bromoalkanoic acid to 2-methylbenzoselenazole (**1**), with triethyl orthoformate in dry pyridine, furnished directly symmetric selenacarbocyanines **5a–d**, in moderate yields. These were additionally characterized by conversion to their corresponding methyl ester derivatives **6a–d**, upon Fisher's esterification.

Reaction of the quaternary bromides **3a–d** with the vinylacetanilide salts **4a–d**, using ethanol as solvent, in the presence of triethylamine, afforded the asymmetric selenacarbocyanines **7a–d** almost quantitatively. The required precursors **4a–d** were obtained by the reaction of the *N*-alkylbenzoselenazolium iodides **2a–d** with *N*,*N*′-diphenylformamidine, in acetic anhydride. Benzoselenazolium **2a–d** salts were achieved through the classical basic alkylation of 2-methylbenzoselenazole (**1**) with an alkyl iodide [8].

Some of the primarily obtained forms **5–7** were found to be considerably insoluble in common organic solvents and, therefore, were isolated as so or, when considered convenient, converted to the more soluble hydrogensulphate or iodide salts by treatment with H_2SO_4 or 14% aqueous KI, respectively. The different salts of the same compound differ only in solubility, melting point and yield, the spectroscopic data being practically superimposable.

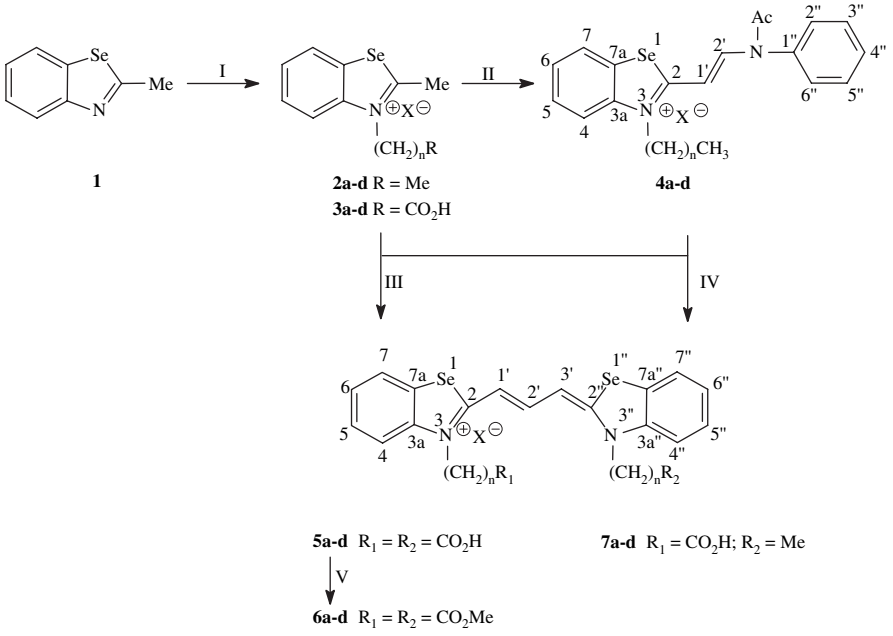
Apart from *N*-alkylbenzoselenazolium iodides **2a** and **2c**, all the remaining precursors and dyes prepared haven't hitherto been described. Consequently, their full spectroscopic characterization, including ^1H and ^{13}C NMR shift assignments, which were established with the aid of Heteronuclear Multiple Quantum Coherence (HMQC), Heteronuclear Multiple Bond Correlation (HMBC) and Correlated Spectroscopy (COSY) experiments, is reported.

3. Experimental

3.1. General

All reagents were of the highest purity available, purchased from Sigma–Aldrich Company, and used as received. Solvents were of analytical grade. Methanol, ethanol, triethylamine, acetic anhydride, acetonitrile and pyridine were dried over 3 Å molecular sieves prior to use.

All reactions were monitored by thin-layer chromatography (TLC) on aluminum plates precoated with Merck silica gel 60 F_{254} (0.25 mm), using dichloromethane or dichloromethane/methanol (5–10%) as eluent and the spots have been examined under 254, 312 and 365 nm UV light.



Scheme 1. Reagents and conditions. (I) – **2a–d**: $I(CH_2)_nMe$ (3.2–5.0 eq.), MeCN (reflux); **3a–d**: $Br(CH_2)_nCO_2H$ (1.1–1.2 eq.), 150 °C; (II) – **4a–d**: PhN=CHNHPh (1.1–1.2 eq.), Ac_2O, 145 °C; (III) – **5a–d**: $CH(OEt)_3$ (2.0–2.1 eq.), pyridine (reflux); (IV) – **7a–d**: triethylamine (2.1–2.2 eq.), ethanol (reflux); (V) – **6a–d**: MeOH, H_2SO_4 (5% v/v) (reflux).

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 or CD_3CN solutions on a Brüker ACP 250 (250.13 and 62.90 MHz) or Brüker ARX 400 (400.13 and 100.61 MHz) spectrometer. Chemical shifts are reported in ppm relative to residual solvent signals or Me_4Si and coupling constants (J) are given in Hz. HMQC, HMBC and COSY spectra were acquired on the Brüker ARX 400 spectrometer.

Infrared spectra (IR) were performed on a Mattson 5000-FTS FTIR spectrometer. All samples were prepared by mixing FTIR-grade KBr with 1% (w/w) compound and grinding to a fine powder. Spectra were recorded over the 400–4000 cm^{-1} range without baseline corrections. More intensive bands are given in cm^{-1}.

Visible spectra (Vis) were recorded on a Perkin–Elmer Lambda 6 spectrophotometer using ethanol as a solvent. Wavelength of maximum absorption is reported in nm.

High Resolution Fast Atom Bombardment Mass Spectra (HR-FAB-MS) were recorded in a Micromass AutoSpec M, operating at 70 eV, using a matrix of 3-nitrobenzyl alcohol (3-NBA).

Melting points were determined in open capillary tubes in a Büchi 530 melting point apparatus and are uncorrected.

3.2. Synthesis of N-alkylbenzoselenazolium salts **2**

3.2.1. 2-Methyl-3-undecylbenzoselenazol-3-ium iodide (**2d**): typical procedure

A solution of 1.06 g (5.38 mmol) of 2-methylbenzoselenazole (**1**) and 4.88 g (4.00 ml, 1.73 mmol) of 1-iodoundecane in 25 ml of dry acetonitrile was heated under reflux for 96 h. After cooling to room temperature, diethyl ether was added to allow complete precipitation. The resulting crystalline product was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry acetonitrile. Yield: 27%. M.p. 147–148 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 0.84 (3H, t, $J = 7.1$ Hz, CH_2CH_3), 1.22–1.35 (14H, m, CH_2), 1.39–1.47 (2H, m, 3-N$(CH_2)_2CH_2$), 1.81 (2H, qui, $J = 7.3$ Hz, 3-NCH_2CH_2), 3.37 (3H, s, 2-CH_3), 4.67 (2H, t, $J = 7.1$ Hz, 3-NCH_2), 7.74 (1H, t, $J = 8.3$ Hz, 6-CH), 7.82 (1H, t, $J = 8.0$ Hz, 5-CH), 8.30 (1H, d, $J = 8.0$ Hz, 4-CH), 8.48 (1H, d, $J = 7.7$ Hz, 7-CH). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 13.9 (CH_2CH_3), 19.6 (2-CH_3), 22.0 (CH_2CH_3), 25.8 (3-N$(CH_2)_8CH_2$), 27.6 (3-N$(CH_2)_7CH_2$), 28.5 (3-N$(CH_2)_6CH_2$), 28.6 (3-N$(CH_2)_5CH_2$), 28.8 (3-N$(CH_2)_4CH_2$), 28.9 (3-N$(CH_2)_2CH_2CH_2$), 31.2 (3-NCH_2CH_2), 49.2 (3-NCH_2), 118.4 (4-CH), 127.4 (6-CH), 127.7 (7-CH), 128.7 (5-CH), 131.8 (7a-C), 141.8 (3a-C), 188.1 (2-C). IR (KBr) ν (cm^{-1}): 2921, 2852, 1579 (C=C), 1513 (C=C), 1457, 1442, 1324, 1189, 758. HR-FAB-MS (3-NBA): $C_{19}H_{30}N^{78}Se$: calc. 350.1551; found 350.1536; $C_{19}H_{30}N^{80}Se$: calc. 352.1543; found 352.1531.

