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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 $MeNH_2$ were selected. The obtained dyes with ammonium groups capable of hydrogen bonding are promising as components of light-sensitive supramolecular systems.

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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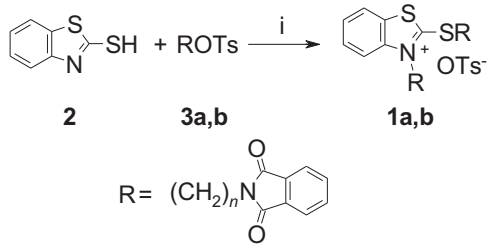
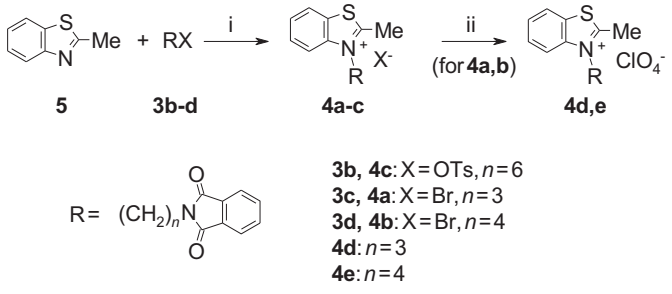
Some unsymmetrical mono-, *meso*-methyltri- and pentamethine cyanine dyes containing phthalimide groups or amino group hydrobromides as terminal groups on the *N*-substituents of heterocyclic residues have been reported.[11] However, these dyes have not been isolated in a pure state and their structures 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-phthalimidohexyl 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).

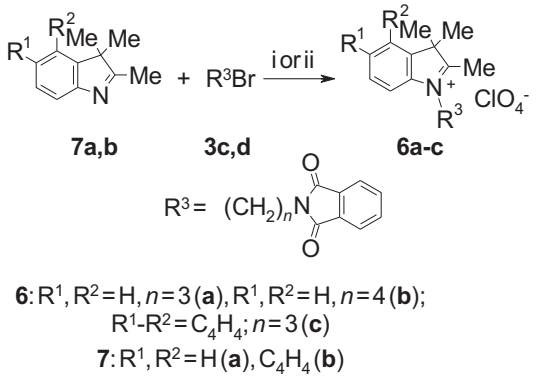


Scheme 2. Synthesis of 2-methylbenzothiazolium salts **4a**–**e**. Reagents and conditions: (i) heating, 140–150 °C (**4a**: 92%; **4b**: 80%; **4c**: 67% yield); (ii) $HClO_4$ (70%, aq), MeOH (**4d**: 96%; **4e**: 94% yield).

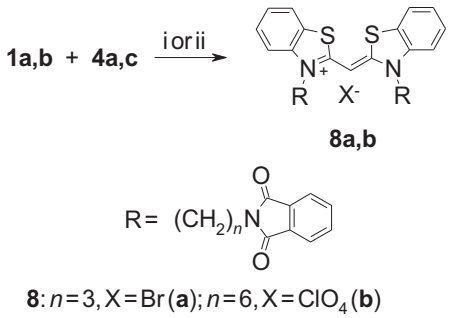
Salts **6a**–**c** were prepared by the reaction of heterocyclic bases **7a**,**b** with phthalimidoalkyl derivatives **3c**,**d**; the reaction was carried out in acetonitrile under inert atmosphere (Scheme 3).

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).

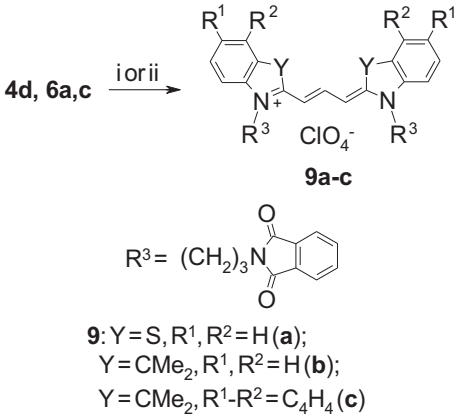
Trimethine dyes **9a**–**c** containing phthalimidoalkyl substituents at nitrogen atoms were prepared using a described procedure[14] by the reaction of quaternary salts **4d**, **6a**,**c** with triethyl orthoformate in pyridine or in acetic anhydride induced by triethylamine (Scheme 5). The use of 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. $HClO_4$ (70%, aq), EtOH (**6a**: 51%; **6b**: 85% yield); (ii) 1. MeCN, argon, sealed tube, 110 °C; 2. $HClO_4$ (70%, aq), EtOH (**6c**: 40% yield).

