Phenothiazine−Bipyridinium Cyclophanes[‡]

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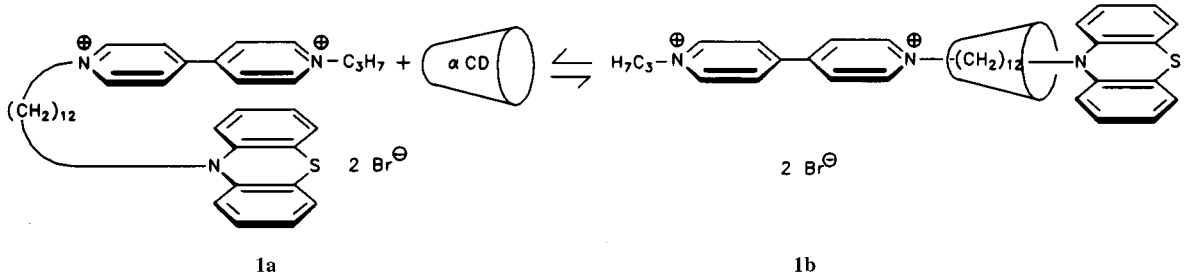
The syntheses of oligooxa[8.8]-, -[11.11]-, -[14,14]-, -[17.17]- and -[20.20]cyclophanes with phenothiazine as donor and bipyridinium dication as acceptor are described, together with preparations of the corresponding oligomethylene-[3.3]- and -[4.4]cyclophanes. While the large [8.8]-, [11.11]- and [14.14]cyclophanes in particular show well-defined charge-transfer (CT) absorption maxima, the smallest [3.3]cyclophane does not exhibit any CT effect. For the large cyclophanes, a preferred conformation with crossed donor and acceptor units is proposed. The fluorescence quenching and electrochemical behaviour of all phenothiazine–bipyridinium cyclophanes is discussed.

Introduction

Intermolecular interactions of *N*-substituted phenothiazines as donors and bipyridinium dications as acceptors have been studied with regard to their photoinduced electron-transfer reactions.[2] Corresponding intramolecular interactions have been described in compounds with phenothiazine and bipyridinium components linked through their N atoms by flexible polymethylene chains[3,4] (Scheme 1). For the dodecamethylene-linked phenothiazine−bipyridinium compound **1a**, a conformer with a face-to-face orientation of the donor and acceptor units has been suggested. Compound **1a** was reported to display a weak and broad charge-transfer absorption band (λ_{max} = 550 nm, extinction coefficient and solvent not given), which disappeared on addition of α-cyclodextrin (α-CD), giving rise to the open, flat rotaxane-like structure of complex **1b**.[3]

Scheme 1 shows the outer pyridinium unit of the bipyridinium part lying in a planar fashion above the thiazine ring of the phenothiazine moiety, positioning its nitrogen atom over the sulfur atom of the thiazine ring. Another, very similar, face-to-face orientation of donor and acceptor, with even better HOMO−LUMO overlap, is possible if the inner pyridinium nitrogen atom of the bipyridinium unit is above the phenothiazine nitrogen atom (Figure 1).

Obviously, the face-to-face conformers of the monolinked phenothiazine−bipyridinium system should constitute only a fraction of all the extended non-overlapping conformers. Thus, for better investigation of the charge-transfer interaction between the phenothiazine donor and the bipyridinium acceptor, the donor−acceptor units should be linked by two bridges. Were these bridges long enough, face-to-face orientations with crossed long axes of the phenothiazine−bipyridinium units, similar to that



1a **1b**

Scheme 1. Reaction of monolinked phenothiazine−bipyridinium compounds with α-cyclodextrine

shown in Scheme 1, might be formed (Figure 2). In order to meet that requirement, polyethylene glycol chains of different lengths were chosen, as shown in compounds **2**−**7**. Complexation of such macrocycles with suitable metal ions might make it possible to generate crown-ether-like structures exhibiting charge-transfer absorptions of higher intensity, as found with oligooxa[*n.n*]paracyclophane quinhydrones.[5] The two positive charges of the bipyridinium

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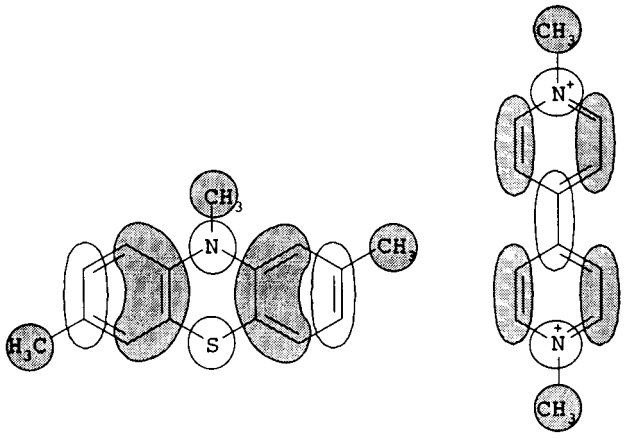


Figure 1. HOMO of *N*,2,7-trimethylphenothiazine and LUMO of *N,N′*-dimethyl-4,4′-bipyridinium

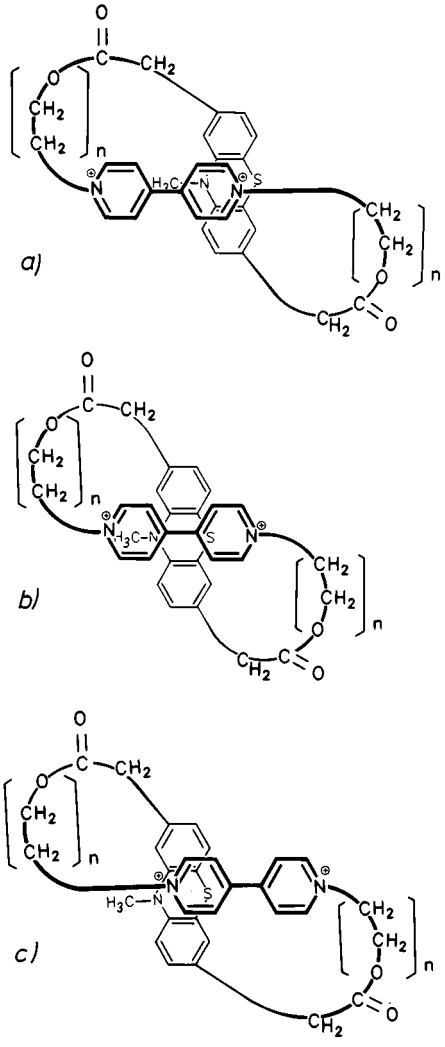
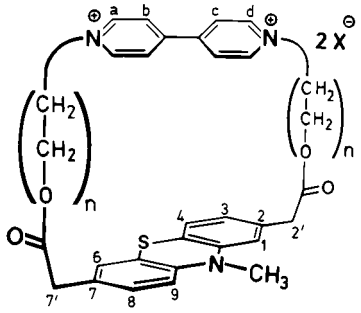


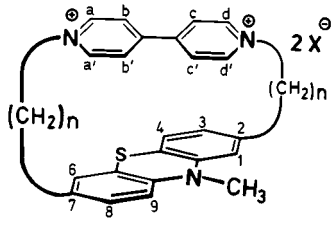
Figure 2. Some orientations of the phenothiazine−bipyridinium oligooxa[3*n*+2]cyclophanes

component, however, would certainly be a hindrance for the complexation reactions.

It would also be advisable to compare the oligooxacyclophanes **2**−**7** against the phenothiazine−bipyridinium cyclophanes **8** and **9**, containing short (trimethylene and tetramethylene) bridges, with the long axes of the donor−acceptor components forced to be nearly parallel.



2–**7**: n = 1–6
a: X = I
b: X = BF_4
c: X = ClO_4
d: X = PF_6



8: n = 3; **9**: n = 4
a: X = I
b: X = BF_4

In a preliminary communication, the syntheses of the first doubly bridged macrocyclic phenothiazine−bipyridinium diiodide systems **3a**−**7a**, with an oligooxacyclophane − or more precisely cyclophanium − structure (another name is oligooxabipyridinophenothiazino-[3*n*+2]phanium diiodides), were reported.[6] In these compounds, the phenothiazine 2- and 7-positions are connected with the bipyridine 4- and 4′-positions. Linkage through simple $(CH_2OCH_2)_n$ bridges could not be achieved in test attempts with model compounds such as 2,7-bis(alkoxymethyl)-*N*-methylphenothiazines. The ether groups of 2,7-bis-(methoxyethyl)-*N*-methylphenothiazine would cleave even in water, yielding the corresponding diol. Thus, the oligooxa bridges were connected with the phenothiazine framework through ester functions, as shown in the oligooxa[3*n*+2]cyclophanes **3**−**7**. In the cyclophanes **3a**−**7a**, charge-transfer interactions between the iodide anions and the bipyridinium moiety are possible. The iodide anion in the cyclophanium iodides therefore needed to be exchanged for anions that do not donate electrons − BF_4^-, ClO_4^- and PF_6^- anions − if the intramolecular charge-transfer interactions between the phenothiazine donor and the bipyridinium acceptor were to be studied exclusively.

