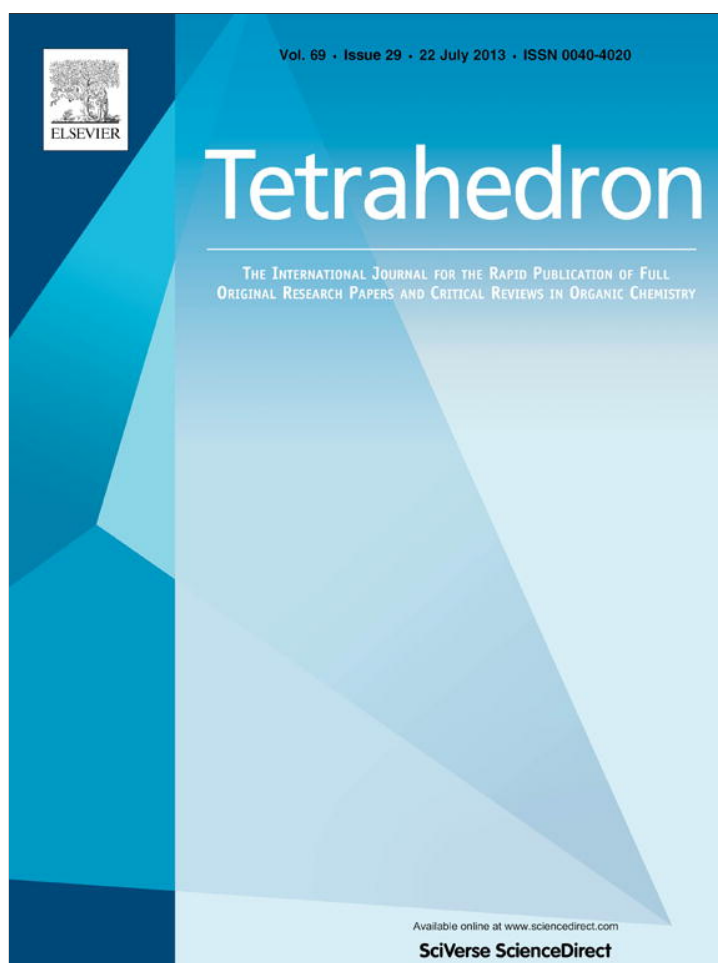


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Synthesis of symmetrical cyanine dyes with two *N*-ammonioalkyl groups



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ABSTRACT

Synthesis of new symmetrical mono-, tri-, and pentamethine cyanine dyes with two *N*-ammonioalkyl substituents was developed. In the last step of the synthesis, conditions for the removal of the phthalimide protecting group in cyanine dyes using hydrazine monohydrate and an ethanol solution of MeNH₂ were selected. The obtained dyes with ammonium groups capable of hydrogen bonding are promising as components of light-sensitive supramolecular systems.

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1. Introduction

Cyanine dyes are well-known for their wide use in photographic materials;¹ however, the interest in this class of compounds persists because they have found use as luminophores,² luminescence labels in biology and medicine,³ as parts of the recording medium in optical discs,⁴ and components of supramolecular structures.⁵ The sensitivity of absorption and fluorescence of cyanine dyes to the medium determines good prospects for their use as probes, not only to study endogenous biomolecules but also to study the structure, kinetics, and thermodynamics of the formation of aggregates, supramolecular complexes and assemblies.^{5e,6}

The hydrogen bond is a principal intermolecular interaction, resulting in the formation of stable supramolecular systems.⁷ Using hydrogen bonds, which are rather strong and definitely directed, for supramolecular assembly, it is possible to design promising supramolecular objects with a specified structure and diverse properties. Published data describe supramolecular complexes and assemblies that have been made by means of hydrogen bonds involving amide, hydroxyl, carboxyl, amino, and other groups. The strength of the obtained structures regularly increases following an

increase in the number of intermolecular hydrogen bonds formed.⁸ However, published examples of using a primary ammonium group able to form three hydrogen bonds, which are often encountered in natural systems, for self-assembly of supramolecular light-sensitive systems are very few.

In this regard, of particular interest are cyanine dyes containing ammonioalkyl substituents at the nitrogen atoms of the heterocyclic residues, which creates new opportunities for their self-assembly to light-sensitive supramolecular systems based on hydrogen bonding.

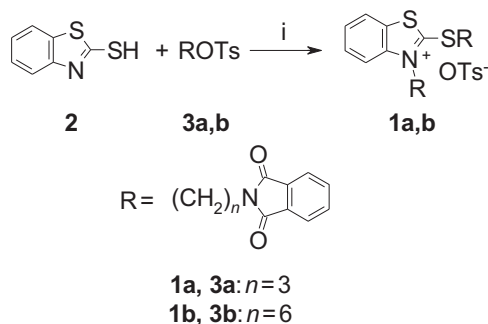
2. Results and discussion

Methods for the preparation of cyanine dyes are now well developed, and are based on the condensation of quaternary salts of heterocyclic bases containing an active methyl group in position 2 or 4 with C-electrophiles. The condensation is performed in the presence of bases.^{1b,c,9} Cyanine dyes containing terminal ammonium groups in *N*-substituents cannot be prepared by direct condensation of quaternary heterocyclic salts containing ammonioalkyl groups due to side reactions. The use of a protecting group makes it possible to avoid undesirable processes. In our investigations, phthalimide protection, which is stable against the bases and electrophilic reagents used, proved to be most suitable.¹⁰

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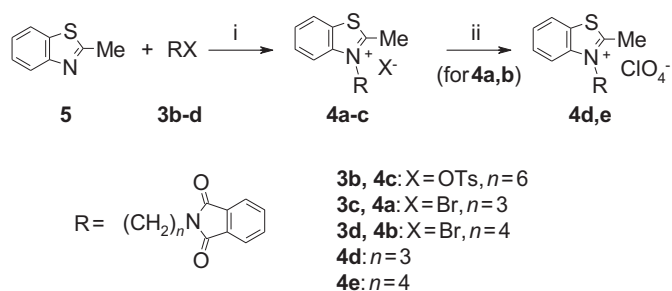
Some unsymmetrical mono-, *meso*-methyltri- and pentamethine cyanine dyes containing phthalimide groups or amino group hydrobromides as terminal groups on the *N*-substituents of heterocyclic residues have been reported.¹¹ However, these dyes have not been isolated in a pure state and their structures have not been confirmed by physicochemical characteristics. In this connection, the purpose of our study is the development of synthesis, isolation methods, and characterization of symmetrical cyanine dyes with ammonium groups on the *N*-substituents of the heterocyclic residues. The quaternary benzothiazolium, 3*H*-indolium, and 1*H*-benzo[*e*]indolium salts needed for dye synthesis were obtained based on known procedures by quaternization of heterocyclic bases.¹²

The initial 2-thiobenzothiazolium salts **1a,b** were prepared by fusing together benzothiazole-2-thiol **2** with 3-phthalimidopropyl or 6-phthalimidoethyl tosylate (**3a,b**) (Scheme 1).



Scheme 1. Synthesis of 2-thiobenzothiazolium salts **1a,b**. Reagents and conditions: (i) heating, 140 °C (**1a**: 70%; **1b**: 54% yield).

Quaternary salts **4a–c** were prepared by fusing together phthalimidoalkyl derivatives **3b–d** with 2-methylbenzothiazole **5**. Perchlorate salts **4d,e** were obtained by treating the corresponding bromides with perchloric acid in methanol (Scheme 2).

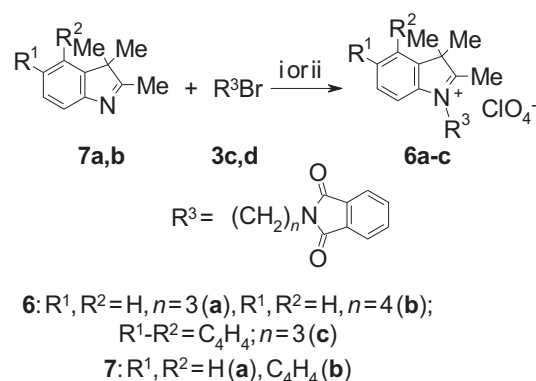


Scheme 2. Synthesis of 2-methylbenzothiazolium salts **4a–e**. Reagents and conditions: (i) heating, 140–150 °C (**4a**: 92%; **4b**: 80%; **4c**: 67% yield); (ii) HClO₄ (70%, aq), MeOH (**4d**: 96%; **4e**: 94% yield).

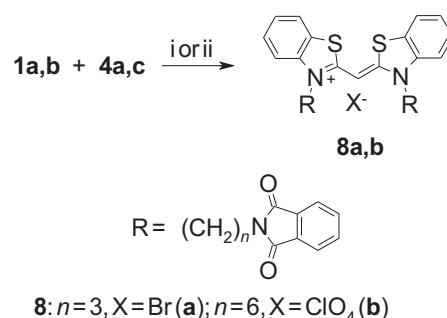
Salts **6a–c** were prepared by the reaction of heterocyclic bases **7a,b** with phthalimidoalkyl derivatives **3c,d**; the reaction was carried out in acetonitrile under inert atmosphere (Scheme 3).

Benzothiazole monomethine dyes **8a,b** containing phthalimidoalkyl substituents at the nitrogen atoms were synthesized using a known procedure,¹³ by triethylamine-induced condensation of heterocyclic salts **1a,b** and **4a,c** in ethanol (Scheme 4).

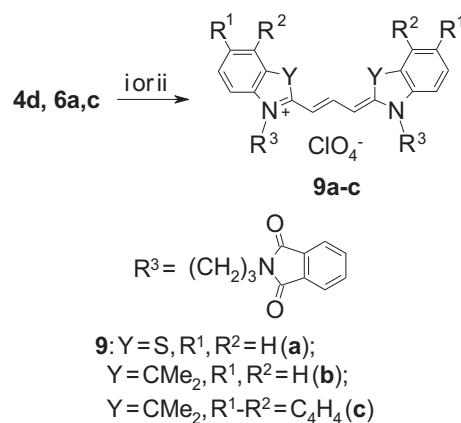
Trimethine dyes **9a–c** containing phthalimidoalkyl substituents at nitrogen atoms were prepared using a described procedure¹⁴ by the reaction of quaternary salts **4d, 6a,c** with triethyl orthoformate in pyridine or in acetic anhydride induced by triethylamine (Scheme 5). The use of a fourfold excess of triethyl orthoformate increased the yields of the target dyes.