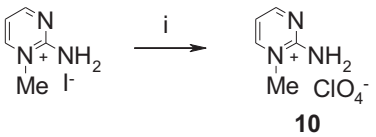


Scheme 4. Synthesis of monomethine cyanine dyes **8a**,**b**. Reagents and conditions: (i) Et_3N, EtOH, reflux (**8a**: 60% yield); (ii) 1. Et_3N, EtOH, reflux; 2. $HClO_4$ (70%, aq), EtOH (**8b**: 61% yield).



Scheme 5. Synthesis of trimethine cyanine dyes **9a**–**c**. Reagents and conditions: (i) $CH(OEt)_3$, Py, reflux (**9a**: 60%; **9b**: 33% yield); (ii) $CH(OEt)_3$, Et_3N, Ac_2O, reflux (**9c**: 63% yield).

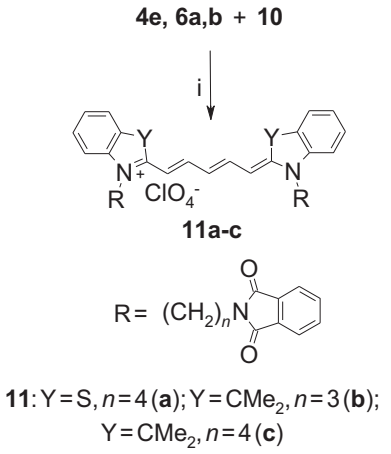
Pentamethine dyes were prepared using 2-amino-1-methylpyrimidinium perchlorate. For this purpose, 2-amino-1-methylpyrimidinium iodide, prepared by a known procedure,[15] was converted to perchlorate **10** by treatment with an excess of $HClO_4$ in methanol (Scheme 6).



Scheme 6. Synthesis of salt **10**. Reagents and conditions: (i) $HClO_4$ (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) Et_3N, Py or Ac_2O, 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 CH_2N^+ protons in the NOESY spectra of dyes **9a**,**b**, whereas cross-peaks due to coupling of CH_2N^+ with *meso*-H are absent. Contrarily, in the case of monomethine dye **8b**, the expected NOESY cross-peak due to the CH_2N^+ 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

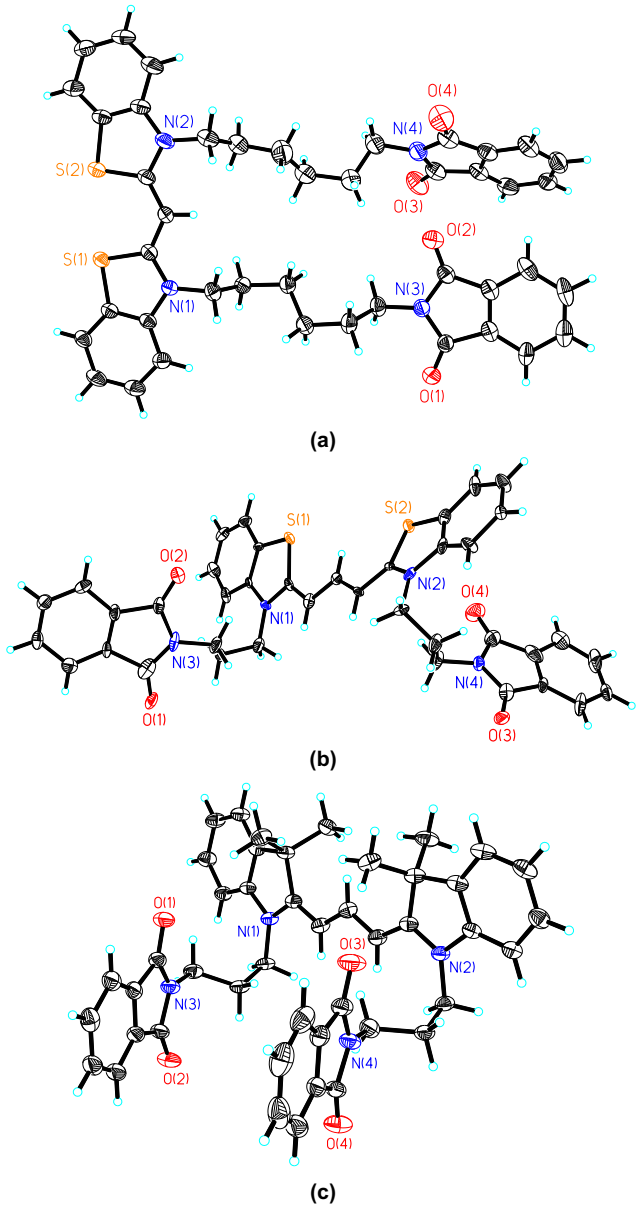
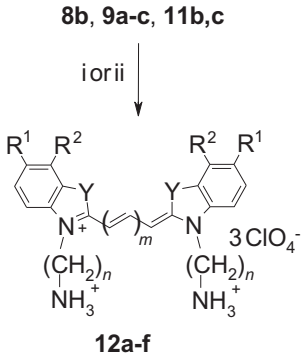