The *N*-alkylbenzoselenazolium iodides **2a–c** were prepared using a similar procedure (24–96 h). The spectroscopic characterization of **2a** and **2c** has already been reported [8].

3.2.2. 2-Methyl-3-propylbenzoselenazol-3-ium iodide (**2b**)

Yield: 29%. M.p. 186–187 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 1.00 (3H, t, $J = 7.4$ Hz, CH_2CH_3), 1.85 (2H, sxt, $J = 7.7$ Hz, CH_2CH_3), 3.24 (3H, s, 2-CH_3), 4.66 (2H, t, $J = 7.8$ Hz, 3-NCH_2), 7.71 (1H, t, $J = 7.8$ Hz, 6-CH), 7.82 (1H, t, $J = 8.2$ Hz, 5-CH), 8.34 (1H, d, $J = 8.5$ Hz, 4-CH), 8.51 (1H, d, $J = 8.0$ Hz, 7-CH). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 10.7 (CH_2CH_3), 19.8 (2-CH_3), 21.1 (CH_2CH_3), 51.2 (3-NCH_2), 118.4 (4-CH), 127.4 (6-CH), 127.7 (7-CH), 128.6 (5-CH), 131.7 (7a-C), 141.8 (3a-C), 188.1 (2-C). IR (KBr) ν (cm^{-1}): 2964, 2874, 1624 (C=C), 1577 (C=C), 1509 (C=C), 1459, 1441, 1324, 1191, 776. HR-FAB-MS (3-NBA): $C_{11}H_{14}N^{78}Se$: calc. 238.0299; found 238.0306; $C_{11}H_{14}N^{80}Se$: calc. 240.0291; found 240.0288.

3.3. Synthesis of N-carboxyalkylbenzoselenazolium salts **3**

3.3.1. 3-(10-Carboxydecyl)-2-methylbenzoselenazol-3-ium bromide (**3d**): typical procedure

A mixture of 1.08 g (5.51 mmol) of 2-methylbenzoselenazole (**1**) and 1.60 g (6.03 mmol) of 11-bromoundecanoic acid was heated at 150 °C for 48 h. After cooling to room temperature, diethyl ether was added to the reaction mixture until complete precipitation. The crystalline product so formed was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry acetonitrile. Yield: 53%. M.p. 155–157 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 1.12–1.28 (10H, m, CH_2), 1.36–1.44 (4H, m, 3-N$(CH_2)_2CH_2$, 3-N$(CH_2)_7CH_2$), 1.72–1.83 (2H, m, 3-NCH_2CH_2), 2.14 (2H, t, $J = 7.5$ Hz, CH_2COOH), 3.20 (3H, s, 2-CH_3), 4.64 (2H, t, $J = 7.5$ Hz, 3-NCH_2), 7.66 (1H, t, $J = 7.7$ Hz, 6-CH), 7.78 (1H, t, $J = 7.3$ Hz, 5-CH), 8.27 (1H, d, $J = 8.4$ Hz, 4-CH), 8.53 (1H, d, $J = 8.0$ Hz, 7-CH). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 19.6 (2-CH_3), 24.4 (CH_2), 25.8 (CH_2), 27.6 (CH_2), 28.4 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 28.7 (CH_2), 33.6 (CH_2COOH), 50.0 (3-NCH_2), 118.3 (4-CH), 127.6 (6-CH, 7-CH), 128.6 (5-CH), 131.9 (7a-C), 141.8 (3a-C), 174.4 (CO), 188.2 (2-C). IR (KBr) ν (cm^{-1}): 2927, 2853, 1721 (C=O), 1578 (C=C), 1519 (C=C), 1469, 1440, 1402, 1172, 775. HR-FAB-MS (3-NBA): $C_{19}H_{28}NO_2^{78}Se$: calc. 380.1293; found 380.1289; $C_{19}H_{28}NO_2^{80}Se$: calc. 382.1285; found 382.1277.

The *N*-carboxyalkylbenzoselenazolium bromides **3a–c** were prepared using a similar procedure (2–48 h).

3.3.2. 3-Carboxymethyl-2-methylbenzoselenazol-3-ium bromide (**3a**)

Yield: 91%. M.p. 229–230 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 3.19 (3H, s, 2-CH_3), 5.72 (2H, s, 3-NCH_2COOH), 7.72 (1H, t, $J = 7.3$ Hz, 6-CH), 7.82 (1H, t, $J = 7.2$ Hz, 5-CH), 8.23 (1H, d, $J = 8.3$ Hz, 4-CH), 8.53 (1H, d, $J = 8.0$ Hz, 7-CH). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 19.6 (2-CH_3), 50.5 (3-NCH_2COOH), 117.5 (4-CH), 127.4 (6-CH), 127.5 (7-CH), 128.5 (5-CH), 131.2 (7a-C), 141.8 (3a-C), 166.3 (CO), 190.4 (2-C). IR (KBr) ν (cm^{-1}): 2943, 1723 (C=O), 1509 (C=C), 1442, 1345, 1244, 1189, 762. HR-FAB-MS (3-NBA): $C_{10}H_{10}NO_2^{78}Se$: calc. 253.9885; found 253.9886; $C_{10}H_{10}NO_2^{80}Se$: calc. 255.9877; found 255.9880.

*3.3.3. 3-(2-Carboxyethyl)-2-methylbenzoselenazol-3-ium bromide (**3b**)*

Yield: 81%. M.p. 204–206 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 2.96 (2H, t, $J = 7.3$ Hz, CH_2COOH), 3.27 (3H, s, 2-CH_3), 4.86 (2H, t, $J = 7.3$ Hz, 3-NCH_2), 7.69 (1H, t, $J = 7.7$ Hz, 6-C*H*), 7.80 (1H, t, $J = 8.2$ Hz, 5-C*H*), 8.31 (1H, d, $J = 8.4$ Hz, 4-C*H*), 8.59 (1H, d, $J = 8.0$ Hz, 7-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 19.8 (2-*C*H$_3$), 31.7 (*C*H$_2$COOH), 45.8 (3-NCH$_2$), 118.3 (4-*C*H), 127.6 (6-*C*H), 127.7 (7-*C*H), 128.7 (5-*C*H), 131.8 (7a-*C*), 141.7 (3a-*C*), 171.4 (*C*O), 189.6 (2-*C*). IR (KBr) ν (cm^{-1}): 2831, 2496, 1713 (C=O), 1511 (C=C), 1444, 1398, 1195, 773. HR-FAB-MS (3-NBA): $C_{11}H_{12}NO_2^{78}Se$: calc. 268.0041; found 268.0047; $C_{11}H_{12}NO_2^{80}Se$: calc. 270.0033; found 270.0044.