Scheme 3. Synthesis of 3*H*-indolium and 1*H*-benzo[*e*]indolium salts **6a–c**. Reagents and conditions: (i) 1. MeCN, argon, reflux; 2. HClO₄ (70%, aq), EtOH (**6a**: 51%; **6b**: 85% yield); (ii) 1. MeCN, argon, sealed tube, 110 °C; 2. HClO₄ (70%, aq), EtOH (**6c**: 40% yield).

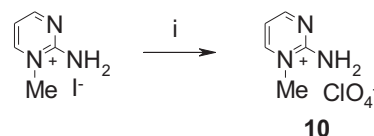


Scheme 4. Synthesis of monomethine cyanine dyes **8a,b**. Reagents and conditions: (i) Et₃N, EtOH, reflux (**8a**: 60% yield); (ii) 1. Et₃N, EtOH, reflux; 2. HClO₄ (70%, aq), EtOH (**8b**: 61% yield).



Scheme 5. Synthesis of trimethine cyanine dyes **9a–c**. Reagents and conditions: (i) CH(OEt)₃, Py, reflux (**9a**: 60%; **9b**: 33% yield); (ii) CH(OEt)₃, Et₃N, Ac₂O, reflux (**9c**: 63% yield).

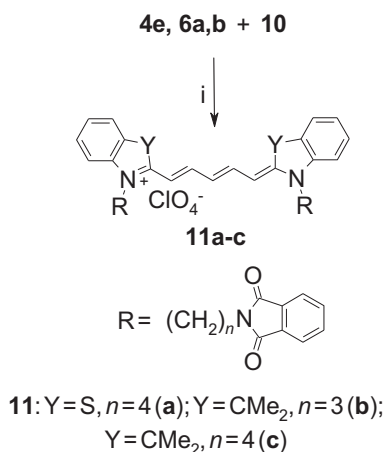
Pentamethine dyes were prepared using 2-amino-1-methylpyrimidinium perchlorate. For this purpose, 2-amino-1-methylpyrimidinium iodide, prepared by a known procedure,¹⁵ was converted to perchlorate **10** by treatment with an excess of HClO₄ in methanol (Scheme 6).



Scheme 6. Synthesis of salt **10**. Reagents and conditions: (i) HClO₄ (70%, aq), MeOH (**10**: 76% yield).

In the synthesis of pentamethine dyes, it is desirable to use 2-amino-1-methylpyrimidinium salt as the perchlorate, because the second heterocyclic salt is used as the perchlorate, and thus iodide impurity in the target dye can be avoided. Furthermore, the conversion of 2-amino-1-methylpyrimidinium iodide to the perchlorate is an additional procedure for purifying this salt.

Pentamethine dyes **11a–c** were synthesized by condensation of heterocyclic salts **4e**, **6a,b** with 2-amino-1-methylpyrimidinium perchlorate **10** induced by triethylamine similarly to the method reported previously.¹⁵ The reaction was carried out in pyridine in the case of thiadicarbocyanine **11a** or in acetic anhydride in the case of indodicarbocyanines **11b,c** (Scheme 7).



Scheme 7. Synthesis of pentamethine cyanine dyes **11a–c**. Reagents and conditions: (i) Et₃N, Py or Ac₂O, reflux (**11a**: 30%; **11b**: 48%; **11c**: 70% yield).

The dyes **8b** and **9a,b** were prepared as single crystals, which were studied by X-ray diffraction. These structures are shown in Fig. 1. The chromophore part of **8b** is strictly planar, the dihedral angle between the planes of the benzothiazole residues is only 3.8°. In both trimethine dyes, the chromophore moieties are non-planar: the dihedral angles between the planes of the heterocyclic residues in molecules **9a** and **9b** are 27.0° and 11.7°, respectively. The bond lengths in the polymethine chain of **9b** are nearly equal [1.384(3)–1.393(3) Å], indicating effective conjugation throughout the chromophore. The lower accuracy of the experiments for dyes **8b** and **9a** precludes drawing definite conclusions about the distribution of the bond lengths in the polymethine bridges, although a tendency for greater difference between them can be noted for **9a** and **9b**. This may be a consequence of greater twisting of the chromophore in **9a** caused apparently by the specific features of packing of this dye.

In dyes **9a,b**, the trimethine bridge exists in the *transoid* configuration, the α -H atoms pointing in the same direction as the *N*-substituents. Another common structural feature of all dyes is orientation of both *N*-substituents in the same direction in the chromophore plane. This geometry of the cyanine dyes in the crystals is characteristic.¹⁶ It follows from NMR data that this geometry is retained in solution, as indicated by intense cross-peaks between the α -H and CH₂N⁺ protons in the NOESY spectra of dyes **9a,b**, whereas cross-peaks due to coupling of CH₂N⁺ with *meso*-H are absent. Contrarily, in the case of monomethine dye **8b**, the expected NOESY cross-peak due to the CH₂N⁺ and *meso*-H interaction was found.

In the crystal of **8b**, the dye cations form rather isolated centrosymmetric dimers with stacking interaction between the chromophore units, which are arranged at distance of ~ 3.5 Å. The dye cations in the crystal of **9a** are packed into strongly skewed stacks with a centrosymmetric arrangement; the stacking interaction

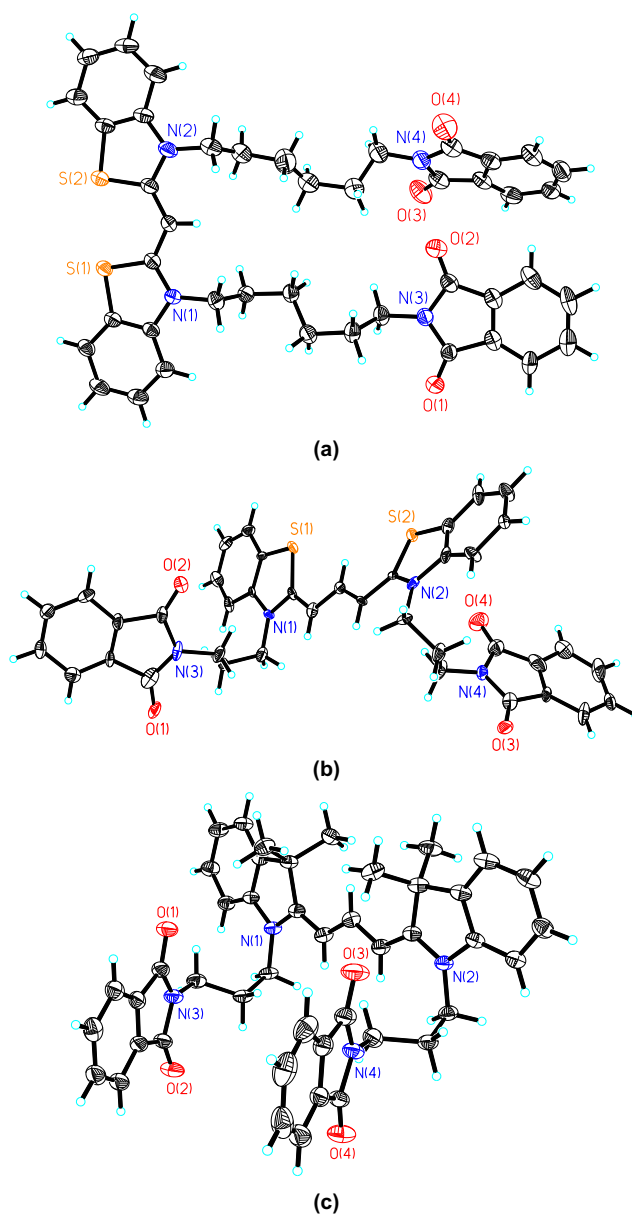
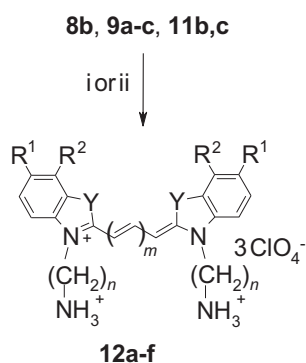


Fig. 1. The cations of dyes in structures of (a) **8b** · 1.75H₂O, (b) **9a** · 0.6CH₂Cl₂ · 0.4CHCl₃ and (c) **9b** · 2MeCN. Thermal anisotropic ellipsoids are drawn at the (a) 40% and (b, c) 50% probability level.

region in these stacks involves mainly the benzothiazolium residues. The distances between the planes of the adjacent molecules of **9a** is ~ 3.4 Å. In the crystal packing of dye **9b**, the chromophores of the neighbouring molecules are remote from one another, which is probably attributable to the steric hindrance created by the CMe₂ groups of the indoleninium residues.

Cyanine dyes **12a–f** with ammonioalkyl substituents at the heterocyclic nitrogen atoms were prepared after removal of the protecting groups from **8b**, **9a–c**, and **11b,c**. The most common method for removing the phthalimide protecting group is hydrazinolysis, which proceeds rather readily.^{10a,17} While selecting conditions for deprotection, we looked to the procedure reported previously.¹⁸ The reaction was carried out with a tenfold excess of hydrazine monohydrate in a boiling CH₂Cl₂–MeOH mixture; the reaction time varied from 3 to 6 h. The reaction afforded dyes amino derivatives. The subsequent treatment of these products with a solution of HClO₄ gave the desired dyes **12b,c,f** in 17–45% yield. However, this method is not free from drawbacks, namely, the

laborious procedure of dye separation from 1,4-phthalazinedione formed in the reaction and the unreacted hydrazine monohydrate. The purification procedure must be repeated many times, and this decreases the yields of target dyes. The phthalimide group can also be removed by treatment with other, milder nucleophilic reagents such as aqueous methylamine.^{11a} While selecting the deprotection conditions, we found that on treatment of dyes **8b**, **9b,c**, and **11b,c** with a 38% solution of MeNH₂ in absolute ethanol, the reaction occurs under milder conditions and remaining methylamine is easily distilled off under reduced pressure. *N,N'*-Dimethylphthalimide is removed from the reaction mixture by extraction into ethyl acetate. This workup is fairly facile and efficient. The subsequent treatment of dye amino derivatives with a solution of HClO₄ provides the desired dyes in high purity in good yields (up to 51%) (Scheme 8, Table 1).