Fig. 1. The cations of dyes in structures of (*a*) **8b**·1.75H_2O, (*b*) **9a**·0.6CH_2Cl_2·0.4$CHCl_3$ and (*c*) **9b**·2MeCN. Thermal anisotropic ellipsoids are drawn at the (*a*) 40% and (*b*, *c*) 50% probability level.

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 CMe_2 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 CH_2Cl_2–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 $HClO_4$ 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 $MeNH_2$ in absolute ethanol, the reaction occurs under milder conditions and remaining methylamine is easily distilled off under reduced pressure. *N*,*N*′-Dimethylphthalamide 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 $HClO_4$ 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 $MeNH_2$ in abs EtOH; 2. $HClO_4$ (70%, aq), EtOH; (ii) 1. $N_2H_4{\cdot}H_2O$, CH_2Cl_2/MeOH, reflux; 2. $HClO_4$ (70%, aq), EtOH.

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

Dye	*m*	*n*	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_4H_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 ^{13}C 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 $^1H-^{13}C$ 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 ($C_{dye}=1\times10^{-5}$ 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 ($C_{dye}=1\times10^{-5}$ 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. $C_{36}H_{31}N_3O_7S_3{\cdot}TsOH{\cdot}H_2O$ 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 $C_{29}H_{24}N_3O_4S_2^+$ 542.1208); δ_H (DMSO-d_6) 2.14–2.24 (4H, m, $2CH_2$), 2.28 (3H, s, Me), 3.65 (2H, br t, CH_2S), 3.74–3.81 (4H, m, $2CH_2N$), 4.69–4.72 (2H, m, CH_2N^+), 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 ($2CH_2$), 33.67 and 34.81 ($2CH_2N$), 35.98 (CH_2S), 47.91 (CH_2N^+), 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. $C_{42}H_{43}N_3O_7S_3{\cdot}TsOH{\cdot}H_2O$ 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 $C_{35}H_{36}N_3O_4S_2^+$: 626.2147); δ_H (DMSO-d_6) 1.29–1.64 (12H, m, $6CH_2$), 1.80–1.83 (2H, m, CH_2), 1.88–1.91 (2H, m, CH_2), 2.28 (3H, s, Me), 3.53–3.58 (4H, m, $2CH_2N$), 3.59–3.62 (2H, m, CH_2S), 4.58 (2H, br t, CH_2N^+), 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 (8CH_2), 35.88 (CH_2S), 37.11 (2CH_2N), 49.87 (CH_2N^+), 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. $C_{19}H_{17}BrN_2O_2S$ 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, C$H_2$$CH_2$N), 3.20 (3H, s, Me), 3.85 (2H, br t, CH_2N), 4.80–4.83 (2H, m, CH_2N^+), 7.77–7.80 (1H, m, 6-H), 7.84–7.90 (5H, m, 5-H, 4′-H, 5′-H, 6′-H, 7′-H), 8.36 (1H, d, *J* 8.3 Hz, 4-H), 8.41 (1H, d, *J* 7.8 Hz, 7-H); δ_C (DMSO-d_6) 16.69 (Me), 26.49 (C$H_2$$CH_2$N), 34.87 ($CH_2$N), 47.17 ($CH_2N^+$), 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. $C_{20}H_{19}BrN_2O_2S$ 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, C$H_2$$CH_2$N), 1.87–1.93 (2H, m, C$H_2$$CH_2N^+$), 3.21 (3H, s, Me), 3.64 (2H, t, *J* 6.8 Hz, CH_2N), 4.72–4.75 (2H, m, CH_2N^+), 7.77–7.80 (1H, m, 6-H), 7.83–7.89 (5H, m, 5-H, 4′-H, 5′-H, 6′-H, 7′-H), 8.36 (1H, d, *J* 8.5 Hz, 4-H), 8.44 (1H, d, *J* 8.0 Hz, 7-H); δ_C (DMSO-d_6) 16.72 (Me), 25.01 and 25.11 ($CH_2$$CH_2$), 36.80 ($CH_2$N), 48.67 ($CH_2N^+$), 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. $C_{29}H_{30}N_2O_5S_2$ 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, 4CH_2), 2.26 (3H, s, *Me*Ar), 3.19 (3H, s, *Me*Het), 3.56 (2H, t, *J* 7.0 Hz, CH_2N), 4.68 (2H, br t, CH_2N^+), 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 (*Me*Het), 20.65 (*Me*Ar), 25.29, 25.74, 27.48 and 27.61 (4CH_2), 37.16 (CH_2N), 48.98 (CH_2N^+), 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. $C_{19}H_{17}ClN_2O_6S$ 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, C$H_2$$CH_2$N), 3.20 (3H, s, Me), 3.85 (2H, t, *J* 6.8 Hz, CH_2N), 4.80–4.83 (2H, m, CH_2N^+), 7.77–7.80 (1H, m, 6-H), 7.84–7.90 (5H, m, 5-H, 4′-H, 5′-H, 6′-H, 7′-H), 8.37 (1H, d, *J* 8.5 Hz, 4-H), 8.41 (1H, d, *J* 8.2 Hz, 7-H); δ_C (DMSO-d_6) 16.69 (Me), 26.49 (C$H_2$$CH_2$N), 34.87 ($CH_2$N), 47.17 ($CH_2N^+$), 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. $C_{20}H_{19}ClN_2O_6S$ 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, C$H_2$$CH_2$N), 1.88–1.94 (2H, m, C$H_2$$CH_2N^+$), 3.21 (s, 3H, Me), 3.64 (2H, t, *J* 6.8 Hz, CH_2N), 4.72–4.75 (2H, m, CH_2N^+), 7.79 (m, 1H, 6-H), 7.82–7.89 (5H, m, 5-H, 4′-H, 5′-H, 6′-H, 7′-H), 8.35 (1H, d, *J* 8.5 Hz, 4-H), 8.42 (1H, d, *J* 8.2 Hz, 7-H); δ_C (DMSO-d_6) 16.72 (Me), 25.01 and 25.11 ($CH_2$$CH_2$), 36.80 ($CH_2$N), 48.67 ($CH_2N^+$), 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 3*H*-indolium and 1*H*-benzo[*e*]indolium salts 6a–c