*3.3.4. 3-(4-Carboxybutyl)-2-methylbenzoselenazol-3-ium bromide (**3c**)*

Yield: 58%. M.p. 165–167 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 1.66 (2H, qui, $J = 7.4$ Hz, 3-N(CH$_2$)$_2$CH_2), 1.85 (2H, qui, $J = 7.2$ Hz, 3-NCH$_2$CH_2), 2.30 (2H, t, $J = 7.4$ Hz, CH_2COOH), 3.23 (3H, s, 2-CH_3), 4.71 (2H, t, $J = 7.6$ Hz, 3-NCH_2), 7.70 (1H, t, $J = 7.2$ Hz, 6-C*H*), 7.81 (1H, t, $J = 7.2$ Hz, 5-C*H*), 8.31 (1H, d, $J = 8.2$ Hz, 4-C*H*), 8.57 (1H, d, $J = 8.0$ Hz, 7-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 19.7 (2-*C*H$_3$), 21.5 (3-N(CH$_2$)$_2$CH$_2$), 27.1 (3-NCH$_2$*C*H$_2$), 33.1 (*C*H$_2$COOH), 49.8 (3-N*C*H$_2$), 118.4 (4-*C*H), 127.7 (6-*C*H, 7-*C*H), 128.8 (5-*C*H), 132.1 (7a-*C*), 141.9 (3a-*C*), 174.3 (*C*O), 188.5 (2-*C*). IR (KBr) ν (cm^{-1}): 3095, 3008, 2947, 1731 (C=O), 1584 (C=C), 1551 (C=C), 1458, 1417, 1213, 1010, 758. HR-FAB-MS (3-NBA): $C_{13}H_{16}NO_2^{78}Se$: calc. 296.0354; found 296.0365; $C_{13}H_{16}NO_2^{80}Se$: calc. 298.0346; found 298.0343.

*3.4. Synthesis of acetanilide derivatives **4a–d***

*3.4.1. 2-[2-(Acetylphenylamino)vinyl]-3-ethylbenzoselenazol-3-ium iodide (**4a**): typical procedure*

A solution of 0.86 g (2.45 mmol) of 3-ethyl-2-methylbenzoselenazol-3-ium iodide (**2a**) and 0.56 g (2.87 mmol) of *N*, *N*′-diphenylformamidine in 10 ml of dry acetic anhydride was heated under reflux for 2 h. After cooling to room temperature, diethyl ether was added to the reaction mixture until complete precipitation. The crystalline product so formed was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry acetonitrile. Yield: 88%. M.p. 189–191 °C. ^{1}H NMR (250.13 MHz, CD$_3$CN/5% DMSO-d_6) δ (ppm): 1.19 (3H, t, $J = 7.4$ Hz, CH$_2$CH_3), 2.04 (3H, s, COCH_3), 4.27 (2H, q, $J = 7.3$ Hz, 3-NCH_2CH$_3$), 5.69 (1H, d, $J = 13.7$ Hz, 1′-C*H*), 7.44 (2H, d, $J = 7.9$ Hz, 2″-C*H*, 6″-C*H*), 7.52–7.64 (4H, m, 6-C*H*, 3″-C*H*, 4″-C*H*, 5″-C*H*), 7.70 (1H, t, $J = 7.9$ Hz, 5-C*H*), 7.90 (1H, d, $J = 8.6$ Hz, 4-C*H*), 8.27 (1H, d, $J = 8.0$ Hz, 7-C*H*), 8.83 (1H, d, $J = 13.5$ Hz, 2′-C*H*). ^{13}C NMR (62.90 MHz, CD$_3$CN/5% DMSO-d_6) δ (ppm): 13.3 (CH$_2$*C*H$_3$), 23.7 (COCH_3), 46.0 (3-N*C*H$_2$CH$_3$), 100.2 (1′-*C*H), 118.1 (4-*C*H), 128.7 (7-*C*H), 128.9 (6-*C*H), 129.0 (2″-*C*H, 6″-*C*H), 129.5 (7a-*C*), 129.7 (5-*C*H), 131.1 (4″-*C*H), 131.6 (3″-*C*H, 5″-*C*H), 138.2 (1″-*C*), 143.3 (3a-*C*), 148.5 (2′-*C*H), 171.0 (*C*O), 180.4 (2-*C*). IR (KBr) ν (cm^{-1}): 3040, 2982, 1713 (C=O), 1604 (C=C), 1587 (C=C), 1544 (C=C), 1487, 1455, 1417, 1360, 1259, 1234, 1208, 1129, 761. Vis (EtOH): 383 nm. HR-FAB-MS (3-NBA): $C_{19}H_{19}N_2O^{78}Se$: calc. 369.0670; found 369.0655; $C_{19}H_{19}N_2O^{80}Se$: calc. 371.0663; found 371.0646.

The *N*-acetanilide derivatives **4b–d** were prepared using a similar procedure (0.5–2 h).

*3.4.2. 2-[2-(Acetylphenylamino)vinyl]-3-propylbenzoselenazol-3-ium iodide (**4b**)*

Yield: 66%. M.p. 192–194 °C. ^{1}H NMR (400.13 MHz, CD$_3$CN/5% DMSO-d_6) δ (ppm): 0.76 (3H, t, $J = 7.4$ Hz, CH$_2$CH_3), 1.66 (2H, sxt, $J = 7.3$ Hz, CH_2CH$_3$), 2.05 (3H, s, COCH_3), 4.18 (2H, t, $J = 7.3$ Hz, 3-NCH_2), 5.68 (1H, d, $J = 13.6$ Hz, 1′-C*H*), 7.43 (2H, d, $J = 6.5$ Hz, 2″-C*H*, 6″-C*H*), 7.59 (1H, t, $J = 7.7$ Hz, 6-C*H*), 7.63–7.71 (4H, m, 5-C*H*, 3″-C*H*, 4″-C*H*, 5″-C*H*), 7.88 (1H, d, $J = 8.6$ Hz, 4-C*H*), 8.28 (1H, d, $J = 8.2$ Hz, 7-C*H*), 8.84 (1H, d, $J = 13.6$ Hz, 2′-C*H*). ^{13}C NMR (100.61 MHz, CD$_3$CN/5% DMSO-d_6) δ (ppm): 10.3 (CH$_2$*C*H$_3$), 21.3 (*C*H$_2$CH$_3$), 22.8 (COCH_3), 50.9 (3-NCH_2), 99.8 (1′-*C*H), 117.5 (4-*C*H), 127.0 (7-*C*H), 127.9 (6-*C*H), 128.2 (2″-*C*H, 6″-*C*H), 128.5 (7a-*C*), 128.9 (5-*C*H), 130.3 (4″-*C*H), 130.8 (3″-*C*H, 5″-*C*H), 137.4 (1″-*C*), 142.6 (3a-*C*), 147.5 (2′-*C*H), 170.1 (*C*O), 180.0 (2-*C*). IR (KBr) ν (cm^{-1}): 3064, 3000, 2958, 2870, 1714 (C=O), 1605 (C=C), 1587 (C=C), 1553 (C=C), 1457, 1421, 1231, 1202, 998, 746. Vis (EtOH): 384 nm. HR-FAB-MS (3-NBA): $C_{20}H_{21}N_2O^{78}Se$: calc. 383.0827; found 383.0822; $C_{20}H_{21}N_2O^{80}Se$: calc. 385.0819; found 385.0808.