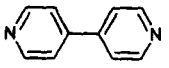
In this paper we report on the syntheses and the spectroscopic and electrochemical properties of phenothiazine−bipyridinium oligooxa[8.8]-, -[11.11]-, -[14.14]-, -[17.17]-, and -[20.20]cyclophanes **3**−**7**, with iodide, tetrafluoroborate, perchlorate and hexafluorophosphate anions. These compounds were compared with the corresponding oligomethylene-bridged [3.3]- and [4.4]cyclophanes **8** and **9**.

Results and Discussion

Syntheses

1. Syntheses of Phenothiazine−Bipyridinium Oligooxacyclophanes

To achieve cyclizations affording the phenothiazine−bipyridinium oligooxacyclophanes **3a−7a** with X = I {oligooxa-(1,1′)(4,4′)-bipyridino(2,7)phenothiazino[3*n*+2]-phanium diiodides}, 4,4′-bipyridine (**10**) was doubly alkylated with the appropriate 2,7-bis(ω-iodooligooxaalkylcarbonylmethyl)-*N*-methylphenothiazines **11−16** in refluxing nitromethane over 4−5 d, using a two-channel syringe pump.



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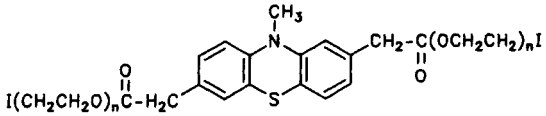


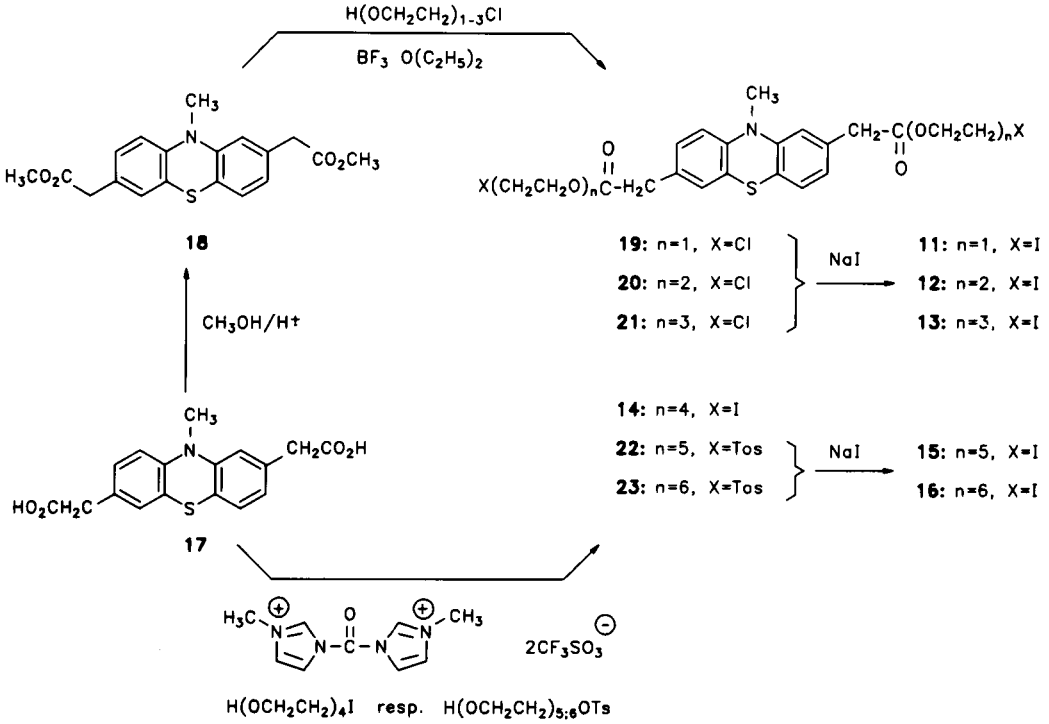
11-16: n = 1-6

For the preparation of the corresponding 4,4′-bipyridino-2,7-phenothiazino[3*n*+2]phanium bis(tetrafluoroborates) and bis(perchlorates) **3b/c−7b/c**, four methods were used, involving treatment of the cyclophanium diiodides

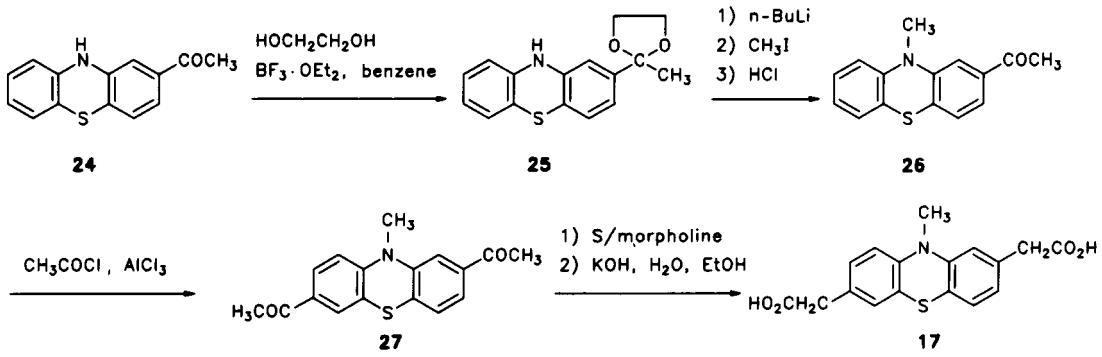
1. with silver tetrafluoroborate or silver perchlorate,
2. with silver oxide and tetrafluoroboric acid or perchloric acid,
3. with sodium perchlorate, and
4. with a Dowex 1 × 8 column loaded with tetrafluoroborate or perchlorate.

The [8.8]cyclophanium bis(tetrafluoroborate) **3b** and bis(perchlorate) **3c** were obtained as blue-green powders, the [11.11]- to [20.20]cyclophanium bis(tetrafluoroborates) and bis(perchlorates) **4b/c−7b/c** as dark violet powders slightly contaminated (1−2%) with inorganic materials. Because of these contaminants it was not possible to obtain correct elemental analyses for the cyclophanium salts.

The cyclization components **11−16** were prepared by two routes (Scheme 2). The first route involved the transesterification of 2,7-bis(methoxycarbonylmethyl)-*N*-methylphenothiazine (**18**) with polyethylene glycol chlorohydrins in the presence of $BF_3{\cdot}OEt_2$ to give the dichlorides **19−21**, which were readily converted into the more reactive diiodides **11−13** by means of a Finkelstein reaction with sodium iodide. The second route involved the esterification of *N*-methylphenothiazine-2,7-diacetic acid (**17**) with monoiodo- or mono(*p*-toluenesulfonyl)oligoethylene glycols to give the diiodide **14** or the ditosylates **22** and **23**, employing the azolide 1,1′-carbonylbis(methylimidazolium trifluoromethanesulfonate) as condensing agent. Like the dichlorides, compounds **22** and **23** were treated with sodium iodide to give the diiodides **15** and **16**.



Scheme 2. Preparation of the phenothiazine cyclization components of the phenothiazine−bipyridinium oligooxacyclophanes



Scheme 3. Synthesis of *N*-methylphenothiazine-2,7-diacetic acid

The synthesis of bis(methoxycarbonylmethyl)-*N*-methylphenothiazine (**18**) started from the commercially available 2-acetylphenothiazine (**24**), which was converted into the known 2,7-diacetyl-*N*-methylphenothiazine (**27**) by a circuitous route by way of the ketal **25** (Scheme 3). The methylation of the ketal **25** was followed by a Friedel–Crafts acetylation with $CH_3COCl/AlCl_3$. This route is strongly recommended, since the alternative direct methylation of 2-acetylphenothiazine (**24**) resulted in one case in a large explosion. An easy synthesis of the dicarboxylic acid **17** and its esterification to **18** was then accomplished by means of a Willgerodt–Kindler reaction on **27**, using sulfur and morpholine.

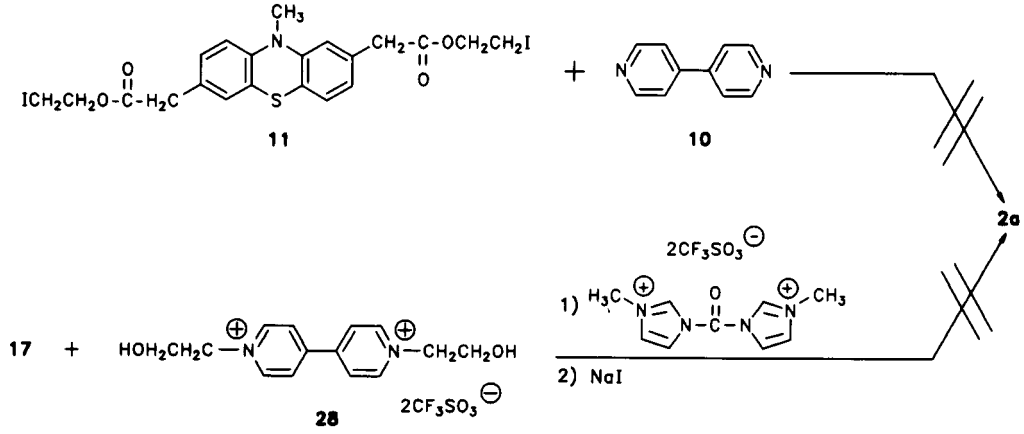
Under the same reaction conditions as used for the synthesis of the cyclophanium diiodides **3a**–**7a**, it was found not to be possible to cyclize diiodide **11** and bipyridine **10** to the [5.5]cyclophanium diiodide **2a** (Scheme 4). No cyclization product could be isolated even when using *N*-methylphenothiazine-2,7-diacetic acid (**17**), 1,1′-bis(2′-hydroxyethyl)-4,4′-bipyridinium bis(trifluorosulfonate) (**28**) and condensing agent carbonylbis(*N*-methylimidazolium trifluorosulfonate) at room temperature.