Method A. A mixture of 2,3,3-trimethyl-3*H*-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-1*H*-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 $HClO_4$ (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. $C_{22}H_{23}ClN_2O_6$ 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, CMe_2), 2.20–2.26 (2H, m, CH_2), 2.83 (3H, s, Me), 3.81 (2H, t, *J* 6.7 Hz, CH_2N), 4.55–4.58 (2H, m, CH_2N^+), 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 (CMe_2), 26.19 (C$H_2$$CH_2$N), 34.76 ($CH_2$N), 45.58 ($CH_2N^+$), 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. $C_{23}H_{25}ClN_2O_6$ requires C, 59.94; H, 5.47; N, 6.08%. Mp 240–243 °C. IR (KBr) 1709 (C=O) cm^{-1}; δ_H (DMSO-d_6) 1.53 (6H, s, CMe_2), 1.75–1.80 (2H, m, CH_2CH_2N), 1.87–1.93 (2H, m, $CH_2CH_2N^+$), 2.83 (3H, s, Me), 3.64 (2H, t, *J* 6.6 Hz, CH_2N), 4.47 (2H, br t, CH_2N^+), 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-d_6) 13.84 (Me), 21.91 (CMe_2), 24.46 and 24.94 (CH_2CH_2), 36.77 (CH_2N), 47.05 (CH_2N^+), 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. $C_{26}H_{25}ClN_2O_6$ requires C, 62.84; H, 5.07; N, 5.64%. Mp 231–232 °C. IR (KBr) 1711 (C=O) cm^{-1}; δ_H (DMSO-d_6) 1.77 (6H, s, CMe_2), 2.26–2.32 (2H, m, CH_2CH_2N), 2.94 (3H, s, Me), 3.85 (2H, t, *J* 6.7 Hz, CH_2N), 4.69 (2H, br t, CH_2N^+), 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-d_6) 13.70 (Me), 21.49 (CMe_2), 26.36 (CH_2CH_2N), 34.76 (CH_2N), 45.80 (CH_2N^+), 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 $HClO_4$ (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. $C_{37}H_{29}BrN_4O_4S_2\cdot H_2O$ 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-d_6) 2.16–2.23 (4H, m, $2CH_2CH_2N$), 3.77 (4H, br t, $2CH_2N$), 4.80 (4H, br t, $2CH_2N^+$), 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-d_6) 25.42 ($2CH_2CH_2N$), 34.80 ($2CH_2N$), 43.82 ($2CH_2N^+$), 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. $C_{43}H_{41}ClN_4O_8S_2\cdot H_2O$ 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-d_6) 1.27–1.33, 1.44–1.49, 1.51–1.57 and 1.72–1.78 (16H, 4m, $8CH_2$), 3.49 (4H, t, *J* 7.0 Hz, $2CH_2N$), 4.62 (4H, br t, $2CH_2N^+$), 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-d_6) 25.54, 26.01, 26.78 and 27.70 ($8CH_2$), 37.12 ($2CH_2N$), 46.05 ($2CH_2N^+$), 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. $C_{39}H_{31}ClN_4O_8S_2$ 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-d_6) 2.10–2.16 (4H, m, $2CH_2CH_2N$), 3.77 (4H, t, *J* 7.1 Hz, $2CH_2N$), 4.41–4.46 (4H, m, $2CH_2N^+$), 4.62 (4H, br t, $2CH_2N^+$),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-d_6) 26.05 ($2CH_2CH_2N$), 35.03 ($2CH_2N$), 44.07 ($2CH_2N^+$), 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. $C_{45}H_{43}ClN_4O_8$ 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-d_6) 1.72 (12H, s, $2CMe_2$), 2.10–2.15 (4H, m, $2CH_2CH_2N$), 3.72 (4H, t, *J* 7.1 Hz, $2CH_2N$), 4.25 (4H, br t, $2CH_2N^+$), 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 (2*C*H$_2$CH$_2$N), 27.32 (2*C*Me$_2$), 35.03 (2CH$_2$N), 41.52 (2CH$_2$N$^+$), 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-[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. $C_{53}H_{47}ClN_4O_8 \cdot H_2O$ 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, λ^f_{max} 612 nm. IR (KBr) 1710 (C=O) cm^{-1}; δ_H (DMSO-d_6) 2.03 (12H, s, 2CMe$_2$), 2.17–2.23 (4H, m, 2C*H*$_2$CH$_2$N), 3.76 (4H, br t, 2CH$_2$N), 4.40 (4H, br t, 2CH$_2$N$^+$), 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 (2*C*H$_2$CH$_2$N), 26.99 (2*C*Me$_2$), 35.05 (2CH$_2$N), 41.71 (2CH$_2$N$^+$), 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. $C_5H_8ClN_3O_4$ requires C, 28.65; H, 3.85; N, 20.05%. Mp 190–193 °C (decomp.). IR (KBr) 3344, 3289 (NH$_2$) 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, NH$_2$).