*3.4.3. 2-[2-(Acetylphenylamino)vinyl]-3-pentylbenzoselenazol-3-ium iodide (**4c**)*

Yield: 81%. M.p. 170–172 °C. ^{1}H NMR (250.13 MHz, CD$_3$CN/5% DMSO-d_6) δ (ppm): 0.80 (3H, t, $J = 6.8$ Hz, CH$_2$CH_3), 1.09–1.16 (4H, m, 3-N(CH$_2$)$_2$CH_2CH_2CH$_3$), 1.60 (2H, qui, $J = 7.2$ Hz, 3-NCH$_2$CH_2), 2.06 (3H, s, COCH_3), 4.18 (2H, t, $J = 7.7$ Hz, 3-NCH_2), 5.64 (1H, d, $J = 13.6$ Hz, 1′-C*H*), 7.44 (2H, d, $J = 8.0$ Hz, 2″-C*H*, 6″-C*H*), 7.57 (1H, t, $J = 8.1$ Hz, 6-C*H*), 7.64–7.72 (4H, m, 5-C*H*, 3″-C*H*, 4″-C*H*, 5″-C*H*), 7.88 (1H, d, $J = 8.4$ Hz, 4-C*H*), 8.38 (1H, d, $J = 8.1$ Hz, 7-C*H*), 8.83 (1H, d, $J = 13.6$ Hz, 2′-C*H*). ^{13}C NMR (62.90 MHz, CD$_3$CN/5% DMSO-d_6) δ (ppm): 14.2 (CH$_2$*C*H$_3$), 22.7 (*C*H$_2$CH$_3$), 23.7 (COCH_3), 28.3 (3-N(CH$_2$)$_2$*C*H$_2$), 29.1 (3-NCH$_2$*C*H$_2$), 50.5 (3-NCH_2), 100.7 (1′-*C*H), 118.3 (4-*C*H), 128.1 (7-*C*H), 128.7 (6-*C*H), 129.2 (2″-*C*H, 6″-*C*H), 129.5 (7a-*C*), 129.8 (5-*C*H), 131.2 (4″-*C*H), 131.8 (3″-*C*H, 5″-*C*H), 138.3 (1″-*C*), 143.4 (3a-*C*), 148.4 (2′-*C*H), 170.9 (*C*O), 180.5 (2-*C*). IR (KBr) ν (cm^{-1}): 3041, 2997, 2953, 2925, 2858, 1724 (C=O), 1605 (C=C), 1588 (C=C), 1490, 1456, 1421, 1368, 1336, 1265, 1203, 1146, 990, 952, 772, 703. Vis (EtOH): 384 nm. HR-FAB-MS (3-NBA): $C_{22}H_{25}N_2O^{78}Se$: calc. 411.1140; found 411.1143; $C_{22}H_{25}N_2O^{80}Se$: calc. 413.1132; found 413.1130.

*3.4.4. 2-[2-(Acetylphenylamino)vinyl]-3-undecylbenzoselenazol-3-ium iodide (**4d**)*

Yield: 54%. M.p. 141–143 °C. ^{1}H NMR (250.13 MHz, CD_3CN/5% DMSO-d_6) δ (ppm): 0.88 (3H, t, $J = 6.9$ Hz, CH_2CH_3), 1.05–1.29 (16H, m, CH_2), 1.59 (2H, qui, $J = 6.9$ Hz, 3-NCH_2CH_2), 2.06 (3H, s, $COCH_3$), 4.18 (2H, t, $J = 7.7$ Hz, 3-NCH_2), 5.64 (1H, d, $J = 13.6$ Hz, 1′-CH), 7.44 (2H, d, $J = 8.1$ Hz, 2″-CH, 6″-CH), 7.57 (1H, t, $J = 8.2$ Hz, 6-CH), 7.62–7.72 (4H, m, 5-CH, 3″-CH, 4″-CH, 5″-CH), 7.87 (1H, d, $J = 8.5$ Hz, 4-CH), 8.39 (1H, d, $J = 8.1$ Hz, 7-CH), 8.83 (1H, d, $J = 13.6$ Hz, 2′-CH). ^{13}C NMR (62.90 MHz, CD_3CN/5% DMSO-d_6) δ (ppm): 14.4 (CH_2CH_3), 23.3 (CH_2CH_3), 23.7 ($COCH_3$), 27.0 (3-$N(CH_2)_8CH_2$), 28.6 (CH_2), 29.4 (CH_2), 29.9 (CH_2CH_2), 30.0 (CH_2), 30.2 (CH_2), 32.5 (3-NCH_2CH_2), 50.5 (3-NCH_2), 100.7 (1′-CH), 118.2 (4-CH), 128.1 (7-CH), 128.6 (6-CH), 129.1 (2″-CH, 6″-CH), 129.4 (7a-C), 129.7 (5-CH), 131.1 (4″-CH), 131.7 (3″-CH, 5″-CH), 138.2 (1″-C), 143.3 (3a-C), 148.3 (2′-CH), 170.9 (CO), 180.4 (2-C). IR (KBr) ν (cm^{-1}): 2923, 2853, 1712 (C=O), 1602 (C=C), 1588 (C=C), 1577 (C=C), 1492, 1454, 1366, 1337, 1262, 1217, 1143, 922, 774, 702. Vis (EtOH): 384 nm. HR-FAB-MS (3-NBA): $C_{28}H_{37}N_2O^{78}Se$: calc. 495.2079; found 495.2082; $C_{28}H_{37}N_2O^{80}Se$: calc. 497.2071; found 497.2075.

*3.5. Synthesis of symmetric carboxyalkylselenacarbocyanine dyes **5***

*3.5.1. 3-(10-Carboxydecyl)-2-{3-[3-(10-carboxydecyl)-3H-benzoselenazol-2-ylidene]propenyl}benzoselenazol-3-ium hydrogensulphate (**5d**): typical procedure*

A solution of 0.60 g (1.30 mmol) of 3-(10-carboxydecyl)-2-methylbenzoselenazol-3-ium bromide (**3d**) and 0.40 g (0.45 ml, 2.71 mmol) of triethyl orthoformate in 5 ml of dry pyridine was heated under reflux for 24 h. After cooling to room temperature, diethyl ether was added and the resulting mixture refrigerated to allow complete precipitation. The crystalline product obtained was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry acetonitrile.

Yield: 24%. M.p. 104–106 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6/5% D_2SO_4) δ (ppm): 1.18–1.30 (20 H, m, CH_2), 1.39–1.51 (8H, m, CH_2), 1.67–1.76 (4H, m, 3-NCH_2CH_2, 3″-NCH_2CH_2), 2.16 (4H, t, $J = 7.3$ Hz, CH_2COO), 4.31 (4H, t, $J = 7.4$ Hz, 3-NCH_2, 3″-NCH_2), 6.74 (2H, d, $J = 12.7$ Hz, 1′-CH, 3′-CH), 7.34 (2H, t, $J = 7.8$ Hz, 6-CH, 6″-CH), 7.54 (2H, t, $J = 8.3$ Hz, 5-CH, 5″-CH), 7.65–7.79 (3H, m, 4-CH, 2′-CH, 4″-CH), 8.07 (2H, d, $J = 7.8$ Hz, 7-CH, 7″-CH). ^{13}C NMR (62.90 MHz, DMSO-d_6/5% D_2SO_4) δ (ppm): 24.6 (3-$N(CH_2)_8CH_2$, 3″-$N(CH_2)_8CH_2$), 26.1 (3-$N(CH_2)_2CH_2$, 3″-$N(CH_2)_2CH_2$), 27.4 (3-NCH_2CH_2, 3″-NCH_2CH_2), 28.6 (CH_2), 28.8 (CH_2CH_2), 28.8 (CH_2), 28.9 (CH_2), 33.7 (CH_2COO), 47.0 (3-NCH_2, 3″-NCH_2), 103.4 (1′-CH, 3′-CH), 115.0 (4-CH, 4″-CH), 125.1 (6-CH, 6″-CH), 125.3 (7a-C, 7a″-C), 126.5 (7-CH, 7″-CH), 128.0 (5-CH, 5″-CH), 142.7 (3a-C, 3a″-C), 150.8 (2′-CH), 169.3 (2-C, 2″-C), 174.6 (CO). IR (KBr) ν (cm^{-1}): 2923, 2852, 1710 (C=O), 1550 (C=C), 1455, 1416, 1220, 1161, 1044, 753. Vis (EtOH): 575 nm. HR-FAB-MS (3-NBA): $C_{39}H_{53}N_2O_4^{78}Se_2$: calc. 769.2351; found 769.2365; $C_{39}H_{53}N_2O_4^{78}Se^{80}Se$: calc. 771.2344; found 771.2328; $C_{39}H_{53}N_2O_4^{80}Se_2$: calc. 773.2336; found 773.2319.