2. Syntheses of the Phenothiazine–Bipyridinium [3.3]- and [4.4]Cyclophanes

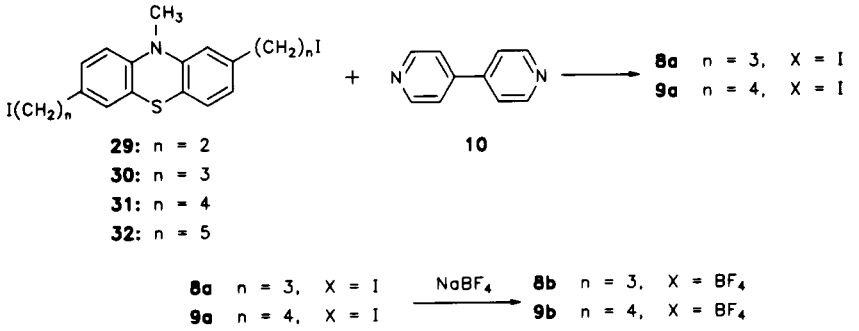
The phenothiazine–bipyridinium [3.3]- and [4.4]cyclophanes **8b** and **9b** {correct names: 4,4′-bipyridino[2,7]-*N*-methylphenothiazino[3.3 or 4.4]phanium bis(tetrafluoroborates)} were obtained in analogous fashion to the oligooxacyclophanes **3b**–**7b**, by cyclization of 2,7-bis(iodoalkyl)-*N*-methylphenothiazine **30** and **31** with 4,4′-bipyridine and subsequent exchange of the iodide anions for tetrafluoroborate (Scheme 5).

Treatment of 2,7-bis(iodoethyl or iodopentyl)-*N*-methylphenothiazine **29** and **32** with bipyridine **10** did not yield the cyclized products, because of decomposition of the starting diiodides under the reaction conditions. The iodo compounds **29**–**31** were prepared through the dialcohols **35**–**37** and the dibromides **38**–**40** (Scheme 6). Elongation of the 2,7-side chains of *N*-methylphenothiazinediacetate **18** by one CH_2 group, giving **33**, was achieved by conversion of the dibromide **38** to the dicyanide **41** (with sodium cyanide) and subsequent alcoholysis. Elongation of **18** by two CH_2 groups, producing **34**, was accomplished through a malonic ester synthesis with 2,7-bis(iodoethyl)-*N*-methylphenothiazine (**29**), by way of the diester **42**.

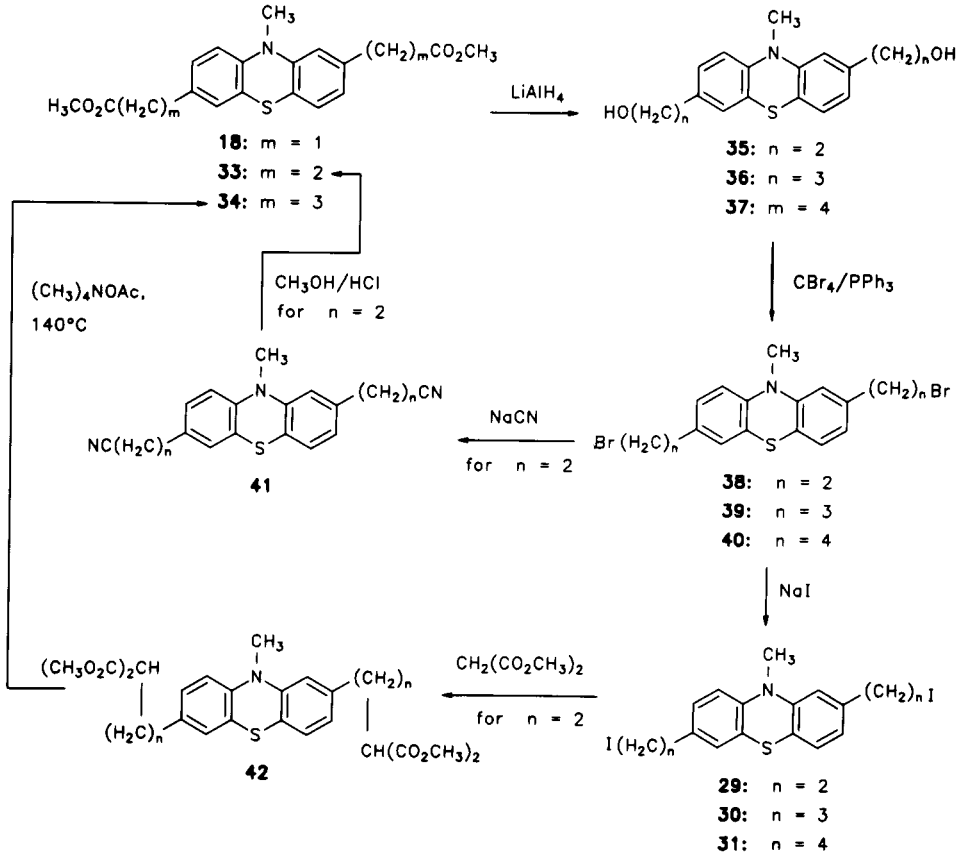
2,7-Bis(iodopentyl)-*N*-methylphenothiazine (**32**) was obtained by cross-coupling of diiodide **29** with allylmagnesium bromide in the presence of nickel dichloride/bis(diphenylphosphanyl)ethane as catalyst, followed by hydroboration of the diolefin **43** and cleavage of the bis(borane) with iodine chloride (Scheme 7). The diiodide **29** could easily be reduced with lithium aluminium hydride, to yield 2,7-



Scheme 4. Attempts to synthesize the [5.5]cyclophanium diiodide **2a**



Scheme 5. Preparation of the phenothiazine−bipyridinium [3.3]- and [4.4]cyclophanes **8** and **9**



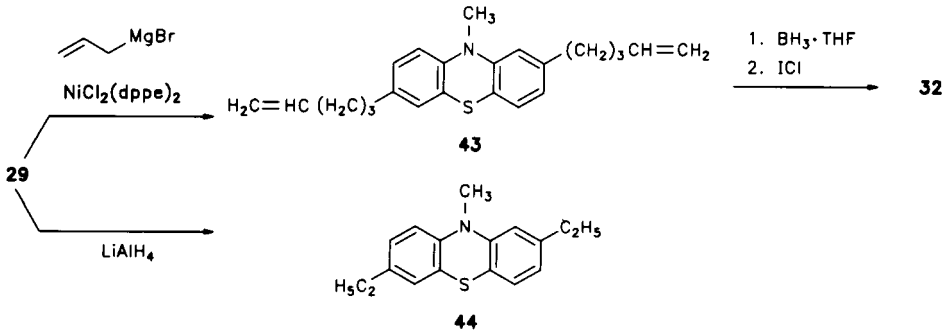
Scheme 6. Preparation of the 2,7-bis(iodoalkyl)-*N*-methylphenothiazines

diethyl-*N*-methylphenothiazine (**44**), which was used as a reference compound in cyclic voltammetric examination of [3.3]- and [4.4]cyclophanes **8b** and **9b**.

Electron Spectra

The UV absorptions of all oligooxa[3*n*+2]cyclophanes [$\lambda_{max} \approx 250$ (strong) and 310−313 nm (weak)] are practically identical and appear to be composed simply of the spectra of the two subunits.

In the cyclophanium diiodides **3a**−**7a**, CT absorption between the phenothiazine donor and the bipyridinium acceptor is superimposed by CT absorptions between the iodide anion and the bipyridinium moiety. The [14.14]cyclophanium diiodide **5a** (in acetonitrile), for example, shows two CT absorptions at $\lambda = 483$ nm ($\varepsilon = 180$) and 550 nm (sh, $\varepsilon = 150$), the first of which is attributable to the CT between iodide and bipyridinium, and the second to the CT between phenothiazine and bipyridinium. In the less polar solvent dichloromethane, a strongly enhanced absorption is observed [$\lambda_{CT} = 477$ nm ($\varepsilon = 920$)], composed mainly of the CT absorption deriving from the less solvated iodide donor and only to a minor extent of the CT between phenothiazine and bipyridinium. This assignment is based on comparison with *N*,*N*′-dioctyl-4,4′-bipyridinium diiodide, the absorption maximum of which was found at $\lambda =$



Scheme 7. Preparation of 2,7-bis(5′-iodopentyl)-*N*-methylphenothiazine (**32**) and 2,7-diethyl-*N*-methylphenothiazine (**44**)

453 nm ($\varepsilon = 119$) in acetonitrile, but at $\lambda = 506$ nm (with a much higher intensity at $\varepsilon = 1276$) in dichloromethane.