4.9. Synthesis of pentamethine cyanine dyes 11a–c

Method A. Triethylamine (139 μL, 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 μL, 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. $C_{43}H_{37}ClN_4O_8S_2$ 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, λ^f_{max} 685 nm. IR (KBr) 1710 (C=O) cm^{-1}; δ_H (DMSO-d_6) 1.73–1.78 (8H, m, 2CH$_2$CH$_2$), 3.63–3.65 (4H, m, 2CH$_2$N), 4.33–4.35 (4H, m, 2CH$_2$N$^+$), 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 (4CH$_2$CH$_2$), 36.88 (2CH$_2$N), 45.48 (2CH$_2$N$^+$), 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. $C_{47}H_{45}ClN_4O_8 \cdot 1.5H_2O$ 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, λ^f_{max} 671 nm. IR (KBr) 1709 (C=O) cm^{-1}; δ_H (DMSO-d_6) 1.69 (12H, s, 2CMe$_2$), 2.03–2.09 (4H, m, 2C*H*$_2$CH$_2$N), 3.71 (4H, br t, 2CH$_2$N), 4.22–4.25 (4H, m, 2CH$_2$N$^+$), 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 (2*C*H$_2$CH$_2$N), 26.98 (2*C*Me$_2$), 34.97 (2CH$_2$N), 41.10 (2CH$_2$N$^+$), 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. $C_{49}H_{49}ClN_4O_8 \cdot 2H_2O$ 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, λ^f_{max} 671 nm. IR (KBr) 1709 (C=O) cm^{-1}; δ_H (DMSO-d_6) 1.66 (12H, s, 2CMe$_2$), 1.71–1.76 (8H, m, 2CH$_2$CH$_2$), 3.61–3.64 (4H, m, 2CH$_2$N), 4.11–4.16 (4H, m, 2CH$_2$N$^+$), 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 (2CH$_2$CH$_2$), 27.01 (2*C*Me$_2$), 36.90 (2CH$_2$N), 42.81 (2CH$_2$N$^+$), 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 MeNH$_2$ 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 HClO$_4$ (70% (aq), 260 μL, 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 CH_2Cl_2 (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 $HClO_4$ (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. $C_{27}H_{39}Cl_3N_4O_{12}S_2$ 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^{f}_{max} 477 nm; δ_H (DMSO-d_6) 1.32–1.38, 1.41–1.46, 1.47–1.52 and 1.57–1.81 (16H, 4m, 8CH_2), 2.71–2.77 (4H, m, 2$CH_2NH_3^+$), 4.65 (4H, br t, 2CH_2N^+), 6.68 (1H, s, *meso*-H), 7.51–7.54 (2H, m, 2×6-H), 7.57 (6H, br s, 2NH_3^+), 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-d_6) 25.37, 25.43, 26.65 and 26.74 (8CH_2), 38.64 (2$CH_2NH_3^+$), 45.97 (2CH_2N^+), 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. $C_{23}H_{29}Cl_3N_4O_{12}S_2\cdot 0.5HClO_4\cdot 0.5$DMSO 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^{f}_{max} 580 nm; δ_H (DMSO-d_6) 2.01–2.08 (4H, m, 2$CH_2CH_2NH_3^+$), 2.94–3.00 (4H, m, 2$CH_2NH_3^+$), 4.39–4.44 (4H, m, 2CH_2N^+), 