Scheme 8. Deprotection of the phthalimide group. Reagents and conditions: (i) 1. 38% solution of MeNH₂ in abs EtOH; 2. HClO₄ (70%, aq), EtOH; (ii) 1. N₂H₄·H₂O, CH₂Cl₂/MeOH, reflux; 2. HClO₄ (70%, aq), EtOH.

Table 1
Yields of dyes **12a–f** produced via Scheme 8

Dye	<i>m</i>	<i>n</i>	Y	R ¹ , R ²	Yield % (i)	Yield % (ii)
12a	0	6	S	H, H	44	0
12b	1	3	S	H, H		17
12c	1	3	CMe ₂	H, H	40	45
12d	1	3	CMe ₂	C ₄ H ₄	25	
12e	2	3	CMe ₂	H, H	42	
12f	2	4	CMe ₂	H, H	51	37

The obtained cyanine dyes with terminal ammonium groups on the *N*-substituents of heterocyclic residues can be employed as components for the design of light-sensitive supramolecular systems. The presence of primary ammonium groups capable of functioning as proton donors in hydrogen bonds creates the possibility for self-assembly of the dyes to supramolecular complexes with crown or cavitand molecules having proton-acceptor groups, for example, ether or carbonyl oxygens. We have shown that this type of interaction gives rise to highly stable supramolecular complexes in which unusual photochemical processes may take place.¹⁹

3. Conclusions

We have developed the synthesis of high-purity symmetrical mono-, tri-, and pentamethine cyanine dyes with two ammonioalkyl substituents on the heterocyclic nitrogen atoms in good yields. Conditions for the removal of the phthalimide protection in cyanine dyes of this type were selected. This approach to the synthesis of symmetrical cyanine dyes with ammonioalkyl substituents may also open up a way to novel groups of dyes promising as luminophores and luminescent labels in biology and medicine.

4. Experimental section

4.1. General

Melting points were determined with a MEL-Temp II apparatus in a capillary and are uncorrected. 1D ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-500 instrument (500.13 and 125.76 MHz, respectively) as solutions in DMSO-*d*₆ using the solvent as an internal reference (δ_{H} 2.50, δ_{C} 39.40, respectively); 2D homonuclear ¹H–¹H COSY and NOESY spectra and heteronuclear ¹H–¹³C COSY spectra (HSQC and HMBC) were used to assign the proton and carbon signals. Absorption spectra were recorded on Shimadzu UV-3101PC and Agilent Cary 4000 spectrophotometers in the range of 250–800 nm with an increment of 1 nm (*C*_{dye} = 1 × 10^{−5} M, 1-cm quartz cell, room temperature). Emission spectra were recorded on a Shimadzu RF-5301PC spectrofluorimeter in the range of 430–800 nm with an increment of 1 nm (*C*_{dye} = 1 × 10^{−5} M, 1-cm quartz cell, room temperature). IR spectra in KBr pellets were recorded on a Bruker IFS-113V spectrophotometer. High resolution ESI mass spectra were measured on a MicrOTOF II instrument (Bruker Daltonics) in the range of *m/z* = 50–3000 for positive ions (MeOH solution inlet, nitrogen gas flow, 4500 V capillary voltage). Elemental analyses were performed at the Microanalytical Laboratory of A.N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federation). Tosylates **3a,b** and 2-amino-1-methylpyrimidin-1-ium iodide were prepared by known procedures.^{11a,15,20}

4.2. Synthesis of 2-thiobenzothiazolium salts **1a,b**

A mixture of 2-mercaptobenzothiazole **2** (167 mg, 1 mmol) and compounds **3a,b** (2 mmol) was heated at 140 °C (oil bath) for 20 h. After cooling to room temperature, the resulting mass was washed with benzene and dried in vacuo. Yield **1a**: 499 mg (70%). Yield **1b**: 430 mg (54%). Compounds **1a,b** were used without further purification.

4.2.1. 3-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-[[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]thio]-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (1a**).** Salt **1a** was isolated as a brownish oil. Found C, 57.38; H, 4.57; N, 4.37. C₃₆H₃₁N₃O₇S₃·TsOH·H₂O requires C, 57.13; H, 4.57; N, 4.65%. IR (KBr) 1711 (C=O) cm^{−1}; MS (ESI): found *m/z* 542.1190 (calcd for C₂₉H₂₄N₃O₄S₂⁺ 542.1208); δ_{H} (DMSO-*d*₆) 2.14–2.24 (4H, m, 2CH₂), 2.28 (3H, s, Me), 3.65 (2H, br t, CH₂S), 3.74–3.81 (4H, m, 2CH₂N), 4.69–4.72 (2H, m, CH₂N⁺), 7.12 (2H, d, *J* 7.7 Hz, 3''-H, 5''-H), 7.50 (2H, d, *J* 7.7 Hz, 2''-H, 6''-H), 7.70–7.73 (1H, m, 6-H), 7.81–7.87 (9H, m, 5-H, 4'-H, 5'-H, 6'-H, 7'-H, 4''-H, 5''-H, 6''-H, 7''-H), 8.29 (1H, d, *J* 8.6 Hz, 4-H), 8.37 (1H, d, *J* 8.2 Hz, 7-H); δ_{C} (DMSO-*d*₆) 20.70 (Me), 25.88 and 26.70 (2CH₂), 33.67 and 34.81 (2CH₂N), 35.98 (CH₂S), 47.91 (CH₂N⁺), 115.60 (4-C), 122.97 and 123.01 (2 × 5'-C, 2 × 6'-C), 124.12 (7-C), 125.43 (2''-C, 6'''-C), 128.08 (3'''-C, 5'''-C), 128.24 (6-C), 128.64 (7a-C), 129.27 (5-C), 131.59 and 131.68 (3a'-C, 7a'-C, 3a''-C, 7a''-C), 134.32 and 134.36 (4'-C, 7'-C, 4''-C, 7''-C), 137.84 (4'''-C), 141.41 (3a-C), 145.21 (1'''-C), 167.96 and 168.02 (1'-C, 3'-C, 1''-C, 3''-C), 179.30 (2-C).

4.2.2. 3-[6-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)hexyl]-2-[[6-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)hexyl]thio]-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (1b**).** Salt **1b** was isolated as a brownish oil. Found C, 59.54; H, 5.33; N, 4.01. C₄₂H₄₃N₃O₇S₃·TsOH·H₂O requires C, 59.55; H, 5.41; N, 4.25%. IR (KBr) 1709 (C=O) cm^{−1}; MS (ESI): found *m/z* 626.2147 (calcd for C₃₅H₃₆N₃O₄S₂⁺ 626.2147); δ_{H} (DMSO-*d*₆) 1.29–1.64 (12H, m, 6CH₂), 1.80–1.83 (2H, m, CH₂), 1.88–1.91 (2H, m, CH₂), 2.28 (3H, s, Me), 3.53–3.58 (4H, m, 2CH₂N), 3.59–3.62 (2H, m, CH₂S), 4.58 (2H, br t, CH₂N⁺), 7.10 (2H, d, *J* 7.6 Hz, 3''-H, 5''-H), 7.48 (2H, d, *J* 7.6 Hz,

2'''-H, 6'''-H), 7.70–7.74 (1H, m, 6-H), 7.80–7.86 (9H, m, 5-H, 4'-H, 5'-H, 6'-H, 7'-H, 4''-H, 5''-H, 6''-H, 7''-H), 8.21 (1H, d, *J* 8.3 Hz, 4-H), 8.36 (1H, d, *J* 8.3 Hz, 7-H); δ_{C} (DMSO-*d*₆) 20.63 (Me), 25.30, 25.43, 25.64, 26.56, 27.16, 27.34, 27.55 and 27.68 (8CH₂), 35.88 (CH₂S), 37.11 (2CH₂N), 49.87 (CH₂N⁺), 115.67 (4-C), 122.83 (2×5''-C, 2×6'-C), 123.97 (7-C), 125.37 (2×2''-C, 6''-C), 127.91 (3''-C, 5''-C, 6-C), 128.58 (7a-C), 129.14 (5-C), 131.44 (3a'-C, 7a'-C, 3a''-C, 7a''-C), 134.25 (4'-C, 7'-C, 4''-C, 7''-C), 137.49 (4'''-C), 141.44 (3a-C), 145.60 (1'''-C), 167.81 and 167.83 (1'-C, 3'-C, 1''-C, 3''-C), 179.33 (2-C).

4.3. Synthesis of 2-methylbenzothiazolium salts 4a–c

A mixture of 2-methylbenzothiazole **5** (0.19 mL, 1.5 mmol) and compounds **3b–d** (1.0 mmol) was heated at 140–150 °C (oil bath) for 20 h. After cooling to room temperature, the resulting solid was washed with hot benzene, acetone, diethyl ether and dried in air. Yield **4a**: 383 mg (92%). Yield **4b**: 344 mg (80%). Yield **4c**: 368 mg (67%).

4.3.1. 3-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-methyl-1,3-benzothiazol-3-ium bromide (**4a**). Salt **4a** was isolated as a white powder. Found C, 54.78; H, 4.07; N, 6.53. C₁₉H₁₇BrN₂O₂S requires C, 54.68; H, 4.11; N, 6.71%. Mp 225 °C (decomp.). IR (KBr) 1705 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 2.23–2.29 (2H, m, CH₂CH₂N), 3.20 (3H, s, Me), 3.85 (2H, br t, CH₂N), 4.80–4.83 (2H, m, CH₂N⁺), 7.77–7.80 (1H, m, 6-H), 7.84–7.90 (5H, m, 5-H, 4'-H, 5'-H, 6'-H, 7'-H), 8.36 (1H, d, *J* 8.3 Hz, 4-H), 8.41 (1H, d, *J* 7.8 Hz, 7-H); δ_{C} (DMSO-*d*₆) 16.69 (Me), 26.49 (CH₂CH₂N), 34.87 (CH₂N), 47.17 (CH₂N⁺), 116.67 (4-C), 122.90 (5'-C, 6'-C), 124.47 (7-C), 127.99 (6-C), 128.96 (7a-C), 129.24 (5-C), 131.70 (3a'-C, 7a'-C), 134.22 (4'-C, 7'-C), 140.62 (3a-C), 168.04 (1'-C, 3'-C), 177.51 (2-C).