The symmetric selenacarbocyanine dyes **5a–c** were prepared using a similar procedure (2–18 h).

In order to increase their solubility, dyes **5a**,**b**,**d** underwent counter-ion exchange to hydrogensulphate. To a solution of the dye in a minimum amount of methanol or acetonitrile was added 5% (v/v) H_2SO_4. The resulting mixture was heated to reflux, cooled to room temperature and equal volume of water was added. The organic solvent was removed under reduced pressure, and the resulting solution was refrigerated overnight. The precipitated crystalline product was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry acetonitrile or dry methanol.

*3.5.2. 3-Carboxymethyl-2-[3-(3-carboxymethyl-3H-benzoselenazol-2-ylidene)propenyl]benzoselenazol-3-ium hydrogensulphate (**5a**)*

Yield: 52%. M.p. 236–238 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 5.23 (4H, s, 3-NCH_2COOH, 3″-NCH_2COOH), 6.66 (2H, d, $J = 12.8$ Hz, 1′-CH, 3′-CH), 7.35 (2H, t, $J = 7.4$ Hz, 6-CH, 6″-CH), 7.52 (2H, t, $J = 7.3$ Hz, 5-CH, 5″-CH), 7.64 (2H, d, $J = 8.1$ Hz, 4-CH, 4″-CH), 7.83 (1H, t, $J = 12.3$ Hz, 2′-CH), 8.09 (2H, d, $J = 7.6$ Hz, 7-CH, 7″-CH). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 48.2 (3-NCH_2COOH, 3″-NCH_2COOH), 104.0 (1′-CH, 3′-CH), 114.7 (4-CH, 4″-CH), 124.9 (6-CH, 6″-CH), 125.3 (7a-C, 7a″-C), 126.4 (7-CH, 7″-CH), 128.0 (5-CH, 5″-CH), 142.8 (3a-C, 3a″-C), 151.2 (2′-CH), 167.8 (CO), 170.7 (2-C, 2″-C). IR (KBr) ν (cm^{-1}): 1729 (C=O), 1586 (C=C), 1554 (C=C), 1458, 1439, 1414, 1319, 1262, 1224, 1189, 1162, 1024, 941, 832, 746. Vis (EtOH): 573 nm. HR-FAB-MS (3-NBA): $C_{21}H_{17}N_2O_4^{78}Se_2$: calc. 516.9534; found 516.9529; $C_{21}H_{17}N_2O_4^{78}Se^{80}Se$: calc. 518.9527; found 518.9510; $C_{21}H_{17}N_2O_4^{80}Se_2$: calc. 520.9519; found 520.9516.

*3.5.3. 3-(2-Carboxyethyl)-2-{3-[3-(2-carboxyethyl)-3H-benzoselenazol-2-ylidene]propenyl}benzoselenazol-3-ium hydrogensulphate (**5b**)*

Yield: 77%. M.p. 233–235 °C. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 2.77 (4H, t, $J = 7.4$ Hz, CH_2COO), 4.52 (4H, t, $J = 7.3$ Hz, 3-NCH_2, 3″-NCH_2), 6.78 (2H, d, $J = 12.4$ Hz, 1′-CH, 3′-CH), 7.35 (2H, t, $J = 7.5$ Hz, 6-CH, 6″-CH), 7.54 (2H, t, $J = 7.5$ Hz, 5-CH, 5″-CH), 7.72 (2H, d, $J = 8.5$ Hz, 4-CH, 4″-CH), 7.76 (1H, t, $J = 12.4$ Hz, 2′-CH), 8.07 (2H, d, $J = 7.5$ Hz, 7-CH, 7″-CH). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ (ppm): 31.4 (CH_2COO), 42.8 (3-NCH_2, 3″-NCH_2), 103.6 (1′-CH, 3′-CH), 114.9 (4-CH, 4″-CH), 125.0 (6-CH, 6″-CH), 125.1 (7a-C, 7a″-C), 126.2 (7-CH, 7″-CH), 127.9 (5-CH, 5″-CH), 142.3 (3a-C, 3a″-C), 150.9 (2′-CH), 169.5 (2-C, 2″-C), 171.5 (CO). IR (KBr) ν (cm^{-1}): 1730 (C=O), 1586 (C=C), 1556 (C=C), 1457, 1424, 1220, 1176, 1121, 1009, 751. Vis (EtOH): 575 nm. HR-FAB-MS (3-NBA): $C_{23}H_{21}N_2O_4^{78}Se_2$: calc. 544.9847;

found 544.9847; $C_{23}H_{21}N_2O_4^{78}Se^{80}Se$: calc. 546.9840; found 546.9836; $C_{23}H_{21}N_2O_4^{80}Se_2$: calc. 548.9832; found 548.9814.

3.5.4. 3-(4-Carboxybutyl)-2-{3-[3-(4-carboxybutyl)-3H-benzoselenazol-2-ylidene]propenyl}benzoselenazol-3-ium inner salt (**5c**)

Yield: 29%. M.p. 240–241 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 1.60–1.80 (8H, m, CH_2), 2.31 (4H, t, $J = 7.0$ Hz, CH_2COO), 4.32 (4H, t, $J = 7.0$ Hz, 3-NCH_2, 3″-NCH_2), 6.77 (2H, d, $J = 12.3$ Hz, 1′-C*H*, 3′-C*H*), 7.34 (2H, t, $J = 7.4$ Hz, 6-C*H*, 6″-C*H*), 7.53 (2H, t, $J = 7.6$ Hz, 5-C*H*, 5″-C*H*), 7.67–7.80 (3H, m, 4-C*H*, 2′-C*H*, 4″-C*H*), 8.09 (2H, d, $J = 8.1$ Hz, 7-C*H*, 7″-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 21.6 (3-N(CH$_2$)$_2$*C*H$_2$, 3″-N(CH$_2$)$_2$*C*H$_2$), 26.7 (3-NCH$_2$*C*H$_2$, 3″-NCH$_2$*C*H$_2$), 33.2 (*C*H$_2$COO), 46.6 (3-N*C*H$_2$, 3″-N*C*H$_2$), 103.3 (1′-*C*H, 3′-*C*H), 114.9 (4-*C*H, 4″-*C*H), 125.0 (6-*C*H, 6″-*C*H), 125.2 (7a-*C*, 7a″-*C*), 126.4 (7-*C*H, 7″-*C*H), 127.9 (5-*C*H, 5″-*C*H), 142.6 (3a-*C*, 3a″-*C*), 150.7 (2′-*C*H), 169.3 (2-*C*, 2″-*C*), 174.2 (*C*O). IR (KBr) ν (cm^{-1}): 2943, 1722 (C=O), 1583 (C=C), 1550 (C=C), 1456, 1417, 1319, 1240, 1217, 1161, 754. Vis (EtOH): 575 nm. HR-FAB-MS (3-NBA): $C_{27}H_{29}N_2O_4^{78}Se_2$: calc. 601.0473; found 601.0482; $C_{27}H_{29}N_2O_4^{78}Se^{80}Se$: calc. 603.0466; found 603.0470; $C_{27}H_{29}N_2O_4^{80}Se_2$: calc. 605.0458; found 605.0464.