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, 2NH_2^+), 7.81–7.88 (3H, m, *meso*-H, 2×4-H), 8.03–8.04 (2H, m, 2×7-H); δ_C (DMSO-d_6) 25.34 (2$CH_2CH_2NH_3^+$), 36.22 (2$CH_2NH_3^+$), 43.34 (2CH_2N^+), 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. $C_{29}H_{41}Cl_3N_4O_{12}\cdot 2H_2O$ 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^{f}_{max} 569 nm; δ_H (DMSO-d_6) 1.73 (12H, s, H, s, 2CMe_2), 2.02–2.07 (4H, m, 2$CH_2CH_2NH_3^+$), 2.94–2.97 (4H, m, 2$CH_2NH_3^+$), 4.21 (4H, br t, 2CH_2N^+), 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, 2NH_3^+), 8.40 (1H, t, *J* 13.6 Hz, *meso*-H); δ_C (DMSO-d_6) 25.12 (2$CH_2CH_2NH_3^+$), 27.32 (2CMe_2), 36.38 (2$CH_2NH_3^+$), 41.96 (2CH_2N^+), 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. $C_{37}H_{45}Cl_3N_4O_{12}\cdot H_2O$ 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^{f}_{max} 611 nm; δ_H (DMSO-d_6) 2.07 (12H, s, 2CMe_2), 2.12–2.18 (4H, m, 2$CH_2CH_2NH_3^+$), 2.99–3.08 (4H, m, 2$CH_2NH_3^+$), 4.36–4.38 (4H, m, 2CH_2N^+), 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, 2NH_3^+), 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-d_6) 26.16 (2$CH_2CH_2NH_3^+$), 26.89 (2CMe_2), 36.28 (2$CH_2NH_3^+$), 41.02 (2CH_2N^+), 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. $C_{31}H_{43}Cl_3N_4O_{12}\cdot H_2O$ 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^{f}_{max} 667 nm; δ_H (DMSO-d_6) 1.70 (12H, s, 2CMe_2), 1.95–2.01 (4H, m, 2$CH_2CH_2NH_3^+$), 2.88–2.96 (4H, m, 2$CH_2NH_3^+$), 4.19–4.22 (4H, m, 2CH_2N^+), 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, 2NH_3^+, 2×4-H), 8.36–8.41 (2H, m, 2×β-H); δ_C (DMSO-d_6) 25.09 (2$CH_2CH_2NH_3^+$), 27.22 (2CMe_2), 36.84 (2$CH_2NH_3^+$), 42.86 (2CH_2N^+), 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. $C_{33}H_{47}Cl_3N_4O_{12}\cdot H_2O$ 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^{f}_{max} 668 nm; δ_H (DMSO-d_6) 1.70 (12H, s, 2CMe_2), 1.58–1.64 and 1.73–1.77 (8H, 2m, 2CH_2CH_2), 2.81–2.86 (4H, m, 2$CH_2NH_3^+$), 4.14–4.17 (4H, m, 2CH_2N^+), 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, 2NH_3^+), 7.63–7.64 (2H, m, 2×4-H), 8.33–8.38 (2H, m, 2×β-H); δ_C (DMSO-d_6) 24.02 and 24.23 (2CH_2CH_2), 27.05 (2CMe_2), 38.51 (2$CH_2NH_3^+$), 42.73 (2CH_2N^+), 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 $CHCl_3$–CH_2Cl_2–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 F^2 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**·1.75H_2O; 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**·1.75H_2O, **9a**·0.6CH_2Cl_2·0.4$CHCl_3$ and **9b**·2MeCN