4.3.2. 3-[4-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)butyl]-2-methyl-1,3-benzothiazol-3-ium bromide (**4b**). Salt **4b** was isolated as a yellow powder. Found C, 55.75; H, 4.45; N, 6.46. C₂₀H₁₉BrN₂O₂S requires C, 55.69; H, 4.44; N, 6.49%. Mp 257 °C (decomp.). IR (KBr) 1716 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 1.77–1.83 (2H, m, CH₂CH₂N), 1.87–1.93 (2H, m, CH₂CH₂N⁺), 3.21 (3H, s, Me), 3.64 (2H, t, *J* 6.8 Hz, CH₂N), 4.72–4.75 (2H, m, CH₂N⁺), 7.77–7.80 (1H, m, 6-H), 7.83–7.89 (5H, m, 5-H, 4'-H, 5'-H, 6'-H, 7'-H), 8.36 (1H, d, *J* 8.5 Hz, 4-H), 8.44 (1H, d, *J* 8.0 Hz, 7-H); δ_{C} (DMSO-*d*₆) 16.72 (Me), 25.01 and 25.11 (CH₂CH₂), 36.80 (CH₂N), 48.67 (CH₂N⁺), 116.76 (4-C), 122.91 (5'-C, 6'-C), 124.47 (7-C), 127.99 (6-C), 128.96 (7a-C), 129.24 (5-C), 131.52 (3a'-C, 7a'-C), 134.28 (4'-C, 7'-C), 140.71 (3a-C), 167.93 (1'-C, 3'-C), 177.26 (2-C).

4.3.3. 3-[6-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)hexyl]-2-methyl-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**4c**). Salt **4c** was isolated as a white powder. Found C, 63.14; H, 5.44; N, 5.03. C₂₉H₃₀N₂O₅S₂ requires C, 63.25; H, 5.49; N, 5.09%. Mp 180 °C (decomp.). IR (KBr) 1709 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 1.30–1.36, 1.43–1.49, 1.56–1.62 and 1.79–1.85 (8H, 4m, 4CH₂), 2.26 (3H, s, MeAr), 3.19 (3H, s, MeHet), 3.56 (2H, t, *J* 7.0 Hz, CH₂N), 4.68 (2H, br t, CH₂N⁺), 7.08 (2H, d, *J* 7.6 Hz, 3''-H, 5''-H), 7.47 (2H, d, *J* 7.6 Hz, 2''-H, 6''-H), 7.77–7.80 (1H, m, 6-H), 7.82–7.88 (5H, m, 5-H, 4'-H, 5'-H, 6'-H, 7'-H), 8.31 (1H, d, *J* 8.6 Hz, 4-H), 8.42 (1H, d, *J* 8.5 Hz, 7-H); δ_{C} (DMSO-*d*₆) 16.64 (MeHet), 20.65 (MeAr), 25.29, 25.74, 27.48 and 27.61 (4CH₂), 37.16 (CH₂N), 48.98 (CH₂N⁺), 116.75 (4-C), 122.88 (5'-C, 6'-C), 124.47 (7-C), 125.37 (2''-C, 6''-C), 127.91 (3''-C, 5''-C), 127.96 (6-C), 128.99 (7a-C), 129.24 (5-C), 131.45 (3a'-C, 7a'-C), 134.31 (4'-C, 7'-C), 137.43 (4''-C), 140.71 (3a-C), 145.70 (1'''-C), 167.85 (1'-C, 3'-C), 176.98 (2-C).

4.4. Synthesis of perchlorates 4d,e

Perchloric acid (70% (aq), 0.30 mL) was added to a solution of salt **4a,b** (1 mmol) in MeOH (30 mL). The reaction mixture was heated and water was added dropwise until complete dissolution

of the substance was attained. After cooling to 5 °C, the precipitate that formed was filtered off and washed with MeOH. Yield **4d**: 420 mg (96%). Yield **4e**: 423 mg (94%).

4.4.1. 3-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-methyl-1,3-benzothiazol-3-ium perchlorate (**4d**). Salt **4d** was isolated as white crystals. Found C, 52.29; H, 3.74; N, 6.32. C₁₉H₁₇ClN₂O₆S requires C, 52.24; H, 3.92; N, 6.41%. Mp 248–249 °C. IR (KBr) 1719 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 2.23–2.29 (2H, m, CH₂CH₂N), 3.20 (3H, s, Me), 3.85 (2H, t, *J* 6.8 Hz, CH₂N), 4.80–4.83 (2H, m, CH₂N⁺), 7.77–7.80 (1H, m, 6-H), 7.84–7.90 (5H, m, 5-H, 4'-H, 5'-H, 6'-H, 7'-H), 8.37 (1H, d, *J* 8.5 Hz, 4-H), 8.41 (1H, d, *J* 8.2 Hz, 7-H); δ_{C} (DMSO-*d*₆) 16.69 (Me), 26.49 (CH₂CH₂N), 34.87 (CH₂N), 47.17 (CH₂N⁺), 116.67 (4-C), 122.90 (5'-C, 6'-C), 124.47 (7-C), 127.99 (6-C), 128.96 (7a-C), 129.24 (5-C), 131.70 (3a'-C, 7a'-C), 134.22 (4'-C, 7'-C), 140.62 (3a-C), 168.04 (1'-C, 3'-C), 177.51 (2-C).

4.4.2. 3-[4-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)butyl]-2-methyl-1,3-benzothiazol-3-ium perchlorate (**4e**). Salt **4e** was isolated as white crystals. Found C, 53.36; H, 4.26; N, 6.61. C₂₀H₁₉ClN₂O₆S requires C, 53.28; H, 4.25; N, 6.21%. Mp 221–225 °C. IR (KBr) 1714 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 1.78–1.83 (2H, m, CH₂CH₂N), 1.88–1.94 (2H, m, CH₂CH₂N⁺), 3.21 (s, 3H, Me), 3.64 (2H, t, *J* 6.8 Hz, CH₂N), 4.72–4.75 (2H, m, CH₂N⁺), 7.79 (m, 1H, 6-H), 7.82–7.89 (5H, m, 5-H, 4'-H, 5'-H, 6'-H, 7'-H), 8.35 (1H, d, *J* 8.5 Hz, 4-H), 8.42 (1H, d, *J* 8.2 Hz, 7-H); δ_{C} (DMSO-*d*₆) 16.72 (Me), 25.01 and 25.11 (CH₂CH₂), 36.80 (CH₂N), 48.67 (CH₂N⁺), 116.76 (4-C), 122.91 (5'-C, 6'-C), 124.47 (7-C), 127.99 (6-C), 128.96 (7a-C), 129.24 (5-C), 131.52 (3a'-C, 7a'-C), 134.28 (4'-C, 7'-C), 140.71 (3a-C), 167.93 (1'-C, 3'-C), 177.26 (2-C).

4.5. Synthesis of 3H-indolium and 1H-benzo[e]indolium salts 6a–c

Method A. A mixture of 2,3,3-trimethyl-3H-indole **7a** (240 μL, 1.5 mmol) and compounds **3c,d** (1.0 mmol) in dry MeCN (3.5 mL) was stirred under reflux for 20 h in argon flow. The solvent was evaporated in vacuo and the residue was dissolved in acetone and poured into diethyl ether (100 mL). The precipitate that formed was filtered off and washed with acetone and diethyl ether and dried in air to give the bromide salt as a crystalline powder. Perchloric acid (70% (aq), 130 μL, 1.5 mmol) was added to a solution of the bromide salt in hot EtOH (5 mL). The reaction mixture was cooled to 5 °C and the precipitate that formed was filtered off and washed with EtOH. Yield **6a**: 228 mg (51%). Yield **6b**: 391 mg (85%).

Method B. A mixture of 1,1,2-trimethyl-1H-benzo[e]indole **7b** (209 mg, 1 mmol) and compound **3c** (268 mg, 1.0 mmol) in dry MeCN (1 mL) was sealed in a glass tube under argon and heated at 110 °C (oil bath) for 45 h. After tube opening, the solvent was evaporated in vacuo, and the residue was dissolved in acetone and poured into diethyl ether (150 mL). The precipitate that formed was filtered off and the procedure was repeated. The precipitate was dissolved in EtOH (7 mL) and HClO₄ (70% (aq), 100 μL, 1.15 mmol) was added to this solution. After cooling to 5 °C, the precipitate that formed was filtered off and washed with benzene and diethyl ether and dried in air. Yield **6c**: 198 mg (40%).

4.5.1. 1-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2,3,3-trimethyl-3H-indolium perchlorate (**6a**). Salt **6a** was isolated as a yellow powder. Found C, 59.01; H, 5.14; N, 6.12. C₂₂H₂₃ClN₂O₆ requires C, 59.13; H, 5.19; N, 6.27%. Mp 190–193 °C. IR (KBr) 1710 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 1.54 (6H, s, CMe₂), 2.20–2.26 (2H, m, CH₂), 2.83 (3H, s, Me), 3.81 (2H, t, *J* 6.7 Hz, CH₂N), 4.55–4.58 (2H, m, CH₂N⁺), 7.59–7.64 (2H, m, Ar), 7.82–7.89 (5H, m, Ar, 4'-H, 5'-H, 6'-H, 7'-H), 7.99–8.01 (1H, m, Ar); δ_{C} (DMSO-*d*₆) 13.88 (Me), 21.89 (CMe₂), 26.19 (CH₂CH₂N), 34.76 (CH₂N), 45.58 (CH₂N⁺), 54.12 (3-C), 115.29 (7-C), 122.91 (5'-C, 6'-C), 123.39 (4-C), 128.82 (5-C), 129.33

(6-C), 131.73 (3a'-C, 7a'-C), 134.25 (4'-C, 7'-C), 140.93 (3a-C), 141.74 (7a-C), 168.02 (1'-C, 3'-C), 197.08 (2-C).

4.5.2. 1-[4-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)butyl]-2,3,3-trimethyl-3H-indolium perchlorate (**6b**). Salt **6b** was isolated as white crystals. Found C, 59.78; H, 5.38; N, 6.01. C₂₃H₂₅ClN₂O₆ requires C, 59.94; H, 5.47; N, 6.08%. Mp 240–243 °C. IR (KBr) 1709 (C=O) cm⁻¹; δ_H (DMSO-d₆) 1.53 (6H, s, CMe₂), 1.75–1.80 (2H, m, CH₂CH₂N), 1.87–1.93 (2H, m, CH₂CH₂N⁺), 2.83 (3H, s, Me), 3.64 (2H, t, J 6.6 Hz, CH₂N), 4.47 (2H, br t, CH₂N⁺), 7.60–7.61 (2H, m, Ar), 7.82–7.87 (5H, m, Ar, 4'-H, 5'-H, 6'-H, 7'-H), 7.97–7.99 (1H, m, Ar); δ_C (DMSO-d₆) 13.84 (Me), 21.91 (CMe₂), 24.46 and 24.94 (CH₂CH₂), 36.77 (CH₂N), 47.05 (CH₂N⁺), 54.07 (3-C), 115.37 (7-C), 122.93 (5'-C, 6'-C), 123.38 (4-C), 128.82 (5-C), 129.30 (6-C), 131.52 (3a'-C, 7a'-C), 134.31 (4'-C, 7'-C), 140.92 (3a-C), 141.74 (7a-C), 167.95 (1'-C, 3'-C), 196.73 (2-C).