In contrast with the cyclophanium diiodides **3a**−**7a**, selective detection of CT between phenothiazine and bipyridinium moieties is possible in the cyclophanium bis(tetrafluoroborates) **3b**−**7b** and the bis(perchlorates) **3c**−**7c**. In acetonitrile, the cyclophanium bis(perchlorates) and bis(tetrafluoroborates) display CT absorptions between $\lambda = 512$ and 555 nm. The spectra were measured at concentrations of 5×10^{-4} mol in order to preclude intermolecular effects. An acetonitrile solution of the *N*-methylphenothiazine species in the form of **18** and the bipyridinium species in the form of **28** at a concentration of 10^{-2} mol/L did not show CT absorption. Since the Vis spectra of the macrocycles with perchlorate or tetrafluoroborate anions have been shown to be practically independent of these counter-ions, only the absorption spectra of the bis(perchlorates) are discussed below.

In the larger macrocycles, the [20.20]- and [17.17]cyclophanes **7c** and **6c**, an orientation with crossed phenothiazine and bipyridinium components (as illustrated in Figure 2) is possible, but because of their large ring sizes these molecules are rather flexible. Only small CT effects are therefore to be expected in these cases. In fact, the [20.20]cyclophanium bis(perchlorate) **7c** just shows a shoulder at $\lambda = 525$ nm (with $\varepsilon = 75$) (Figure 3).

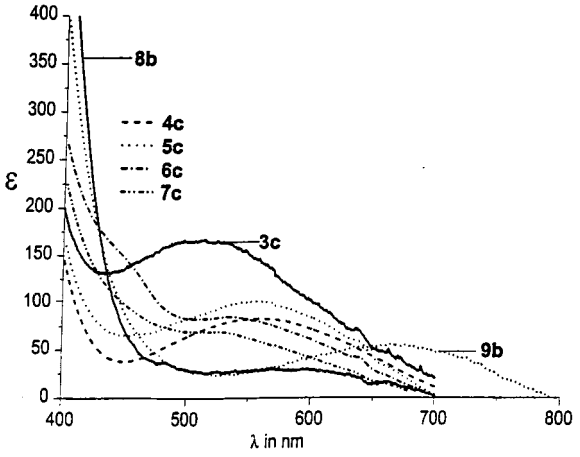


Figure 3. Vis spectra of the [8.8]-, [11.11]-, [14.14]-, [17.17]- and [20.20]cyclophanium bis(perchlorates) **3c**−**7c**, [3.3]cyclophanium bis(tetrafluoroborate) **8b**, and [4.4]cyclophanium bis(tetrafluoroborate) **9b**

The spectrum of the [17.17]cyclophanium bis(perchlorate) **6c** is very similar, also featuring only a shoulder at $\lambda = 530$ nm (with $\varepsilon = 70$). When the [20.20]cyclophanium bis(perchlorate) **7c** was treated with barium perchlorate, no well-defined charge-transfer absorption maximum was observed; the extinction coefficient of the shoulder was merely enhanced from $\varepsilon = 75$ to 105. The [14.14]cyclophanium bis(perchlorate) **5c** exhibits a distinct absorption maximum at $\lambda = 555$ nm (with $\varepsilon = 97$) (Figure 3). In this case, a crossed orientation of the donor−acceptor units − as in Figure 2 − is probably favoured, with a partial overlap of the HOMO−LUMO orbitals of the phenothiazine and bipyridinium units (Figure 1). The position of the absorption maximum corresponds to that of the monolinked phenothiazine−bipyridinium system **1a** ($\lambda_{CT} = 550$ nm) in Scheme 1. In dichloromethane, the CT absorption maximum of [14.14]cyclophane **5c** is bathochromically shifted by 38 nm, to $\lambda = 593$ nm ($\varepsilon = 98$), because the ground state of the cyclophanium bis(perchlorate), which is more polar than the excited state (phenothiazine radical cation − bipyridinium radical cation), is destabilized in the less polar solvent. The CT absorption of the [11.11]cyclophanium bis(perchlorate) **4c**, which shows $\lambda_{CT} = 554$ and $\varepsilon = 83$ in acetonitrile, is similar to that of **5c**.

The CT absorptions of **4c**−**7c** are effectively located in the same region as the bands of the oxidized oligooxacyclophanes containing a phenothiazine radical cation ($\lambda_{max} \approx 530$ nm). However, the nature of the CT absorption (broad, structureless) is quite different from that of the radical trication or of a superposition of the phenothiazine radical cation and the bipyridinium radical cation.

In acetonitrile, the smallest of the oligooxacyclophanes, the [8.8]cyclophanium bis(perchlorate) **3c**, as expected, shows a CT absorption maximum at $\lambda = 512$ nm with the highest extinction coefficient ($\varepsilon = 165$), but the position of the maximum is hypsochromically shifted relative to those of **5c** ($\lambda_{CT} = 555$ nm) and **4c** ($\lambda_{CT} = 554$ nm). This hypsochromic shift is probably due to the fact that in the charge-transfer state (excited state) of the oligooxacyclophanes both the bipyridinium and the phenothiazine should bear positive charges, resulting in a repulsion of the donor and acceptor. The CT state is consequently accompanied by a destabilization, which becomes more pronounced, the smaller the macrocycle. CT absorptions of **3c** and **4c** could

not be measured in dichloromethane, because of poor solubility in this solvent.

The oligomethylene-linked cyclophanes containing short bridges were investigated in the forms of their cyclophanium bis(tetrafluoroborates). Because of its short bridge, the [3.3]cyclophane **8b** exists in a coplanar orientation, with nearly parallel long axes of the phenothiazine and bipyridinium units. Although fixed almost at the van der Waals distance, it does not exhibit charge-transfer absorption at all (Figure 3). This observation can be explained by the unsuitable HOMO−LUMO overlap and the destabilization of the CT state resulting from the Coulombic repulsions of the positive charges on donor and acceptor. The Vis spectrum of the [4.4]cyclophane **9b** showed a very broad and weak absorption maximum at $\lambda = 675$ nm (with $\varepsilon = 60$) (Figure 3). Absorption at such a high wavelength can hardly be assigned to a CT band, because the repulsion of the donor radical cation and acceptor radical cation in the CT state should produce absorption at a wavelength lower than that in the [8.8]cyclophane. The absorption probably originates from some unknown impurity.

From these results it may be assumed that only more or less perpendicular superposition of the phenothiazine and bipyridinium units, best achieved in the larger macrocycles **3c**, **4c** and **5c**, should produce a significant CT effect.

Fluorescence Spectra

Dimethyl *N*-methylphenothiazinediacetate (**18**), a suitable reference compound for the phenothiazine components in the oligooxacyclophanes **3**−**7**, exhibits absorption maxima at $\lambda = 257$ ($\varepsilon = 43.000$) and 310 nm ($\varepsilon = 6.500$) in acetonitrile. A fluorescence band is found at $\lambda = 457$ nm, producing a higher fluorescence quantum yield on excitation at $\lambda = 310$ than at 257 nm. Phenothiazine compounds generally display low fluorescence quantum yields ($\varphi_{rel} \approx 0.1$) because intersystem crossing from $^1(n, \pi^*)$ to $^3(\pi,\pi^*)$ is the main deactivation path.[2] Bipyridinium compounds, such as 1,1′-bis(2′-hydroxyethyl)-4,4′-bipyridinium diiodide, with absorption maxima at $\lambda = 227$ ($\varepsilon = 30.000$) and 264 nm ($\varepsilon = 23.000$), are not fluorescent. In a 10^{-5} molar mixture of the phenothiazine diester and the nonfluorescent bipyridinium salt, phenothiazine fluorescence was not impaired. Phenothiazine fluorescence in all phenothiazine−bipyridinium oligooxacyclophanes, however, was quenched to a large extent ($\varphi_{rel} = 0.04-0.1$) (Table 1). The relative quantum yields φ_{rel} were obtained by integration of the fluorescence intensities at $\lambda = 370-600$ nm.

Table 1. Relative quantum yields φ_{rel} of the [3.3]cyclophane **8b**, the [4.4]cyclophane **9b**, the oligooxa[3*n*+2]cyclophanes **3b**−**7b**, and dimethyl *N*-methylphenothiazine-2,7-diacetate (**18**)

Compound	φ_{rel} (in CH_3CN)
18	1
[3.3]cyclophane (**8b**)	0.35
[4.4]cyclophane **9b**)	0.2
Tetraoxa[8.8]cyclophane (**3b**)	0.07
Hexaoxa[11.11]cyclophane (**4b**)	0.1
Octaoxa[14.14]cyclophane (**5b**)	0.06
Decaoxa[17.17]cyclophane (**6b**)	0.08
Dodecaoxa[20.20]cyclophane (**7b**)	0.04

The quenching is readily explicable in terms of a photoinduced electron transfer process that should be exergonic, with an estimated $\Delta G \approx -40$ kcal mol^{-1}.[2] In the charge-separated states of the oligooxacyclophanes, in which both donor and acceptor bear single positive charges, the donor (phenothiazine radical cation) and acceptor (bipyridinium radical cation) are able to evade one another at relatively large distances. This is not the case with the [3.3]- and [4.4]cyclophanes, in which the positive charges are forced to be at a shorter distance, accompanied by higher energy charge-separated states because of charge repulsion. They therefore display fluorescence quenching weaker than that of the oligooxacyclophanes. In comparison of the fluorescence quenching of the [3.3]- and [4.4]cyclophanes **8b** and **9b** ($\varphi_{rel} = 0.35$ and 0.2, respectively), the latter shows the stronger fluorescence quenching (Table 1, Figure 4). This result can be explained analogously, by the lower energy (larger distance between the positive charges) of the charge-separated state of the [4.4]cyclophane. An example of the geometrical changes accompanying charge separation in a donor−acceptor system containing porphyrin (P) as donor and bipyridinium dication (MV^{++}, methylviologen) as acceptor is described in the literature. In this system the distance between the donor and acceptor in the ground state ($P-MV^{++}$) was found to be shorter than that in the photoinduced charge-separated state (P^+-MV^+).[7]