3.6. Synthesis of symmetric methoxycarbonylalkylselenacarbocyanine dyes **6**

The methoxycarbonylalkylselenacarbocyanines **6a–d** were prepared by heating under reflux a solution of the corresponding carboxyalkylselenacarbocyanines **5a–d** in 5% (v/v) methanolic H_2SO_4 for at least 48 h, to ensure complete esterification. The reaction mixture was then cooled to room temperature and the solvent removed under reduced pressure until complete precipitation of the product. The latter was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry acetonitrile or dry methanol. Since the hydrogensulphate forms of **6c** and **6d** were obtained as an oleum, they were converted to the corresponding iodide salts as previously described for dyes **5**, using 14% (w/v) aqueous potassium iodide.

3.6.1. 3-Methoxycarbonylmethyl-2-{3-[3-methoxycarbonylmethyl-3H-benzoselenazol-2-ylidene]propenyl}benzoselenazol-3-ium hydrogensulphate (**6a**)

Yield: 73%. M.p. 235–236 °C. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 3.76 (6H, s, COOCH_3), 5.37 (4H, s, 3-NCH_2COOCH$_3$, 3″-NCH_2COOCH$_3$), 6.63 (2H, d, $J = 12.2$ Hz, 1′-C*H*, 3′-C*H*), 7.37 (2H, t, $J = 7.6$ Hz, 6-C*H*, 6″-C*H*), 7.52 (2H, t, $J = 7.7$ Hz, 5-C*H*, 5″-C*H*), 7.64 (2H, d, $J = 8.3$ Hz, 4-C*H*, 4″-C*H*), 7.85 (1H, t, $J = 12.4$ Hz, 2′-C*H*), 8.10 (2H, d, $J = 7.7$ Hz, 7-C*H*, 7″-C*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ (ppm): 47.8 (3-N*C*H$_2$COOCH$_3$, 3″-N*C*H$_2$COOCH$_3$), 52.8 (COO*C*H$_3$), 104.0 (1′-*C*H, 3′-*C*H), 114.6 (4-*C*H, 4″-*C*H), 124.7 (7a-*C*, 7a″-*C*), 125.2 (6-*C*H, 6″-*C*H), 126.3 (7-*C*H, 7″-*C*H), 127.9 (5-*C*H, 5″-*C*H), 142.5 (3a-*C*, 3a″-*C*), 151.3 (2′-*C*H), 166.9 (*C*O), 170.8 (2-*C*, 2″-*C*). IR (KBr) ν (cm^{-1}): 1747 (C=O), 1546 (C=C), 1456, 1408, 1256, 1217, 1175, 1155, 1019, 822, 745. Vis (EtOH): 576 nm. HR-FAB-MS (3-NBA): $C_{23}H_{21}N_2O_4^{78}Se_2$: calc. 544.9847; found 544.9860; $C_{23}H_{21}N_2O_4^{78}Se^{80}Se$: calc. 546.9840; found 546.9852; $C_{23}H_{21}N_2O_4^{80}Se_2$: calc. 548.9832; found 548.9833.

3.6.2. 3-(2-Methoxycarbonylethyl)-2-{3-[3-(2-methoxycarbonylethyl)-3H-benzoselenazol-2-ylidene]propenyl}benzoselenazol-3-ium hydrogensulphate (**6b**)

Yield: 74%. M.p. 167–168 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 2.85 (4H, t, $J = 7.1$ Hz, CH_2COOCH$_3$), 3.62 (6H, s, COOCH_3), 4.55 (4H, t, $J = 6.8$ Hz, 3-NCH_2, 3″-NCH_2), 6.75 (2H, d, $J = 12.3$ Hz, 1′-C*H*, 3′-C*H*), 7.35 (2H, t, $J = 7.7$ Hz, 6-C*H*, 6″-C*H*), 7.54 (2H, t, $J = 7.3$ Hz, 5-C*H*, 5″-C*H*), 7.69–7.81 (3H, m, 4-C*H*, 2′-C*H*, 4″-C*H*), 8.06 (2H, d, $J = 7.7$ Hz, 7-C*H*, 7″-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 31.3 (*C*H$_2$COOCH$_3$), 42.8 (3-N*C*H$_2$, 3″-N*C*H$_2$), 51.9 (COO*C*H$_3$), 103.8 (1′-*C*H, 3′-*C*H), 115.0 (4-*C*H, 4″-*C*H), 125.3 (7a-*C*, 7a″-*C*), 125.3 (6-*C*H, 6″-*C*H), 126.4 (7-*C*H, 7″-*C*H), 128.1 (5-*C*H, 5″-*C*H), 142.4 (3a-*C*, 3a″-*C*), 151.0 (2′-*C*H), 169.7 (2-*C*, 2″-*C*), 170.7 (*C*O). IR (KBr) ν (cm^{-1}): 3094, 3007, 2947, 1730 (C=O), 1584 (C=C), 1551 (C=C), 1458, 1416, 1319, 1262, 1213, 1169, 1065, 1011, 932, 835, 758, 731. Vis (EtOH): 576 nm. HR-FAB-MS (3-NBA): $C_{25}H_{25}N_2O_4^{78}Se_2$: calc. 573.0160; found 573.0140; $C_{25}H_{25}N_2O_4^{78}Se^{80}Se$: calc. 575.0153; found 575.0140; $C_{25}H_{25}N_2O_4^{80}Se_2$: calc. 577.0145; found 577.0144.

3.6.3. 3-(4-Methoxycarbonylbutyl)-2-{3-[3-(4-methoxycarbonylbutyl)-3H-benzoselenazol-2-ylidene]propenyl}benzoselenazol-3-ium iodide (**6c**)

Yield: 78%. M.p. 158–160 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 1.64–1.78 (8H, m, CH_2), 2.40 (4H, t, $J = 6.8$ Hz, CH_2COOCH$_3$), 3.57 (6H, s, COOCH_3), 4.33 (4H, t, $J = 6.5$ Hz, 3-NCH_2, 3″-NCH_2), 6.74 (2H, d, $J = 11.9$ Hz, 1′-C*H*, 3′-C*H*), 7.34 (2H, t, $J = 7.4$ Hz, 6-C*H*, 6″-C*H*), 7.53 (2H, t, $J = 7.4$ Hz, 5-C*H*, 5″-C*H*), 7.70 (2H, d, $J = 8.5$ Hz, 4-C*H*, 4″-C*H*), 7.73 (1H, t, $J = 12.3$ Hz, 2′-C*H*), 8.06 (2H, d, $J = 8.0$ Hz, 7-C*H*, 7″-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 21.6 (3-N(CH$_2$)$_2$*C*H$_2$, 3″-N(CH$_2$)$_2$*C*H$_2$), 26.7 (3-NCH$_2$*C*H$_2$, 3″-NCH$_2$*C*H$_2$), 32.9 (*C*H$_2$COOCH$_3$), 46.7 (3-N*C*H$_2$, 3″-N*C*H$_2$), 51.4 (COO*C*H$_3$), 103.4 (1′-*C*H, 3′-*C*H), 115.0 (4-*C*H, 4″-*C*H), 125.0 (6-*C*H, 6″-*C*H), 125.2 (7a-*C*, 7a″-*C*), 126.4 (7-*C*H, 7″-*C*H), 128.0 (5-*C*H, 5″-*C*H), 142.7 (3a-*C*, 3a″-*C*), 150.9 (2′-*C*H), 169.4 (2-*C*, 2″-*C*), 173.2 (*C*O). IR (KBr) ν (cm^{-1}): 2938, 1721 (C=O), 1552 (C=C), 1455, 1420, 1210, 1164, 1056, 754. Vis (EtOH): 575 nm. HR-FAB-MS (3-NBA): $C_{29}H_{33}N_2O_4^{78}Se_2$: calc. 629.0786; found 629.0757; $C_{29}H_{33}N_2O_4^{78}Se^{80}Se$: calc. 631.0779; found 631.0773; $C_{29}H_{33}N_2O_4^{80}Se_2$: calc. 633.0771; found 633.0795.