4.5.3. 3-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-1,1,2-trimethyl-1H-benzo[e]indolium perchlorate (**6c**). Salt **6c** was isolated as a white solid. Found C, 62.71; H, 5.25; N, 5.59. C₂₆H₂₅ClN₂O₆ requires C, 62.84; H, 5.07; N, 5.64%. Mp 231–232 °C. IR (KBr) 1711 (C=O) cm⁻¹; δ_H (DMSO-d₆) 1.77 (6H, s, CMe₂), 2.26–2.32 (2H, m, CH₂CH₂N), 2.94 (3H, s, Me), 3.85 (2H, t, J 6.7 Hz, CH₂N), 4.69 (2H, br t, CH₂N⁺), 7.71–7.74 (1H, m, 7-H), 7.77–7.80 (1H, m, 8-H), 7.83–7.89 (4H, m, 4'-H, 5'-H, 6'-H, 7'-H), 8.17 (1H, d, J 9.1 Hz, 4-H), 8.20 (1H, d, J 7.9 Hz, 6-H), 8.28 (1H, d, J 9.1 Hz, 5-H), 8.36 (1H, d, J 8.5 Hz, 9-H); δ_C (DMSO-d₆) 13.70 (Me), 21.49 (CMe₂), 26.36 (CH₂CH₂N), 34.76 (CH₂N), 45.80 (CH₂N⁺), 55.45 (1-C), 113.09 (4-C), 122.90 (5'-C, 6'-C), 123.26 (9-C), 127.10 and 127.17 (8-C, 9a-C), 128.31 (7-C), 129.59 (6-C), 130.58 (5-C), 131.70 (3a'-C, 7a'-C), 132.93 (5a-C), 134.22 (4'-C, 7'-C), 136.83 (9b-C), 138.35 (3a-C), 168.00 (1'-C, 3'-C), 196.88 (2-C).

4.6. Synthesis of monomethine cyanine dyes **8a,b**

A mixture of salts **1a,b** (1 mmol) and **4a,c** (1 mmol) was dissolved in abs EtOH (20 mL) at heating, and then triethylamine (310 μL, 2.20 mmol) was added to this solution. The reaction mixture was stirred under reflux for 5 h and then cooled to -10 °C. The precipitate that formed was filtered off and washed with cold EtOH and diethyl ether and dried in air. Yield **8a**: 442 mg (60%). In the case of **8b**, the tosylate salt of the dye was dissolved in abs EtOH (15 mL) at heating and then HClO₄ (70% (aq), 80 μL, 0.9 mmol) was added to the solution. After cooling to -10 °C, the precipitate that formed was filtered off and washed with cold abs EtOH and diethyl ether and dried in air. Yield **8b**: 513 mg (61%).

4.6.1. 3-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-((Z)-[3-[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-1,3-benzothiazol-2(3H)-ylidene]methyl)-1,3-benzothiazol-3-ium bromide (**8a**). Dye **8a** was isolated as yellow crystals. Found C, 59.02; H, 4.05; N, 7.48. C₃₇H₂₉BrN₄O₄S₂·H₂O requires C, 58.81; H, 4.14; N, 7.41%. Mp 281 °C; UV-vis (MeCN) λ_{max} 425 nm (ε 82,500 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 415 nm, λ_f^{max} 475 nm. IR (KBr) 1706 (C=O) cm⁻¹; δ_H (DMSO-d₆) 2.16–2.23 (4H, m, 2CH₂CH₂N), 3.77 (4H, br t, 2CH₂N), 4.80 (4H, br t, 2CH₂N⁺), 6.79 (1H, s, meso-H), 7.49–7.52 (2H, m, 2×6-H), 7.64–7.73 (10H, m, 2×5-H, 2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 7.97 (2H, d, J 8.7 Hz, 2×4-H), 8.23 (2H, d, J 8.3 Hz, 2×7-H); δ_C (DMSO-d₆) 25.42 (2CH₂CH₂N), 34.80 (2CH₂N), 43.82 (2CH₂N⁺), 82.66 (meso-C), 113.70 (2×4-C), 122.66 (2×7-C, 2×5'-C, 2×6'-C), 123.52 (2×6-C), 124.83 (2×7a-C), 128.57 (2×5-C), 131.48 (2×3a'-C, 2×7a'-C), 134.08 (2×4'-C, 2×7'-C), 139.98 (2×3a-C), 161.78 (2×2-C), 167.75 (2×1'-C, 2×3'-C).

4.6.2. 3-[6-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)hexyl]-2-((Z)-[3-[6-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)hexyl]-1,3-benzothiazol-2(3H)-ylidene]methyl)-1,3-benzothiazol-3-ium

perchlorate (**8b**). Dye **8b** was isolated as yellow crystals. Found C, 59.96; H, 4.71; N, 6.25. C₄₃H₄₁ClN₄O₈S₂·H₂O requires C, 60.09; H, 5.04; N, 6.52%. Mp 145 °C; UV-vis (MeCN) λ_{max} 426 nm (ε 66,500 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 416 nm, λ_f^{max} 475 nm. IR (KBr) 1709 (C=O) cm⁻¹; δ_H (DMSO-d₆) 1.27–1.33, 1.44–1.49, 1.51–1.57 and 1.72–1.78 (16H, 4m, 8CH₂), 3.49 (4H, t, J 7.0 Hz, 2CH₂N), 4.62 (4H, br t, 2CH₂N⁺), 6.64 (1H, s, meso-H), 7.47–7.50 (2H, m, 2×6-H), 7.65–7.68 (2H, m, 2×5-H), 7.73–7.77 (8H, m, 2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 7.88 (2H, d, J 8.4 Hz, 2×4-H), 8.19 (2H, d, J 7.9 Hz, 2×7-H); δ_C (DMSO-d₆) 25.54, 26.01, 26.78 and 27.70 (8CH₂), 37.12 (2CH₂N), 46.05 (2CH₂N⁺), 82.46 (meso-C), 113.74 (2×4-C), 122.79 (2×7-C, 2×5'-C, 2×6'-C), 123.45 (2×6-C), 124.85 (2×7a-C), 128.51 (2×5-C), 131.40 (2×3a'-C, 2×7a'-C), 134.21 (2×4'-C, 2×7'-C), 140.08 (2×3a-C), 161.49 (2×2-C), 167.75 (2×1'-C, 2×3'-C).

4.7. Synthesis of trimethine cyanine dyes **9a–c**

Method A. Ethyl orthoformate (250 μL, 1.5 mmol) was added to a boiling mixture of salt **4d**, **6a** (1 mmol) and pyridine (10 mL) and the reaction mixture was stirred under reflux for 2 h. Pyridine was evaporated in vacuo, and the residue was washed with benzene and diethyl ether and recrystallized from abs EtOH. Yield **9a**: 234 mg (60%). Yield **9b**: 132 mg (33%).

Method B. Triethylamine (160 μL, 1 mmol) and then ethyl orthoformate (130 μL, 0.8 mmol) were added dropwise to a hot mixture of salt **6c** (496 mg, 1 mmol) and acetic anhydride (20 mL), and the reaction mixture was stirred under reflux for 3 h. The pink reaction mixture was poured into cold water (600 mL) and the crude dye was filtered off and washed with water and cold EtOH. The dye was dissolved in hot EtOH and filtered, and the filtrate was diluted with diethyl ether (600 mL) and cooled to -10 °C. The precipitate that formed was filtered off and washed with diethyl ether. Yield **9c**: 284 mg (63%).

4.7.1. 3-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-((1E,3Z)-3-[3-[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-1,3-benzothiazol-2(3H)-ylidene]prop-1-en-1-yl)-1,3-benzothiazol-3-ium perchlorate (**9a**). Dye **9a** was isolated as purple crystals. Found C, 59.64; H, 4.16; N, 6.98. C₃₉H₃₁ClN₄O₈S₂ requires C, 59.80; H, 3.99; N, 7.15%. Mp 263–264 °C; UV-vis (MeCN) λ_{max} 559 nm (ε 128,300 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 549 nm, λ_f^{max} 584 nm. IR (KBr) 1709 (C=O) cm⁻¹; δ_H (DMSO-d₆) 2.10–2.16 (4H, m, 2CH₂CH₂N), 3.77 (4H, t, J 7.1 Hz, 2CH₂N), 4.41–4.46 (4H, m, 2CH₂N⁺), 4.62 (4H, br t, 2CH₂N⁺), 6.56 (2H, d, J 12.7 Hz, 2×α-H), 7.37–7.40 (2H, m, 2×6-H), 7.52–7.55 (2H, m, 2×5-H), 7.70–7.85 (11H, m, meso-H, 2×4-H, 2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 7.96 (2H, d, J 7.9 Hz, 2×7-H); δ_C (DMSO-d₆) 26.05 (2CH₂CH₂N), 35.03 (2CH₂N), 44.07 (2CH₂N⁺), 98.70 (2α-C), 113.44 (2×4-C), 122.87 (2×5'-C, 2×6'-C), 124.87 (2×7-C), 125.16 (2×6-C), 126.50 (2×7a-C), 127.98 (2×5-C), 131.68 (2×3a'-C, 2×7a'-C), 134.20 (2×4'-C, 2×7'-C), 140.95 (2×3a-C), 146.56 (meso-C), 164.65 (2×2-C), 167.92 (2×1'-C, 2×3'-C).