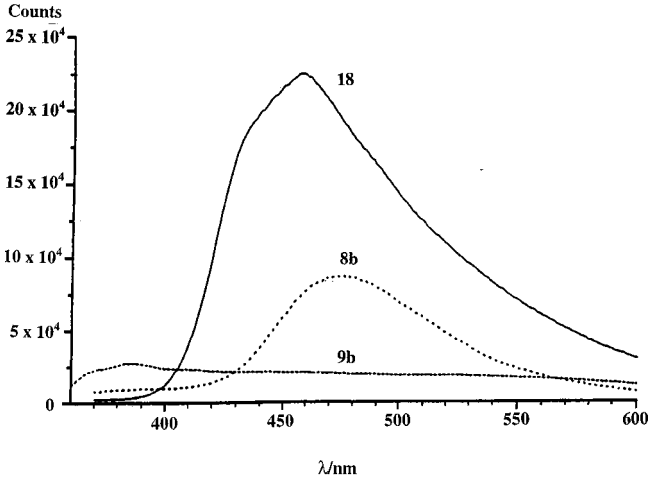


Figure 4. Fluorescence spectra of [3.3]cyclophane **8b**, [4.4]cyclophane **9b**, and of dimethyl *N*-methylphenothiazine-2,7-diacetate (**18**)

NMR Spectra

The two outer (a/d) and the two inner (b/c) protons of *N*,*N*′-dimethylbipyridinium bis(tetrafluoroborate) are equivalent, and so each pair appears as a doublet in the NMR spectrum in CD_3CN (Figure 5). The outer and the inner protons of the bipyridinium components of all oligooxabipyridinophenothiazinocyclophanium bis(tetrafluoroborates), however, each appear as two pairs of doublets, due to the proximity of the unsymmetrical phenothiaz-

ine moiety, and are shifted to higher field relative to *N,N′*-dimethylbipyridinium bis(tetrafluoroborate). In the series from [20,20]cyclophane **7b** to [11.11]cyclophane **4b**, the high-field shifts of the outer and inner protons of the bipyridinium moiety increase, with the shifts of the inner protons being greater than those of the outer protons (Figure 5).

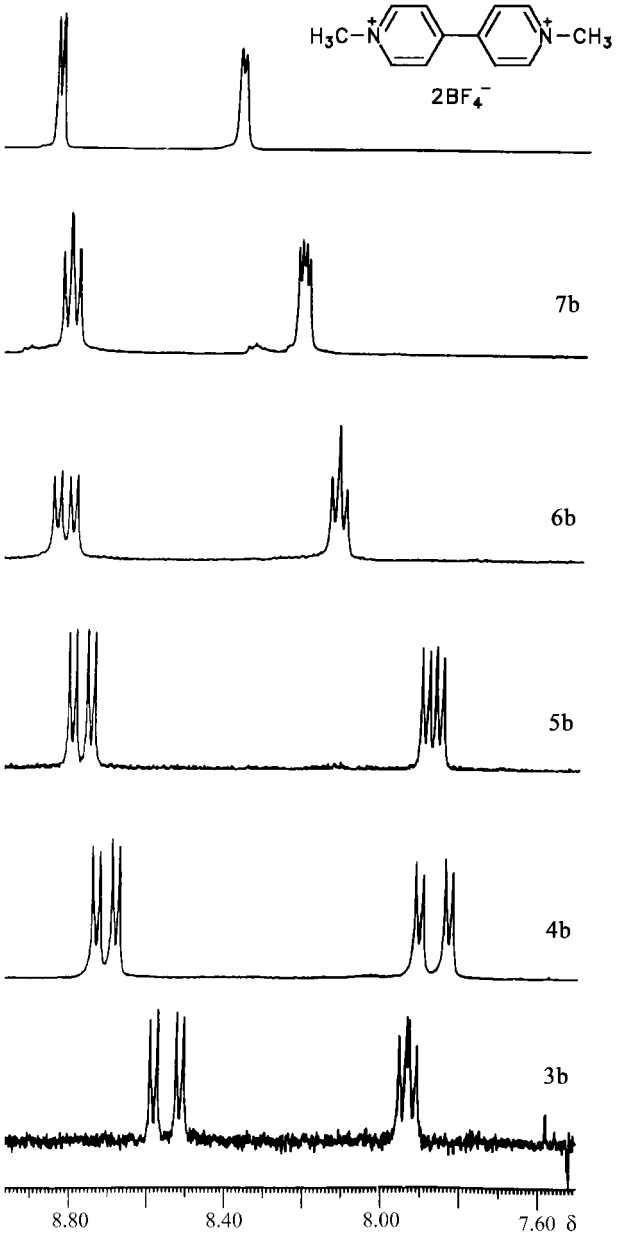


Figure 5. ^{1}H-NMR signals of the bipyridinium units of the [20.20]cyclophane **7b**, the [17.17]cyclophane **6b**, the [14.14]cyclophane **5b**, the [11.11]cyclophane **4b**, the [8.8]cyclophane **3b**, and of the reference compound *N,N′*-dimethylbipyridinium bis(tetrafluoroborate) in CD_3CN

These results indicate a growing tendency of these compounds to form a conformation similar to b in Figure 2. The high-field shifts of the bipyridinium hydrogen atoms of [8.8]cyclophane **3b**, however, are not quite in the line with those of the larger oligooxacyclophanes **4b**−**7b.** As well as this, the signal patterns of the phenothiazine hydrogen atoms of the [8.8]cyclophane (**3b** in CD_3CN, for example: pos. 8-4-6-9-3-1) differ significantly from those of the larger cyclophanes (**6b** in CD_3CN for example: pos. 8-6-4-3-1-9), which are very similar to one another. It is therefore suggested that a somewhat different conformation must be favoured in the [8.8]cyclophane, with no more perpendicular orientation of the bipyridinium and the *N*-methylphenothiazine moieties. In contrast to the larger macrocycles, which feature only two averaged signals for the two pairs of methylene protons $CH_2CH_2N^+$ in the bridge, the [8.8]cyclophanium compounds **3a**−**c** show four separated signals, due to the closer proximity of the unsymmetrical phenothiazine component. Such a differentiation of the two $CH_2CH_2N^+$ pairs in the bridge may also be achieved by conversion of the [20.20]cyclophane **7a** to a dibarium complex by complexation with barium diiodide. This result is unequivocal proof of the coming closer together of the phenothiazine and bipyridinium components of the [20.20]cyclophane as a result of complexation. With the aid of NOE and COSY experiments, it was possible to assign all the phenothiazine hydrogen signals, as well as those of the attached CH_2 groups. On irradiation of the various oligooxacyclophanebipyridinium protons, in addition to enhancement of the neighbouring protons, transannular NOEs arising from the phenothiazine protons were also, surprisingly, observed. These effects were especially pronounced with the oligooxacyclophanes **4**−**7**, both in dichloromethane and acetonitrile (Figure 6). The intensities of the transannular NOEs were about 5−10% of those of the normal NOEs of the neighbouring bipyridinium protons. The enhancements of the phenothiazine hydrogen signals were generally more pronounced on irradiation of the inner bipyridinium hydrogen atoms b/c than on irradiation of the outer bipyridinium hydrogen atoms a/d. These NOEs evidently demonstrate approaches of the donor and acceptor units in the cyclophanes **4**−**7** for at least several hundreds of ms. The preferred conformations might be similar to those in Figure 2.

In the [4.4]cyclophanium diiodide **9a** [PyH a/d: δ = 8.70; PyH b/c: δ = 8.30 (in CD_3CN)], the outer and the inner protons of the bipyridinium moiety are shifted to higher field relative to *N,N′*-didodecylbipyridinium diiodide (δ = 8.95 and 8.42, respectively, in CD_3CN). In contrast to the oligooxacyclophanium diiodides, however, the outer protons are more strongly shifted to higher field (δ = 0.25) in CD_3CN than the inner protons are (δ = 0.12). On irradiation of the outer (a/d) protons of the bipyridinium component of the diiodide **9a** in CD_3OD, NOEs were observed for all phenothiazine hydrogen atoms in positions 1, 3, 4, 6, 8 and 9, and NCH_3. If the inner hydrogen atoms were irradiated, however, only NOEs from the phenothiazine hydrogen atoms at positions 1, 4, 6 and 9 and NCH_3 were observed, with NOEs from 3-H and 8-H being absent. This result can be explained by a conformation of the cyclophane **9a** in which the long axes of the donor and acceptor