3.6.4. 3-(10-Methoxycarbonyldecyl)-2-{3-[3-(10-methoxycarbonyldecyl)-3H-benzoselenazol-2-ylidene]propenyl}benzoselenazol-3-ium iodide (**6d**)

Yield: 51%. M.p. 65–67 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 1.12–1.32 (20H, m, CH_2), 1.38–1.51 (8H, m, CH_2),

1.64–1.76 (4H, m, 3-NCH$_2$CH_2, 3″-NCH$_2$CH_2), 2.25 (4H, t, $J = 7.5$ Hz, CH_2COOCH$_3$), 3.55 (6H, s, COOCH_3), 4.30 (4H, t, $J = 7.5$ Hz, 3-NCH_2, 3″-NCH_2), 6.74 (2H, d, $J = 12.5$ Hz, 1′-C*H*, 3′-C*H*), 7.34 (2H, t, $J = 8.0$ Hz, 6-C*H*, 6″-C*H*), 7.54 (2H, t, $J = 8.3$ Hz, 5-C*H*, 5″-C*H*), 7.66–7.79 (3H, m, 4-C*H*, 2′-C*H*, 4″-C*H*), 8.07 (2H, d, $J = 8.2$ Hz, 7-C*H*, 7″-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 24.4 (3-N(CH$_2$)$_8$CH$_2$, 3″-N(CH$_2$)$_8$CH$_2$), 25.9 (3-N(CH$_2$)$_2$*C*H$_2$, 3″-N(CH$_2$)$_2$*C*H$_2$), 27.2 (3-NCH$_2$*C*H$_2$, 3″-NCH$_2$*C*H$_2$), 28.4 (*C*H$_2$), 28.6 (*C*H$_2$), 28.7 (*C*H$_2$), 28.7 (*C*H$_2$), 28.9 (*C*H$_2$), 33.2 (*C*H$_2$COO), 46.9 (3-N*C*H$_2$, 3″-N*C*H$_2$), 51.1 (COO*C*H$_3$), 103.3 (1′-*C*H, 3′-*C*H), 115.0 (4-*C*H, 4″-*C*H), 125.0 (6-*C*H, 6″-*C*H), 125.2 (7a-*C*, 7a″-*C*), 126.3 (7-*C*H, 7″-*C*H), 127.9 (5-*C*H, 5″-*C*H), 142.6 (3a-*C*, 3a″-*C*), 150.8 (2′-*C*H), 169.3 (2-*C*, 2″-*C*), 173.3 (*C*O). IR (KBr) ν (cm^{-1}): 2925, 2850, 1727 (C═O), 1584 (C═C), 1555 (C═C), 1456, 1419, 1216, 1015, 755. Vis (EtOH): 575 nm. HR-FAB-MS (3-NBA): $C_{41}H_{57}N_2O_4^{78}Se_2$: calc. 797.2664; found 797.2686; $C_{41}H_{57}N_2O_4^{78}Se^{80}Se$: calc. 799.2657; found 799.2668; $C_{41}H_{57}N_2O_4^{80}Se_2$: calc. 801.2649; found 801.2660.

3.7. Synthesis of asymmetric selenacarbocyanine dyes 7

3.7.1. 3-Carboxymethyl-2-[3-(3-ethyl-3H-benzoselenazol-2-ylidene)propenyl]benzoselenazol-3-ium inner salt (7a): typical procedure

A solution of 0.18 g (0.54 mmol) of 3-carboxymethyl-2-methylbenzoselenazol-3-ium bromide (**3a**), 0.19 g (0.38 mmol) of the acetanilide derivative **4a** and 0.09 g (0.12 ml, 0.86 mmol) of dry triethylamine in 5 ml of dry ethanol was refluxed for 2 h. After cooling to room temperature, diethyl ether was added and the resulting mixture refrigerated to allow complete precipitation. The crystalline product obtained was collected by filtration under reduced pressure, washed with diethyl ether and recrystallized from dry acetonitrile.

Yield: 95%. M.p. 174–176 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 1.32 (3H, t, $J = 7.0$ Hz, CH$_2$CH_3), 4.40 (2H, q, $J = 7.0$ Hz, 3″-NCH_2CH$_3$), 5.18 (2H, s, 3-NCH_2COO), 6.63 (1H, d, $J = 12.1$ Hz, 1′-C*H*), 6.80 (1H, d, $J = 12.7$ Hz, 3′-C*H*), 7.28–7.40 (2H, m, 6-C*H*, 6″-C*H*), 7.45–7.60 (2H, m, 5-C*H*, 5″-C*H*), 7.69–7.88 (3H, m, 4-C*H*, 2′-C*H*, 4″-C*H*), 8.08 (1H, d, $J = 7.2$ Hz, 7-C*H*), 8.14 (1H, d, $J = 7.6$ Hz, 7″-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 12.6 (3″-NCH$_2$*C*H$_3$), 42.5 (3″-N*C*H$_2$CH$_3$), 47.9 (3-N*C*H$_2$COO), 102.8 (1′-*C*H), 103.2 (3′-*C*H), 114.2 (4-*C*H), 115.0 (4″-*C*H), 124.8 (6-*C*H), 125.3 (6″-*C*H), 125.9 (7a-*C*), 126.3 (7a″-*C*), 126.4 (7-*C*H), 126.5 (7″-*C*H), 127.8 (5-*C*H), 128.0 (5″-*C*H), 142.1 (3a-*C* or 3a″-*C*), 142.8 (3a-*C* or 3a″-*C*), 150.8 (2′-*C*H), 167.9 (*C*O), 169.0 (2-*C*), 170.3 (2″-*C*). IR (KBr) ν (cm^{-1}): 2928, 2677, 1739 (C═O), 1584 (C═C), 1551 (C═C), 1455, 1417, 1261, 1195, 1160, 1130, 1021, 942, 834, 753. Vis (EtOH): 574 nm. HR-FAB-MS (3-NBA): $C_{21}H_{19}N_2O_2^{78}Se_2$: calc. 486.9793; found 486.9808; $C_{21}H_{19}N_2O_2^{78}Se^{80}Se$: calc. 488.9785; found 488.9778; $C_{21}H_{19}N_2O_2^{80}Se_2$: calc. 490.9777; found 490.9771.

The asymmetric selenacarbocyanine dyes **7b–d** were prepared using a similar procedure (2–18 h).