4.7.2. 1-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-((1E,3E)-3-[1-[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene]prop-1-en-1-yl)-3,3-dimethyl-3H-indolium perchlorate (**9b**). Dye **9b** was isolated as purple crystals. Found C, 67.15; H, 5.45; N, 6.81. C₄₅H₄₃ClN₄O₈ requires C, 67.28; H, 5.40; N, 6.98%. Mp 263–264 °C; UV-vis (MeCN) λ_{max} 548 nm (ε 130,300 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 538 nm, λ_f^{max} 572 nm. IR (KBr) 1714 (C=O) cm⁻¹; δ_H (DMSO-d₆) 1.72 (12H, s, 2CMe₂), 2.10–2.15 (4H, m, 2CH₂CH₂N), 3.72 (4H, t, J 7.1 Hz, 2CH₂N), 4.25 (4H, br t, 2CH₂N⁺), 6.49 (2H, d, J 13.5 Hz, 2×α-H), 7.30 (2H, t, J 7.3 Hz, 2×5-H), 7.43 (2H, t, J 8.0 Hz, 2×6-H), 7.51 (2H, d, J 8.0 Hz, 2×7-H), 7.64 (2H, d, J 7.3 Hz, 2×4-H), 7.79–7.83 (8H, m,

2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 8.37 (1H, t, *J* 13.5 Hz, *meso*-H); δ_C (DMSO-*d*₆) 25.92 (2CH₂CH₂N), 27.32 (2CMe₂), 35.03 (2CH₂N), 41.52 (2CH₂N⁺), 48.90 (2×3-C), 102.70 (2× α -C), 111.48 (2×7-C), 122.45 (2×4-C), 122.86 (2×5'-C, 2×6'-C), 125.24 (2×5-C), 128.56 (2×6-C), 131.63 (2×3a'-C, 2×7a'-C), 134.19 (2×4'-C, 2×7'-C), 140.49 (2×3a-C), 141.69 (2×7a-C), 149.90 (*meso*-C), 167.85 (2×1'-C, 2×3'-C), 173.97 (2×2-C).

4.7.3. 3-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-((1E,3E)-3-[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)prop-1-en-1-yl)-1,1-dimethyl-1H-benzo[e]indolium perchlorate (**9c**). Dye **9c** was isolated as dark purple crystals. Found C, 69.21; H, 5.25; N, 5.73. C₅₃H₄₇ClN₄O₈·H₂O requires C, 69.08; H, 5.36; N, 6.08%. Mp 230 °C; UV–vis (MeCN) λ_{\max} 588 nm (ϵ 96,900 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 578 nm, $\lambda_{\text{max}}^{\text{f}}$ 612 nm. IR (KBr) 1710 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 2.03 (12H, s, 2CMe₂), 2.17–2.23 (4H, m, 2CH₂CH₂N), 3.76 (4H, br t, 2CH₂N), 4.40 (4H, br t, 2CH₂N⁺), 6.55 (2H, d, *J* 13.3 Hz, 2× α -H), 7.53–7.56 (2H, m, 2×7-H), 7.68–7.71 (2H, m, 2×8-H), 7.77–7.84 (10H, m, 2×4-H, 2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 8.07 (2H, d, *J* 8.3 Hz, 2×6-H), 8.10 (2H, d, *J* 8.7 Hz, 2×5-H), 8.30 (2H, d, *J* 8.3 Hz, 2×9-H), 8.59 (1H, t, *J* 13.3 Hz, *meso*-H); δ_C (DMSO-*d*₆) 26.18 (2CH₂CH₂N), 26.99 (2CMe₂), 35.05 (2CH₂N), 41.71 (2CH₂N⁺), 50.59 (2×1-C), 102.23 (2× α -C), 111.63 (2×4-C), 122.08 (2×9-C), 122.87 (2×5'-C, 2×6'-C), 125.04 (2×7-C), 127.27 (2×9a-C), 127.85 (2×8-C), 129.86 (2×6-C), 130.42 (2×5-C), 131.44 (2×5a-C), 131.65 (2×3a'-C, 2×7a'-C), 133.03 (2×9b-C), 134.17 (2×4'-C, 2×7'-C), 139.39 (2×3a-C), 148.46 (*meso*-C), 167.90 (2×1'-C, 2×3'-C), 175.22 (2-C).

4.8. Synthesis of 2-amino-1-methylpyrimidin-1-ium perchlorate (**10**)

Perchloric acid (70%, aq) (0.1 mL, 1.1 mmol) was added to a solution of 2-amino-1-methylpyrimidin-1-ium iodide (237 mg, 1 mmol) in MeOH (2 mL). The reaction mixture was heated and, after cooling to 5 °C, the precipitate that formed was filtered off and washed with MeOH to yield **10** (0.161 mg, 76%) as a white powder. Found C, 28.48; H, 3.72; N, 19.88. C₅H₈ClN₃O₄ requires C, 28.65; H, 3.85; N, 20.05%. Mp 190–193 °C (decomp.). IR (KBr) 3344, 3289 (NH₂) cm⁻¹; δ_{H} (DMSO-*d*₆) 3.71 (3H, s, Me), 7.06–7.09 (1H, m, 5-H), 8.53–8.54 (1H, m, 4-H), 8.82–8.83 (1H, m, 6-H), 9.30 (2H, br s, NH₂).

4.9. Synthesis of pentamethine cyanine dyes **11a–c**

Method A. Triethylamine (139 μ L, 1 mmol) was added to a hot mixture of salts **4e** (451 mg, 1 mmol) and **10** (105 mg, 0.5 mmol) in pyridine (20 mL) and the reaction mixture was stirred under reflux for 4 h. Pyridine was evaporated in vacuo and the residue was washed with EtOH and hot benzene and dissolved in acetone (10 mL). The solution was filtered, the filtrate was concentrated in vacuo to a volume of ~2 mL. The precipitate that formed was filtered off and washed with a mixture of EtOH (20 mL) and water (20 mL), then with diethyl ether, and dried in air. Yield **11a**: 126 mg (30%).

Method B. Triethylamine (139 μ L, 1 mmol) was added to a mixture of salts **6a,b** (1 mmol) and **10** (140 mg, 0.65 mmol) in acetic anhydride (5 mL). The reaction mixture was stirred under reflux for 2 h and then poured into water (600 mL). The precipitate that formed was filtered off and washed with water. The crude dye was dissolved in acetone (~2 mL) and poured into diethyl ether (300 mL). The precipitate that formed was filtered off, washed with diethyl ether and dried in air. Yield **11b**: 205 mg (48%). Yield **11c**: 299 mg (70%).

4.9.1. 3-[4-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)butyl]-2-((1E,3E,5Z)-5-[3-[4-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)butyl]-1,3-benzothiazol-2(3H)-ylidene]penta-1,3-dien-1-yl)-1,3-benzothiazol-3-

ium perchlorate (11a). Dye **11a** was isolated as a blue solid. Found C, 61.79; H, 4.38; N, 6.59. C₄₃H₃₇ClN₄O₈S₂ requires C, 61.68; H, 4.45; N, 6.69%. Mp 220 °C; UV–vis (MeCN) λ_{\max} 655 nm (ϵ 177,000 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 645 nm, $\lambda_{\text{max}}^{\text{f}}$ 685 nm. IR (KBr) 1710 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 1.73–1.78 (8H, m, 2CH₂CH₂), 3.63–3.65 (4H, m, 2CH₂N), 4.33–4.35 (4H, m, 2CH₂N⁺), 6.42 (1H, br t, *meso*-H), 6.50 (2H, d, *J* 13.1 Hz, 2× α -H), 7.34–7.37 (2H, m, 2×6-H), 7.49–7.52 (2H, m, 2×5-H), 7.63–7.72 (4H, m, 2×4-H, 2× β -H), 7.81–7.86 (8H, m, 2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 7.94–7.95 (2H, m, 2×7-H); δ_C (DMSO-*d*₆) 22.56 and 24.95 (4CH₂CH₂), 36.88 (2CH₂N), 45.48 (2CH₂N⁺), 100.28 (2× α -C), 113.23 (2×4-C), 122.86 (*meso*-C), 122.93 (2×7-C), 124.83 (2×5'-C, 2×6'-C), 125.15 (2×6-C), 127.85 (2×7a-C, 2×5-C), 131.45 (2×3a'-C, 2×7a'-C), 134.29 (2×4'-C, 2×7'-C), 141.19 (2×3a-C), 150.25 (2× β -C), 163.42 (2×2-C), 167.96 (2×1'-C, 2×3'-C).

4.9.2. 1-[3-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-2-((1E,3E,5E)-5-[1-[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)propyl]-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene]penta-1,3-dien-1-yl)-3,3-dimethyl-3H-indolium perchlorate (**11b**). Dye **11b** was isolated as a blue solid. Found C, 65.75; H, 5.32; N, 6.86. C₄₇H₄₅ClN₄O₈·1.5H₂O requires C, 65.92; H, 5.65; N, 6.54%. Mp 163–165 °C; UV–vis (MeCN) λ_{\max} 643 nm (ϵ 166,400 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 633 nm, $\lambda_{\text{max}}^{\text{f}}$ 671 nm. IR (KBr) 1709 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 1.69 (12H, s, 2CMe₂), 2.03–2.09 (4H, m, 2CH₂CH₂N), 3.71 (4H, br t, 2CH₂N), 4.22–4.25 (4H, m, 2CH₂N⁺), 6.28 (2H, d, *J* 13.8 Hz, 2× α -H), 6.38 (1H, t, *J* 12.3 Hz, *meso*-H), 7.23–7.26 (2H, m, 2×5-H), 7.37–7.40 (2H, m, 2×7-H), 7.44–7.46 (2H, m, 2×6-H), 7.62 (2H, d, *J* 7.3 Hz, 2×4-H), 7.82–7.86 (8H, m, 2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 8.30–8.35 (2H, m, 2× β -H); δ_C (DMSO-*d*₆) 25.95 (2CH₂CH₂N), 26.98 (2CMe₂), 34.97 (2CH₂N), 41.10 (2CH₂N⁺), 48.87 (2×3-C), 103.17 (2× α -C), 110.97 (2×7-C), 122.37 (2×4-C), 122.91 (2×5'-C, 2×6'-C), 124.68 (*meso*-C), 125.44 (2×5-C), 128.33 (2×6-C), 131.66 (2×3a'-C, 2×7a'-C), 134.21 (2×4'-C, 2×7'-C), 140.96 (2×3a-C), 141.85 (2×7a-C), 154.16 (2× β -C), 167.86 (2×1'-C, 2×3'-C), 172.70 (2×2-C).