Parameter	**8b**·1.75H_2O	**9a**·0.6CH_2Cl_2·0.4$CHCl_3$	**9b**·2MeCN
Empirical formula	$C_{43}H_{44.5}ClN_4O_{9.75}S_2$	$C_{40}H_{32.6}Cl_{3.4}N_4O_8S_2$	$C_{49}H_{49}ClN_6O_8$
Formula weight	872.90	881.95	885.39
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
Unit cell: dimensions (Å),	*a*=20.486(3), *b*=18.008(3), *c*=22.511(3)	*a*=9.5883(11), *b*=14.3371(17), *c*=14.9796(18)	*a*=11.7498(3), *b*=14.0094(4), *c*=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)
Z, D_{calcd} [Mg/m^3]	8, 1.407	2, 1.517	2, 1.338
μ [mm^{-1}]	0.258	0.434	0.150
F(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	$-27\le h\le 27$, $-24\le k\le 24$, $-30\le l\le 30$	$-11\le h\le 11$, $-14\le k\le 17$, $-16\le l\le 17$	$-15\le h\le 16$, $-19\le k\le 19$, $-19\le l\le 19$
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 $I>2\sigma(I)$	4922	5536	6796
Goodness-of-fit on F^2	0.991	1.145	0.999
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0828, wR_2=0.2133	R_1=0.2362, wR_2=0.5266	R_1=0.0680, wR_2=0.1872
R indices (all data)	R_1=0.1831, wR_2=0.2647	R_1=0.2504, wR_2=0.5304	R_1=0.1151, wR_2=0.2044
Largest diff. peak and hole (ē 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**, CH_2Cl_2 and $CHCl_3$ 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**·0.6CH_2Cl_2·0.4$CHCl_3$. 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**·1.75H_2O), CCDC-907649 (**9a**·0.6CH_2Cl_2·0.4$CHCl_3$) 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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