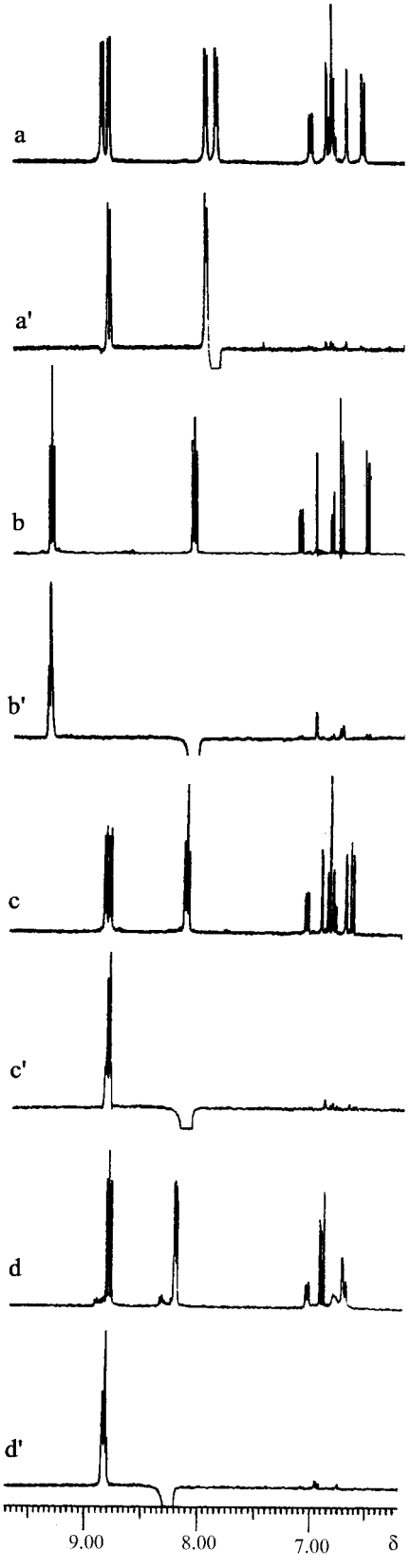


Figure 6. NOE and reference spectra of [11.11]cyclophanium diiodide **4a** in CD_3CN (a′,a), of [14.14]cyclophanium diiodide **5a** in CD_2Cl_2 (b′,b), of [17.17]cyclophanium bis(tetrafluoroborate) **6b** in CD_3CN (c′,c) and of [20.20]cyclophanium bis(tetrafluoroborate) **7b** in CD_3CN (d′,d)

units are not exactly superimposed, but a little distorted relative to each other.

While the donor and acceptor units can rotate at room temperature in the [4.4]cyclophane **9**, this rotation is hindered in the [3.3]cyclophane **8**. Because of this hindered rotation and the unsymmetrical phenothiazine moiety, the four outer bipyridinium protons of the [3.3]cyclophanium diiodide **8a** in DMSO exhibit four separate signals a,a′,d,d′ at $\delta = 9.0-9.4$, while the four inner protons, which experience the unsymmetrical environment less, display a pattern of three signals, resulting from the collapse of the two inner H signals (b,b′) into one. At higher temperature (303 K to 423 K), when rotation of the bipyridinium component is setting in, the signal patterns of the outer and inner protons resemble that in the [4.4]cyclophane, except for the greater shift between these two proton groups (Figure 7).

As far as the signal patterns of the phenothiazine hydrogen atoms between the [3.3]- and [4.4]cyclophane are concerned, there is only one small difference, involving the hydrogen atoms in pos. 6 and 9 (**8b** in CD_3CN, for example: pos. 8-4-3-6-9-1 against **9b** in CD_3CN: pos. 8-4-3-9-6-1).

In [3.3]cyclophanium diiodide **8a**, through-space NOEs are found between the bipyridinium protons d,d′ and the phenothiazine protons 1-H and 3-H, and also between the bipyridinium protons a,a′ and the phenothiazine proton 6-H and 8-H.

Electrochemistry

Under cyclic voltammetry conditions, at scan rates between 50 and 500 mV s^{-1}, the oligooxa[3*n*+2]cyclophanes **3b−6b** display absolute reversible behaviour for oxidation to the radical trications, as well as for reduction to radical cations and the neutral states. Thin layer cyclic voltammograms are stable over several cycles, proving the high stability of the radicals and the doubly reduced uncharged species.

The [3.3]- and [4.4]cyclophanes **8b** and **9b** show reversible oxidation and a quasi-reversible reduction. Thin layer multicycle experiments on the reduction step revealed a subsequent irreversible reaction of the monocation radicals. Spectroelectrochemical measurements on **8b** and **9b** therefore had to be carried out with a photodiode array spectrometer instead of a slowly scanning continuous wave spectrometer.

The oxidation (half-wave) potential of *N*-methylphenothiazine is much lower (325 mV) − or put another way, its donor capacity is much higher − than that of 2,5-dimethoxy-1,4-xylene (778 mV),[8] while the reduction (half-wave) potential (−825 mV) of *N*,*N*′-dimethylbipyridinium bis(tetrafluoroborate) is just a little lower than that of 2,5-dimethylbenzoquinone (−972 mV).[8] Nevertheless, with the *N*-methylphenothiazine and the bipyridinium dication combined in a [3.3]cyclophane, no charge-transfer absorption was found, in contrast to the [3.3]cyclophane with a dimethoxybenzene donor and a benzoquinone acceptor, which exhibited a charge-transfer absorption with an extinction coefficient of about 3000 in the pseudogeminal form.[9] The reason for this behaviour of the phenothiazine−bipyridinium cyclophanes has already been dis-

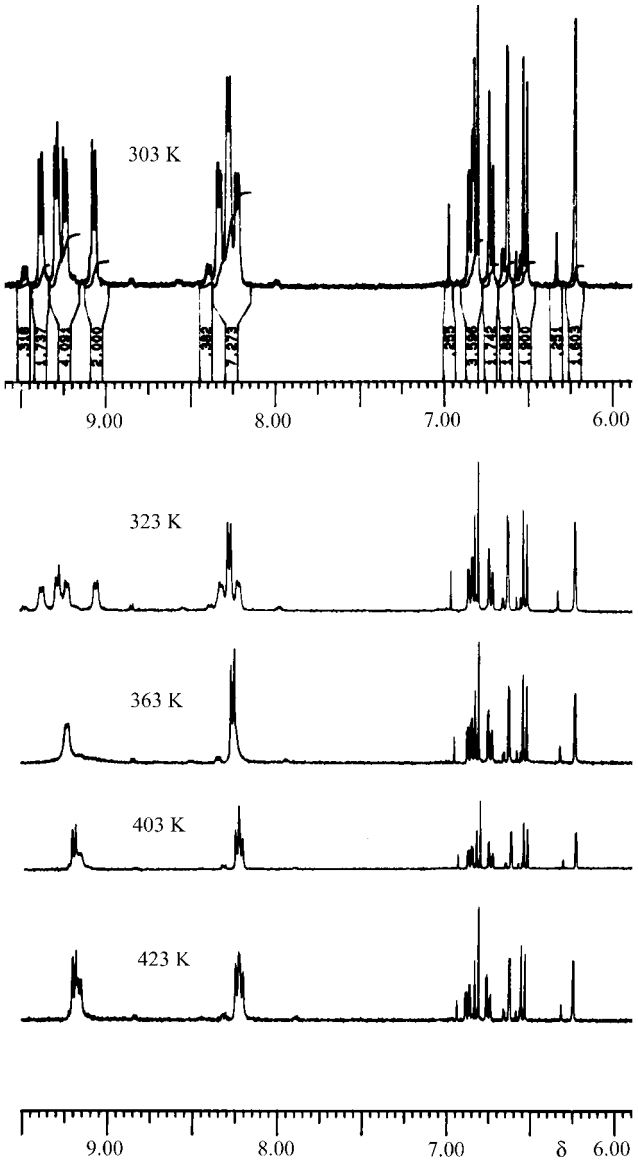


Figure 7. ^{1}H NMR spectrum of [3.3]cyclophanium diiodide **8a** in [D_6]DMSO and temperature dependence of the signals in the bipyridinium part

cussed in the section concerning electronic and fluorescence spectra.

The redox potentials of the phenothiazine−bipyridinium cyclophanes and their reference compounds are summarized in Table 2.

As expected, the oxidation (half-wave) potential of the phenothiazine−bipyridinium [3.3]cyclophane **8b** (410 mV) is higher than that of the corresponding [4.4]cyclophane **9b** (290 mV) because of the stronger Coulombic interaction with the dicationic bipyridinium component in the smaller macrocycle. To a small degree, this Coulombic interaction is also effective in **9b**, as can easily be recognized by comparison with the oxidation potential of 2,7-diethyl-*N*-methylphenothiazine (**44**) (215 mV) as reference compound. Alkyl substituents in the 2- and 7-positions of phenothiazine obviously have a strong influence on the oxidation potential of the phenothiazine compound. This is nicely demonstrated in the oxidation potentials of the series of *N*-methylphenothiazine (325 mV), 2,7-bis(methoxycarbonylmethyl)-*N*-methylphenothiazine (**18**) (300 mV), and 2,7-diethyl-*N*-methylphenothiazine (**44**) (215 mV).

The Coulombic effect of the dicationic bipyridinium component is still effective in the series of the larger oligooxa[3*n*+2]cyclophanes **3b**−**6b**, the oxidation potentials of which (390, 395, 355, 350 mV, respectively) are higher than that of the reference compound 2,7-bis(methoxycarbonylmethyl)-*N*-methylphenothiazine (**18**) (300 mV). It should be noted that the oxidation potentials of the [8.8]- and [11.11]cyclophanes **3b** and **4b** are higher than those of the [14.14]- and [17.17]cyclophanes **5b** and **6b**, but are practically identical within each pair.