4.9.3. 1-[4-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)butyl]-2-((1E,3E,5E)-5-[1-[4-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)butyl]-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene]penta-1,3-dien-1-yl)-3,3-dimethyl-3H-indolium perchlorate (**11c**). Dye **11c** was isolated as a blue solid. Found C, 65.55; H, 5.65; N, 6.95. C₄₉H₄₉ClN₄O₈·2H₂O requires C, 65.87; H, 5.98; N, 6.27%. Mp 125–130 °C; UV–vis (MeCN) λ_{\max} 643 nm (ϵ 168,500 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 633 nm, $\lambda_{\text{max}}^{\text{f}}$ 671 nm. IR (KBr) 1709 (C=O) cm⁻¹; δ_{H} (DMSO-*d*₆) 1.66 (12H, s, 2CMe₂), 1.71–1.76 (8H, m, 2CH₂CH₂), 3.61–3.64 (4H, m, 2CH₂N), 4.11–4.16 (4H, m, 2CH₂N⁺), 6.28 (2H, d, *J* 13.1 Hz, 2× α -H), 6.51 (1H, t, *J* 12.2 Hz, *meso*-H), 7.21–7.24 (2H, m, 2×5-H), 7.36–7.42 (4H, m, 2×6-H, 2×7-H), 7.60 (2H, m, 2×4-H), 7.79–7.85 (8H, m, 2×4'-H, 2×5'-H, 2×6'-H, 2×7'-H), 8.25 (2H, m, 2× β -H); δ_C (DMSO-*d*₆) 24.08 and 24.98 (2CH₂CH₂), 27.01 (2CMe₂), 36.90 (2CH₂N), 42.81 (2CH₂N⁺), 48.76 (2×3-C), 103.12 (2× α -C), 110.98 (2×7-C), 122.29 (2×4-C), 122.91 (2×5'-C, 2×6'-C), 124.57 (*meso*-C), 125.40 (2×5-C), 128.29 (2×6-C), 131.41 (2×3a'-C, 2×7a'-C), 134.27 (2×4'-C, 2×7'-C), 140.95 (2×3a-C), 141.90 (2×7a-C), 153.99 (2× β -C), 167.93 (2×1'-C, 2×3'-C), 172.56 (2×2-C).

4.10. Deprotection of phthalimide group to yield dyes **12a–f**

Method A. A mixture of dye **8b**, **9b,c**, **11b,c** (1 mmol) and a 38% solution of MeNH₂ in abs EtOH (80 mL) was stirred at room temperature for 2 h and then kept overnight at 5 °C. The solvent was evaporated in vacuo, the residue was washed with hot EtOAc and dissolved in EtOH and then HClO₄ (70% (aq), 260 μ L, 3 mmol) was added to this solution. After cooling to –10 °C, the crystalline precipitate was filtered off, washed with EtOAc and diethyl ether and dried in air. Yield **12a**: 344 mg (44%). Yield **12c**: 300 mg (40%).

Yield **12d**: 201 mg (25%). Yield **12e**: 323 mg (42%). Yield **12f**: 407 mg (51%).

Method B. Hydrazine monohydrate (1.00 mL, 20 mmol) was added to a stirred solution of dye **9a,b**, **11c** (1 mmol) in a mixture of CH₂Cl₂ (100 mL) and MeOH (40 mL). The reaction mixture was stirred under reflux for 3–6 h and cooled to room temperature. The precipitate of 2,3-dihydrophthalazine-1,4-dione that formed was filtered off, washed with hot benzene and EtOH. The filtrate was evaporated in vacuo, the residue was dissolved in DMSO (10 mL) (in the case of **12b**) or EtOH (10 mL) (in the case of **12c,f**), and HClO₄ (70% (aq), 260 μL, 3 mmol) was added to this solution. The resulting mixture was diluted with water (200 mL) and the precipitate that formed was filtered off and washed with water, a mixture of EtOH (20 mL) and water (20 mL), then with diethyl ether, and dried in air. Yield **12b**: 89 mg (17%). Yield **12c**: 335 mg (45%). Yield **12f**: 295 mg (37%).

4.10.1. 3-(6-Ammoniohexyl)-2-((Z)-[3-(6-ammoniohexyl)-1,3-benzothiazol-2(3H)-ylidene]methyl)-1,3-benzothiazol-3-ium triperchlorate (**12a**). Dye **12a** was isolated as a yellow solid. Found C, 41.54; H, 5.09; N, 6.98. C₂₇H₃₉Cl₃N₄O₁₂S₂ requires C, 41.46; H, 5.03; N, 7.16%. Mp 142–143 °C; UV–vis (MeCN) λ_{max} 426 nm (ε 66,500 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 416 nm, λ_{max}^f 477 nm; δ_H (DMSO-d₆) 1.32–1.38, 1.41–1.46, 1.47–1.52 and 1.57–1.81 (16H, 4m, 8CH₂), 2.71–2.77 (4H, m, 2CH₂NH₃⁺), 4.65 (4H, br t, 2CH₂N⁺), 6.68 (1H, s, meso-H), 7.51–7.54 (2H, m, 2×6-H), 7.57 (6H, br s, 2NH₃⁺), 7.69–7.72 (2H, m, 2×5-H), 7.91 (2H, d, J 8.5 Hz, 2×4-H), 8.25 (2H, d, J 7.9 Hz, 2×7-H); δ_C (DMSO-d₆) 25.37, 25.43, 26.65 and 26.74 (8CH₂), 38.64 (2CH₂NH₃⁺), 45.97 (2CH₂N⁺), 82.39 (meso-C), 113.73 (2×4-C), 123.53 (2×7-C), 124.81 (2×6-C), 124.97 (2×7a-C), 128.54 (2×5-C), 140.13 (2×3a-C), 161.63 (2×2-C).

4.10.2. 3-(3-Ammoniopropyl)-2-((1E,3Z)-3-[3-(3-ammoniopropyl)-1,3-benzothiazol-2(3H)-ylidene]prop-1-en-1-yl)-1,3-benzothiazol-3-ium triperchlorate (**12b**). Dye **12b** was isolated as violet crystals. Found C, 35.25; H, 3.68; N, 6.67. C₂₃H₂₉Cl₃N₄O₁₂S₂·0.5HClO₄·0.5DMSO requires C, 35.44; H, 4.03; N, 6.89%. Mp 230–231 °C; UV–vis (MeCN) λ_{max} 558 nm (ε 78,000 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 548 nm, λ_{max}^f 580 nm; δ_H (DMSO-d₆) 2.01–2.08 (4H, m, 2CH₂CH₂NH₃⁺), 2.94–3.00 (4H, m, 2CH₂NH₃⁺), 4.39–4.44 (4H, m, 2CH₂N⁺), 6.57 (2H, br d, 2×α-H), 7.45–7.48 (2H, m, 2×6-H), 7.62 (2H, m, 2×5-H), 7.72 (6H, br s, 2NH₃⁺), 7.81–7.88 (3H, m, meso-H, 2×4-H), 8.03–8.04 (2H, m, 2×7-H); δ_C (DMSO-d₆) 25.34 (2CH₂CH₂NH₃⁺), 36.22 (2CH₂NH₃⁺), 43.34 (2CH₂N⁺), 98.50 (2×α-C), 113.33 (2×4-C), 123.11 (2×7-C), 125.01 (2×7a-C), 125.35 (2×6-C), 128.02 (2×5-C), 141.06 (2×3a-C), 146.76 (meso-C), 164.94 (2×2-C).

4.10.3. 1-(3-Ammoniopropyl)-2-((1E,3E)-3-[1-(3-ammoniopropyl)-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene]prop-1-en-1-yl)-3,3-dimethyl-3H-indolium triperchlorate (**12c**). Dye **12c** was isolated as violet crystals. Found C, 44.76; H, 5.79; N, 7.14. C₂₉H₄₁Cl₃N₄O₁₂·2H₂O requires C, 44.65; H, 5.82; N, 7.18%. Mp 261–265 °C; UV–vis (MeCN) λ_{max} 546 nm (ε 106,800 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 536 nm, λ_{max}^f 569 nm; δ_H (DMSO-d₆) 1.73 (12H, s, H, s, 2CMe₂), 2.02–2.07 (4H, m, 2CH₂CH₂NH₃⁺), 2.94–2.97 (4H, m, 2CH₂NH₃⁺), 4.21 (4H, br t, 2CH₂N⁺), 6.50 (2H, d, J 13.6 Hz, 2×α-H), 7.33–7.36 (2H, m, 2×5-H), 7.47–7.50 (2H, m, 2×6-H), 7.53 (2H, d, J 8.0 Hz, 2×7-H), 7.67–7.72 (8H, m, 2×4-H, 2NH₃⁺), 8.40 (1H, t, J 13.6 Hz, meso-H); δ_C (DMSO-d₆) 25.12 (2CH₂CH₂NH₃⁺), 27.32 (2CMe₂), 36.38 (2CH₂NH₃⁺), 41.96 (2CH₂N⁺), 48.92 (2×3-C), 102.33 (2×α-C), 111.31 (2×7-C), 122.52 (2×4-C), 125.35 (2×5-C), 128.51 (2×6-C), 140.51 (2×3a-C), 141.62 (2×7a-C), 150.15 (meso-C), 174.23 (2×2-C).

4.10.4. 3-(3-Ammoniopropyl)-2-((1E,3E)-3-[3-(3-ammoniopropyl)-1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene]prop-1-en-1-yl)-1,1-dimethyl-1H-benzo[e]indolium triperchlorate (**12d**). Dye **12d** was isolated as a violet solid. Found C, 51.66; H, 5.53; N, 6.24.