3.7.2. 3-(2-Carboxyethyl)-2-[3-(3-propyl-3H-benzoselenazol-2-ylidene)propenyl]benzoselenazol-3-ium inner salt (7b)

Yield: 93%. M.p. 220–222 °C. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 1.00 (3H, t, $J = 7.3$ Hz, CH$_2$CH_3), 1.76 (2H, sxt, $J = 7.3$ Hz, CH_2CH$_3$), 2.76 (2H, t, $J = 7.3$ Hz, CH_2COO), 4.30 (2H, t, $J = 7.1$ Hz, 3″-NCH_2), 4.50 (2H, t, $J = 6.9$ Hz, 3-NCH_2), 6.77 (1H, d, $J = 12.5$ Hz, 1′-C*H*), 6.82 (1H, d, $J = 12.6$ Hz, 3′-C*H*), 7.31 (1H, t, $J = 7.6$ Hz, 6-C*H*), 7.36 (1H, t, $J = 7.6$ Hz, 6″-C*H*), 7.50 (1H, t, $J = 8.0$ Hz, 5-C*H*), 7.54 (1H, t, $J = 8.1$ Hz, 5″-C*H*), 7.67–7.76 (3H, m, 4-C*H*, 2′-C*H*, 4″-C*H*), 8.08 (1H, d, $J = 7.5$ Hz, 7-C*H*), 8.12 (1H, d, $J = 7.9$ Hz, 7″-C*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ (ppm): 10.7 (CH$_2$*C*H$_3$), 20.6 (*C*H$_2$CH$_3$), 31.4 (*C*H$_2$COO), 42.7 (3-N*C*H$_2$), 48.2 (3″-N*C*H$_2$), 103.1 (1′-*C*H), 103.9 (3′-*C*H), 114.7 (4-*C*H), 115.0 (4″-*C*H), 124.8 (6-*C*H), 124.9 (7a-*C*), 125.1 (6″-*C*H), 125.3 (7a″-*C*), 126.2 (7-*C*H), 126.4 (7″-*C*H), 127.8 (5-*C*H), 127.9 (5″-*C*H), 142.3 (3a-*C*), 142.6 (3a″-*C*), 150.6 (2′-*C*H), 168.8 (2-*C*), 169.8 (2″-*C*), 171.5 (*C*O). IR (KBr) ν (cm^{-1}): 2973, 2937, 2739, 2678, 2491, 1743 (C═O), 1586 (C═C), 1557 (C═C), 1457, 1426, 1322, 1253, 1207, 1036, 931, 746. Vis (EtOH): 574 nm. HR-FAB-MS (3-NBA): $C_{23}H_{23}N_2O_2^{78}Se_2$: calc. 515.0106; found 515.0122; $C_{23}H_{23}N_2O_2^{78}Se^{80}Se$: calc. 517.0098; found 517.0103; $C_{23}H_{23}N_2O_2^{80}Se_2$: calc. 519.0090; found 519.0096.

3.7.3. 3-(4-Carboxybutyl)-2-[3-(3-pentyl-3H-benzoselenazol-2-ylidene)propenyl]benzoselenazol-3-ium inner salt (7c)

Yield: 94%. M.p. 181–183 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 0.85 (3H, t, $J = 7.1$ Hz, CH$_2$CH_3), 1.32–1.40 (4H, m, CH_2), 1.62–1.76 (6H, m, CH_2), 2.30 (2H, t, $J = 7.1$ Hz, CH_2COO), 4.26–4.35 (4H, m, 3-NCH_2, 3″-NCH_2), 6.77 (1H, d, $J = 11.7$ Hz, 1′-C*H*), 6.82 (1H, d, $J = 12.7$ Hz, 3′-C*H*), 7.32 (2H, t, $J = 7.6$ Hz, 6-C*H*, 6″-C*H*), 7.52 (2H, t, $J = 7.1$ Hz, 5-C*H*, 5″-C*H*), 7.66–7.76 (3H, m, 4-C*H*, 2′-C*H*, 4″-C*H*), 8.10 (2H, d, $J = 7.7$ Hz, 7-C*H*, 7″-C*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 13.9 (CH$_2$*C*H$_3$), 21.7 (*C*H$_2$), 22.0 (*C*H$_2$), 26.8 (*C*H$_2$), 27.1 (*C*H$_2$), 28.2 (*C*H$_2$), 33.3 (*C*H$_2$COO), 46.7 (3-N*C*H$_2$), 47.0 (3″-N*C*H$_2$), 103.4 (1′-*C*H, 3′-*C*H), 115.0 (4-*C*H, 4″-*C*H), 125.0 (6-*C*H, 6″-*C*H), 125.2 (7a-*C*, 7a″-*C*), 126.5 (7-*C*H, 7″-*C*H), 128.0 (5-*C*H, 5″-*C*H), 142.7 (3a-*C*, 3a″-*C*), 150.7 (2′-*C*H), 169.3 (2-*C*, 2″-*C*), 174.3 (*C*O). IR (KBr) ν (cm^{-1}): 2936, 2734, 2677, 2491, 1720 (C═O), 1584 (C═C), 1555 (C═C), 1456, 1423, 1318, 1265, 1214, 1162, 745. Vis (EtOH): 575 nm. HR-FAB-MS (3-NBA): $C_{27}H_{31}N_2O_2^{78}Se_2$: calc. 571.0732; found 571.0732; $C_{27}H_{31}N_2O_2^{78}Se^{80}Se$: calc. 573.0734; found 573.0724; $C_{27}H_{31}N_2O_2^{80}Se_2$: calc. 575.0716; found 575.0736.

3.7.4. 3-(10-Carboxydecyl)-2-[3-(3-undecyl)-3H-benzoselenazol-2-ylidene)propenyl]benzoselenazol-3-ium inner salt (7d)

Yield: 93%. M.p. 108–109 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 0.80 (3H, t, $J = 7.0$ Hz, CH$_2$CH_3), 1.10–1.48 (30H, m, CH_2), 1.61–1.75 (4H, m, CH_2), 2.15 (2H, t, $J = 7.3$ Hz, CH_2COO), 4.21–4.36 (4H, m, 3-NCH_2,

3″-NCH_2), 6.78 (2H, d, $J = 12.6$ Hz, 1′-CH, 3′-CH), 7.32 (2H, t, $J = 7.5$ Hz, 6-CH, 6″-CH), 7.52 (2H, t, $J = 7.5$ Hz, 5-CH, 5″-CH), 7.63–7.77 (3H, m, 4-CH, 2′-CH, 4″-CH), 8.08 (2H, d, $J = 8.1$ Hz, 7-CH, 7″-CH). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 14.0 (CH_2CH_3), 22.2 (CH_2), 24.5 (CH_2), 26.0 (CH_2), 27.3 (CH_2), 28.6 (CH_2), 28.8 (CH_2CH_2), 29.0 (CH_2CH_2), 31.3 (CH_2), 33.7 (CH_2COO), 46.9 (3-NCH_2, 3″-NCH_2), 103.3 (1′-CH, 3′-CH), 115.0 (4-CH, 4″-CH), 125.1(6-CH, 6″-CH), 125.3 (7a-C, 7a″-C), 126.5 (7-CH, 7″-CH), 128.0 (5-CH, 5″-CH), 142.7 (3a-C, 3a″-C), 150.7 (2′-CH), 169.3 (2-C, 2″-C), 174.6 (CO). IR (KBr) ν (cm^{-1}): 2923, 2852, 1726 (C═O), 1584 (C═C), 1553 (C═C), 1455, 1421, 1214, 749. Vis (EtOH): 575 nm. HR-FAB-MS (3-NBA): $C_{39}H_{55}N_2O_2^{78}Se_2$: calc. 739.2610; found 739.2634; $C_{39}H_{55}N_2O_2^{78}Se^{80}Se$: calc. 741.2602; found 741.2626; $C_{39}H_{55}N_2O_2^{80}Se_2$: calc. 743.2594; found 743.2618.

4. Conclusions

Several novel asymmetric *N*-carboxyalkyl-*N*′-alkylselenacarbocyanines and symmetric *N*,*N*′-dicarboxyalkylselenacarbocyanines have been synthesized and fully characterized by ^{1}H and ^{13}C NMR, FTIR and visible spectroscopy and HR-FAB-MS, envisioning their use as ligands for AC. The pendant carboxyalkyl groups present in these cyanine dyes provide a convenient way to easily bind them to hydroxyl-containing chromatographic supports and, simultaneously, can act as convenient spacer arms of different lengths.

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