The first reduction potentials of the [3.3]- and [4.4]cyclophanes (**8b** and **9b**: each −815 mV) and of the oligooxa[8.8]-, -[11.11]-, -[14.14]- and -[17.17]cyclophanes (**3b**−**6b**: −795, −815, −815 and −830 mV, respectively) do not show significant differences within the series or in comparison to the *N*,*N*′-dimethylbipyridinium acceptor (−825 mV). The somewhat less negative value −795 mV for the tetraoxa[8.8]cyclophane **3b** is not indicative of an electronic interaction between the donor and acceptor components, as this should result in a more negative reduction potential. Examples of such an interaction are donor−acceptor catenanes composed of bipyridinium units and phenol ethers.[10]

The second reduction potentials of the [4.4]cyclophane **9b** (−1220 mV) and of the oligooxacyclophanes (−1220 to −1270 mV) are also of the same magnitude as that of *N*,*N*′-dimethylbipyridinium bis(tetrafluoroborate) (−1245 mV). An exception is the smallest cyclophane **8b**, the second reduction potential of which (−1380 mV) differs from that of the reference compound by 135 mV. This result may be explained by conformational strain in the doubly reduced macrocycle containing a bipyridinylidene component.

Table 2. Half-wave redox potentials of phenothiazine−bipyridinium cyclophanes and their reference compounds

$E_{1/2}$ [mV vs. F_c]	**8b**	**9b**	**3b**	**4b**	**5b**	**6b**	*N*-methylphenothiazine	**18**	**44**	*N*,*N*′-dimethylbipyridinium
Ox.	410	290	390	395	355	350	325	300	215	
1. Red.	−815	−815	−795	−815	−815	−830				−825
2. Red.	−1380	−1220	−1250	−1270	−1250	−1250				−1245

Table 3. Absorption maxima of phenothiazine−bipyridinium cyclophanes and their reference compounds from spectroelectrochemical (SEC) measurements

Compound	Oxidation	1st Reduction
3b	528 nm (m), 765 (w), 845 (w)	560 nm (sh), 601 (s), 657 (sh), 722 (m)
4b	528 nm (m), 758 (w), 843 (w)	560 nm (sh), 603 (s), 658 (sh), 722 (m)
5b	527 nm (m), 756 (w), 843 (w)	559 nm (sh), 600 (s), 657 (sh), 724 (m)
6b	527 nm (m), 760 (w), 843 (w)	559 nm (sh), 600 (s), 658 (sh), 723 (w)
8b	553 nm (m), 790 (w), 870 (w)	580 nm (sh), 610 (m), 675 (w), 747 (w)
9b	536 nm (m), 785 (w), 870 (w)	570 nm (sh), 606 (m), 660 (sh), 726 (w)
N-Methylphenothiazine	510 nm (s), 757 (w), 846 (w)	
18	523 nm (m), 751 (w), 841 (w)	
44	536 nm (s), 765 (w), 850 (w)	
N,*N*′-Dimethyl-bipyridinium bistetrafluoroborate		558 nm (sh), 601 (m), 665 (sh), 732 (w)

Spectroelectrochemical (SEC) measurements were carried out to monitor the spectral changes accompanying the oxidations of the oligooxa[8.8]-, -[11.11]-, -[14.14]- and -[17.17]cyclophanes **3b**−**6b**. The positions of the long-wavelength absorptions of the corresponding radical trications ($\lambda \approx 525$, 760, 845 nm) are almost identical within the series and do not differ significantly from those of the reference compound 2,7-bis(methoxycarbonylmethyl)-*N*-methylphenothiazine **18** ($\lambda = 523$, 751, 841 nm) (Table 3). In the spectroelectrogram of the oxidation of [3.3]cyclophane **8b**, a strong band develops at 553 nm, together with two weak bands at 790 nm and 870 nm. The corresponding absorptions of the [4.4]cyclophane radical trication $\mathbf{9b}^{3+}$ are located at 536 (s), 785 (w) and 870 nm (w). These latter absorptions are nearly identical with that of the oxidized reference compound 2,7-diethyl-*N*-methylphenothiazine (**44**) ($\lambda =$ 536, 765 and 850 nm), which indicates that there is no electronic interaction between the chromophores in the radical trication of the [4.4]cyclophane **9b**. However, the absorption of the oxidized [3.3]cyclophane **8b** at $\lambda = 553$ nm shows a bathochromic shift of 17 nm relative to that of the oxidized [4.4]cyclophane **9b** and the reference compound **44**. This may largely be the result of the destabilized ground state of the [3.3]cyclophane radical trication $\mathbf{8b}^{3+}$ (strong Coulombic interaction between the positive charges of the donor and acceptor moieties, which are in closer proximity in comparison to that in the [4.4]cyclophane radical trication $\mathbf{9b}^{3+}$).

The spectroelectrochemistry of the reduction of the oligooxa[3*n*+2]cyclophanes and of the [3.3]- and [4.4]cyclophanes confirmed the typical long wavelength absorption maximum of the bipyridinium monocation at $\lambda \approx 600$ nm (Table 3).The spectroelectrograms of reductions of all oligooxacyclophanes and the bipyridinium reference compound to the neutral species counterpart were identical in the region $\lambda = 300-800$ nm.

These results mean that neither electrochemically nor spectroelectrochemically significant electronic interactions could be established, except for Coulombic effects between the donor and acceptor moieties of the oligooxa[3*n*+2]cyclophanes and of the [3.3]- and [4.4]cyclophanes.

Conclusions

Flexible phenothiazine−bipyridinium oligooxa[3*n*+2]cyclophanium compounds with long (eight-membered to twenty-membered) bridges, enabling superposition of the donor and acceptor units in crossed orientations, exhibit weak but significant CT absorptions. A parallel superposition of the donor−acceptor pair, connected by a very short bridge, as achieved in the rigid phenothiazine−bipyridinium [3.3]cyclophane, does not produce any CT effect. This orientation-dependent behaviour of the phenothiazine−bipyridinium cyclophanes might be the consequence of more or less suitable HOMO−LUMO overlap. Among the oligooxacyclophanes, the smallest one − the [8.8]cyclophane − showed the strongest CT absorption, hypsochromically shifted in comparison to those of the larger oligooxacyclophanes. The hypsochromic shift can be explained by growing destabilization of the CT state as the macrocycle becomes smaller. Quenching of phenothiazine fluorescence in the cyclophanes is explicable in terms of a photoinduced electron transfer process through a charge-separated state, the energy of which should be highest in the [3.3]cyclophane, because of charge repulsion stronger than that in the larger oligooxacyclophanes.

Surprisingly, NOEs were detected in the large macrocyclic oligooxacyclophanes. It may be assumed that the donor−acceptor units may approach in a crossed orientation on the NMR timescale. The electrochemical and spectroelectrochemical behaviour of the oligooxa[3*n*+2]- and of the [3.3]- or [4.4]cyclophanes is dominated by Coulombic interaction between the bipyridinium and phenothiazine units, and does not indicate charge-transfer interaction between the donor and acceptor units in the ground state.

Experimental Section

General: UV/Vis: Varian Cary 2300. − ^{1}H NMR: Bruker HX 360 and AM 500. − Fluorescence: SPEX Fluorolog F 112 XE. − MS:

Jeol JMS SX 102 A (FAB spectra in the matrix *m*-nitrobenzyl alcohol/1% trifluoroacetic acid; EI spectra with given temperature T_P of the probe); Finnigan MAT 212. − IR: Perkin−Elmer FT-IR 1760 X. − Cyclic voltammetry: Amel System 5000 (platinum disc electrode as working electrode, Ag/AgCl electrode as pseudo-reference electrode, internally calibrated vs. ferrocene). Potentiostat EG&G Princeton Applied Research 263 A (glassy carbon electrode as working electrode, platinum wire in 3 M KCl as counter electrode, Ag/AgCl as reference electrode). Solvent: acetonitrile; supporting electrolyte: tetra-*n*-butylammonium hexafluorophosphate. − Spectroelectrochemistry: Perkin−Elmer Lambda 9 and a spectroelectrochemical cell with an optically transparent thin-layer electrode;[11] for measurement of the less stable radical ions a modified Polytec photodiode array spectrometer X-dap was used, coupled to a previously described spectroelectrochemical cell.[12] − Chromatography: Column of Silitech silica gel (60−200 mesh, 60 Å), ICN Biochemicals; TLC with Riedel-de Haën Si F micro cards. − Melting points: Bock monoscope (uncorrected values).

General Procedure for the Synthesis of the Bipyridinophenothiazinophanium Diiodides 3a−7a: Solutions of the diiodides **12**−**16** (1.2 mmol) and of 4,4-bipyridine (**10**) (1.2 mmol) in nitromethane (each 50 mL) were added over 36 h to 50 mL of boiling nitromethane, using a two-channel syringe pump (Fa. B. Braun AG, Melsungen). After the mixture had been heated under reflux for the time indicated, the solvent was removed in vacuo. The residue was dissolved in 80 mL of trichloromethane, the solution shaken with water (3 × 100 mL), and the combined aqueous phases were filtered and subsequently lyophilized. The crude materials were purified and dried in vacuo.