C₃₇H₄₅Cl₃N₄O₁₂·H₂O requires C, 51.55; H, 5.50; N, 6.50%. Mp 274–275 °C; UV–vis (MeCN) λ_{max} 587 nm (ε 90,100 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 577 nm, λ_{max}^f 611 nm; δ_H (DMSO-d₆) 2.07 (12H, s, 2CMe₂), 2.12–2.18 (4H, m, 2CH₂CH₂NH₃⁺), 2.99–3.08 (4H, m, 2CH₂NH₃⁺), 4.36–4.38 (4H, m, 2CH₂N⁺), 6.57 (2H, d, J 13.3 Hz, 2×α-H), 7.56–7.59 (2H, m, 2×7-H), 7.71–7.74 (8H, m, 2×8-H, 2NH₃⁺), 7.83 (2H, d, J 9.0 Hz, 2×4-H), 8.11 (2H, d, J 8.0 Hz, 2×6-H), 8.16 (2H, d, J 9.0 Hz, 2×5-H), 8.31 (2H, d, J 8.0 Hz, 2×9-H), 8.66 (1H, br t, meso-H); δ_C (DMSO-d₆) 26.16 (2CH₂CH₂NH₃⁺), 26.89 (2CMe₂), 36.28 (2CH₂NH₃⁺), 41.02 (2CH₂N⁺), 50.42 (2×1-C), 101.61 (2×α-C), 111.11 (2×4-C), 121.76 (2×9-C), 124.87 (2×7-C), 127.09 (2×9a-C), 127.62 (2×8-C), 129.58 (2×6-C), 130.14 (2×5-C), 131.34 (2×5a-C), 133.06 (2×9b-C), 138.94 (2×3a-C), 148.71 (meso-C), 175.50 (2×2-C).

4.10.5. 1-(3-Ammoniopropyl)-2-((1E,3E,5E)-5-[1-(3-ammoniopropyl)-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene]penta-1,3-dien-1-yl)-3,3-dimethyl-3H-indolium triperchlorate (**12e**). Dye **12e** was isolated as a blue solid. Found C, 47.07; H, 5.47; N, 7.38. C₃₁H₄₃Cl₃N₄O₁₂·H₂O requires C, 47.25; H, 5.76; N, 7.11%. Mp 196–198 °C; UV–vis (MeCN) λ_{max} 640 nm (ε 141,000 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 630 nm, λ_{max}^f 667 nm; δ_H (DMSO-d₆) 1.70 (12H, s, 2CMe₂), 1.95–2.01 (4H, m, 2CH₂CH₂NH₃⁺), 2.88–2.96 (4H, m, 2CH₂NH₃⁺), 4.19–4.22 (4H, m, 2CH₂N⁺), 6.33 (2H, d, J 13.4 Hz, 2×α-H), 6.54–6.56 (1H, m, meso-H), 7.27–7.31 (2H, m, 2×5-H), 7.40–7.43 (4H, m, 2×6-H, 2×7-H), 7.59–7.72 (8H, m, 2NH₃⁺, 2×4-H), 8.36–8.41 (2H, m, 2×β-H); δ_C (DMSO-d₆) 25.09 (2CH₂CH₂NH₃⁺), 27.22 (2CMe₂), 36.84 (2CH₂NH₃⁺), 42.86 (2CH₂N⁺), 48.90 (2×3-C), 103.06 (2×α-C), 111.05 (2×7-C), 122.67 (2×4-C), 124.70 (2×5-C), 125.40 (meso-C), 128.26 (2×6-C), 140.96 (2×3a-C), 141.83 (2×7a-C), 154.13 (2×β-C), 172.77 (2×2-C).

4.10.6. 1-(4-Ammoniobutyl)-2-((1E,3E,5E)-5-[1-(4-ammoniobutyl)-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene]penta-1,3-dien-1-yl)-3,3-dimethyl-3H-indolium triperchlorate (**12f**). Dye **12f** was isolated as a blue solid. Found C, 48.61; H, 5.71; N, 7.08. C₃₃H₄₇Cl₃N₄O₁₂·H₂O requires C, 48.57; H, 6.05; N, 6.87%. Mp >180 °C; UV–vis (MeCN) λ_{max} 641 nm (ε 123,800 L mol⁻¹ cm⁻¹); fluorescence (MeCN) λ_{ex} 631 nm, λ_{max}^f 668 nm; δ_H (DMSO-d₆) 1.70 (12H, s, 2CMe₂), 1.58–1.64 and 1.73–1.77 (8H, 2m, 2CH₂CH₂), 2.81–2.86 (4H, m, 2CH₂NH₃⁺), 4.14–4.17 (4H, m, 2CH₂N⁺), 6.30 (2H, d, J 14.0 Hz, 2×α-H), 6.54 (1H, t, J 12.2 Hz, meso-H), 7.25–7.28 (2H, m, 2×5-H), 7.41–7.44 (4H, m, 2×6-H, 2×7-H), 7.60 (6H, br s, 2NH₃⁺), 7.63–7.64 (2H, m, 2×4-H), 8.33–8.38 (2H, m, 2×β-H); δ_C (DMSO-d₆) 24.02 and 24.23 (2CH₂CH₂), 27.05 (2CMe₂), 38.51 (2CH₂NH₃⁺), 42.73 (2CH₂N⁺), 48.85 (2×3-C), 103.08 (2×α-C), 111.07 (2×7-C), 122.39 (2×4-C), 124.71 (2×5-C), 125.39 (meso-C), 128.31 (2×6-C), 141.00 (2×3a-C), 141.89 (2×7a-C), 154.10 (2×β-C), 172.79 (2×2-C).

4.11. X-ray diffraction study

The crystals of dyes **8b** and **9a,b** were grown using a slow evaporation of a solution of dye in a CHCl₃–CH₂Cl₂–MeCN mixture at ambient temperature. The single crystals were coated with perfluorinated oil and mounted on a Bruker SMART-CCD diffractometer (graphite monochromatized Mo Kα radiation (λ=0.71073 Å), ω scan mode) under a stream of cooled nitrogen (T=120.0(2) K for **9a,b** and 150(2) K for **8b**). The sets of experimental reflections were measured and the structures were solved by direct methods and refined by the full matrix least-squares against R² with anisotropic thermal parameters for all non-hydrogen atoms (except for the oxygen atoms of the disordered perchlorate anions in **8b** and **9b**). The hydrogen atoms were fixed at calculated positions of the carbon atoms and then refined using a riding model. Four water solvate molecules disordered near a symmetry center of the crystal were found in structure **8b**·1.75H₂O; their occupancies are 0.75, 0.50, 0.25, and 0.25. The ISOR command was applied to make better the anisotropic parameters of these oxygen atoms. The hydrogen atoms of the water

Table 2
Crystallographic data and structure refinement details for **8b**·1.75H₂O, **9a**·0.6CH₂Cl₂·0.4CHCl₃ and **9b**·2MeCN

Parameter	8b ·1.75H ₂ O	9a ·0.6CH ₂ Cl ₂ ·0.4CHCl ₃	9b ·2MeCN
Empirical formula	C ₄₃ H _{44.5} Cl ₄ N ₄ O _{9.75} S ₂	C ₄₀ H _{32.6} Cl _{3.4} N ₄ O ₈ S ₂	C ₄₉ H ₄₉ Cl ₆ O ₈
Formula weight	872.90	881.95	885.39
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P $\bar{1}$	P $\bar{1}$
Unit cell: dimensions (Å),	<i>a</i> =20.486(3), <i>b</i> =18.008(3), <i>c</i> =22.511(3)	<i>a</i> =9.5883(11), <i>b</i> =14.3371(17), <i>c</i> =14.9796(18)	<i>a</i> =11.7498(3), <i>b</i> =14.0094(4), <i>c</i> =14.6629(4)
Angle (°)	β =96.954(2)	α =69.794(5), β =87.688(5), γ =89.958(5)	α =107.330(1), β =96.328(1), γ =103.545(1)
Volume (Å ³)	8243(2)	1930.7(4)	2197.44(10)
<i>Z</i> , <i>D</i> _{calcd} [Mg/m ³]	8, 1.407	2, 1.517	2, 1.338
μ [mm ⁻¹]	0.258	0.434	0.150
<i>F</i> (000)	3660	909	932
Crystal size (mm ³)	0.12×0.10×0.08	0.48×0.42×0.38	0.42×0.28×0.16
θ Range (°)	1.51–29.00	1.45–25.00	1.48–29.00
Index ranges	−27≤ <i>h</i> ≤27, −24≤ <i>k</i> ≤24, −30≤ <i>l</i> ≤30	−11≤ <i>h</i> ≤11, −14≤ <i>k</i> ≤17, −16≤ <i>l</i> ≤17	−15≤ <i>h</i> ≤16, −19≤ <i>k</i> ≤19, −19≤ <i>l</i> ≤19
Reflections collected	43,139	11,369	23,403
Independent reflections	10,909 [R(int)=0.0883]	6595 [R(int)=0.0535]	11,519 [R(int)=0.0476]
Reflections with <i>I</i> >2σ(<i>I</i>)	4922	5536	6796
Goodness-of-fit on <i>F</i> ²	0.991	1.145	0.999
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.0828, <i>wR</i> ₂ =0.2133	<i>R</i> ₁ =0.2362, <i>wR</i> ₂ =0.5266	<i>R</i> ₁ =0.0680, <i>wR</i> ₂ =0.1872
<i>R</i> indices (all data)	<i>R</i> ₁ =0.1831, <i>wR</i> ₂ =0.2647	<i>R</i> ₁ =0.2504, <i>wR</i> ₂ =0.5304	<i>R</i> ₁ =0.1151, <i>wR</i> ₂ =0.2044
Largest diff. peak and hole (e [−] Å ^{−3})	0.740 and −0.570	1.755 and −1.345	0.596 and −0.589

molecules were not located. The perchlorate anion in this structure is strongly disordered over four positions (rotation about the center of gravity of the anion) with a 0.40:0.30:0.20:0.10 occupancy ratio. The SADI command was applied to constrain the geometry of this anion. In the crystal of **9a**, CH₂Cl₂ and CHCl₃ solvate molecules were found, which occupy the same position in the unit cell in a 0.60:0.40 ratio. The SADI and ISOR commands were applied in order to constrain the solvate molecules and anisotropic parameters of some non-hydrogen atoms in structure **9a**·0.6CH₂Cl₂·0.4CHCl₃. Disordered structure units have a rather large contribution to structure factors of **8b** and **9b**. Since their positions were determined with a low accuracy, this resulted in a rather low accuracy of these structures as a whole. Nevertheless, the determination of the general structure of the main molecules and relative positions of all structure units in the crystal unit cells does not cast doubt. Two MeCN solvate molecules were found in the crystal of **9b**. The perchlorate anion in this structure is disordered over three positions with a 0.60:0.30:0.10 occupancy ratio. The SADI command was applied to constrain the geometry of this anion. All the calculations were performed using the SHELXTL-Plus software.²¹ The crystal parameters and structure refinement details are given in Table 2. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-933535 (**8b**·1.75H₂O), CCDC-907649 (**9a**·0.6CH₂Cl₂·0.4CHCl₃) and CCDC-907650 (**9b**·2MeCN). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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