Compound 3a: The reaction time after the addition of the cyclization components **12** and **10** was 3 d. The crude product was dissolved in 20 mL of water. After storage of the solution in the refrigerator for some days, a dark microcrystalline precipitate had deposited; this was recrystallized from water to give **3a** (127 mg, 8.2%) as very small, dark green plates, m.p. 262 °C (decomp.) − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.11 (s, 3 H, NCH_3), 3.55 (s, 2 H, 7′-CH_2), 3.63 (s, 2 H, 2′- CH_2), 3.73 (m, 4 H, $N^+CH_2CH_2OCH_2$), 3.92 (“t”, 2 H, $N^+CH_2CH_2$), 3.97 (“t”, 2 H, NCH_2CH_2), 4.18 (m, 4 H,CO_2CH_2), 4.75 (t, ^3J = 4.7 Hz, 2 H, N^+CH_2), 4.84 (t,^3J = 4.7 Hz, 2 H, N^+CH_2), 6.70 (“d”, 1 H, ArH, pos. 1), 6.76 (d, ^3J = 8.2 Hz, 2 H, ArH, pos. 3 and pos. 9), 6.86 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 6.96 (d, ^3J = 7.6 Hz, 1 H, ArH, pos. 4), 7.00 (dd, ^3J = 8.2, ^4J = 1.8 Hz, 1 H, ArH, pos. 8), 8.49 (m, 4 H, PyH), 9.02 (d, ^3J = 6.9 Hz, 2 H, PyH), 9.08 (d, ^3J = 6.9 Hz, 2 H, PyH); assignment of the signals by NOE; in CD_3CN: δ = 3.16 (s, 3 H, NCH_3), 3.52 (s, 2 H, 7′-CH_2), 3.57 (s, 2 H, 2′-CH_2), 3.74 (m, 4 H, $N^+CH_2CH_2OCH_2$), 3.89 (m, 2 H, $N^+CH_2CH_2$), 3.93 (m, 2 H, $N^+CH_2CH_2$), 4.22 (m, 4 H, CO_2CH_2), 4.61 (t^3, J = 4.7 Hz, 2 H, N^+CH_2), 4.74 (t, ^3J = 4.7 Hz, 2 H, N^+CH_2), 6.69 (d, ^3J = 1.6 Hz, 1 H, ArH, pos. 1), 6.75 (dd, ^3J = 7.5, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.77 (d, ^3J = 8.2 Hz, 1 H, ArH, pos. 9), 6.89 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 6.91 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 7.05 (dd, ^3J = 8.2, ^4J = 2.2 Hz, 1 H, ArH, pos. 8), 7.94 (2 d, ^3J = 7.0 Hz, 4 H, PyH), 8.53 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.60 (d, ^3J = 6.9 Hz, 2 H, PyH). − IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1} (νC=O). − MS (FAB): *m*/*z* = 627 [M$^+$ − 2 I]. − $C_{35}H_{37}I_2N_3O_6S$ (881.6): calcd. C 47.69, H 4.23, N 4.77, S 3.64; found C 47.40, H 4.30, N 5.07, S 3.53.

Compound 3b: A solution of silver tetrafluoroborate (44 mg, 0.22 mmol) in 10 mL of water was added to a suspension of [8.8]cyclophanium diiodide **3a** (100 mg, 0.11 mmol) in 50 mL of water, and the mixture was stirred for 30 min at room temperature. The solution was heated under reflux with filter paper and subsequently filtered through a G-4 glass frit to remove the precipitated silver iodide. The solvent was removed in vacuo and the residue taken up in nitromethane. The residual silver iodide was separated by centrifugation (10 h). The precipitate was decanted and the solvent removed in vacuo. After recrystallization from acetonitrile, **3b** (30 mg, 34%) was obtained as a blue-green solid, m.p. 245 °C (decomp.). − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.10 (s, 3 H, NCH_3), 3.55 (s, 2 H, 7′-CH_2), 3.63 (s, 2 H, 2′-CH_2), 3.72 (m, 4 H, $N^+CH_2CH_2$−O−CH_2), 3.91 (t, ^3J = 4.7 Hz, 2 H, $N^+CH_2CH_2$), 3.96 (t, ^3J = 4.9 Hz, 2 H, $N^+CH_2CH_2$), 4.18 (m, 4 H, CO_2CH_2), 4.74 (t, ^3J = 4.8 Hz, 2 H, N^+CH_2), 4.82 (t, ^3J = 4.7 Hz, 2 H, N^+CH_2), 6.70 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.74 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.75 (dd, ^3J = 7.8, ^4J = 1.5 Hz, 1 H, ArH, pos. 3), 6.86 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 6.95 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.99 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.48 (d, ^3J = 6.1 Hz, 4 H, PyH), 9.00 (d, ^3J = 6.9 Hz, 2 H, PyH), 9.07 (d, ^3J = 6.9 Hz, 2 H, PyH). − ^{1}H NMR (360 MHz, CD_3CN): δ = 3.15 (s, 3 H, NCH_3), 3.51 (s, 2 H, 7′-CH_2), 3.57 (s, 2 H, 2′-CH_2), 3.74 (m, 4 H, $N^+CH_2CH_2OCH_2$), 3.89 (“t”, 2 H, $N^+CH_2CH_2$), 3.94 (“t”, 2 H, $N^+CH_2CH_2$), 4.23 (m, 4 H, CO_2CH_2), 4.60 (“t”, 2 H, N^+CH_2), 4.73 (“t”, 2 H, N^+CH_2), 6.69 (d, ^4J = 1.7 Hz, 1 H, ArH, pos. 1), 6.75 (dd, ^3J = 8.4, ^4J = 1.8 Hz, 1 H, ArH, pos. 3), 6.76 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.89 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 6.91 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 7.05 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 7.94 (d, ^3J = 7.0 Hz, 2 H, PyH), 7.92 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.52 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.58 (d, ^3J = 7.0 Hz, 2 H, PyH). − MS (FAB): *m*/*z* (%) = 627 (100) [M$^+$ − 2 BF_4], 714 (28) [M$^+$ − BF_4]. − HRMS calcd. for $C_{35}H_{37}O_6N_3F_4BS$ [M$^+$ − BF_4] 714.2432; found 714.2463.

Compound 3c: Sodium perchlorate (81 mg, 0.66 mmol) was added to a solution of [8.8]cyclophanium diiodide **3a** (100 mg, 0.11 mmol) in 100 mL of water. The mixture was heated to reflux, then cooled in the refrigerator overnight. The deposited precipitate was separated, taken up in 30 mL of water, heated to reflux again and cooled to 4 °C overnight. The precipitate was filtered off and washed with a small amount of water to remove the remaining sodium iodide. The crude material was crystallized from acetonitrile and dried to yield **3c** (40 mg, 44%) as a blue-green powder, m.p. 245 °C (decomp.). − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.11 (s, 3 H, NCH_3), 3.55 (s, 2 H, 7′-CH_2), 3.63 (s, 2 H, 2′-CH_2), 3.72 (m, 4 H, $N^+CH_2CH_2OCH_2$), 3.91 (m, 2 H, $N^+CH_2CH_2$), 3.96 (m, 2 H, $N^+CH_2CH_2$), 4.18 (m, 4 H, CO_2CH_2), 4.74 (“t”, 2 H, N^+CH_2), 4.82 (“t”, 2 H, N^+CH_2), 6.70 (d, ^4J = 1.3 Hz, 1 H, ArH, pos. 1), 6.75 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.76 (dd, ^3J = 7.9, ^4J = 1.4 Hz, 1 H, ArH, pos. 3), 6.86 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 6.95 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 7.00 (dd, ^3J = 8.3, ^4J = 2.2 Hz, 1 H, ArH, pos. 8), 8.48 (d, ^3J = 6.2 Hz, 4 H, PyH), 9.00 (d, ^3J = 7.1 Hz, 2 H, PyH), 9.07 (d, ^3J = 6.7 Hz, 2 H, PyH). − MS (FAB): *m*/*z* (%) = 627 (100) [M$^+$ − 2 ClO_4], 726 (15) [M$^+$ − ClO_4]. − HRMS calcd. for $C_{35}H_{37}O_{10}N_3ClS$ [M$^+$ − ClO_4] 726.1889; found 726.1917.

Compound 4a: The reaction time after the addition of the cyclization components **13** and **10** was 3 d. The crude material was dissolved in 70 mL of water. After storage of the solution for some days at 4 °C, **4a** (224 mg, 18.9%) deposited as fine, black needles, which were dried in vacuo at 110 °C, m.p. 138−139 °C. − ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.11 (s, 3 H, NCH_3), 3.48−3.60 (m, 14 H, 2 × CH_2CH_2OCO, 2 × CH_2CH_2O + 7′-CH_2), 3.66 (s, 2 H, 2′-CH_2), 3.89 (“t”, 2 H, $N^+CH_2CH_2$), 3.92 (“t”, 2 H, $N^+CH_2CH_2$), 4.21 (m, 4 H, CO_2CH_2), 4.79 (“t”, 2 H, N^+CH_2), 4.83 (“t”, 2H

N^+CH_2), 6.70 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.76 ("d", 1 H, ArH, pos. 1), 6.81 ("dd", ^3J = 7.8 Hz, 1 H, ArH, pos. 3), 6.94 ("s", 1 H, ArH, pos. 6), 6.95 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 7.03 (dd, ^3J = 8.3, ^4J = 1.6 Hz, 1 H, ArH, pos. 8), 8.38 (d, ^3J = 6.7 Hz, 2 H, PyH), 8.41 (d, ^3J = 6.7 Hz, 2 H, PyH), 9.12 (m, 4 H, PyH) − ^{1}H NMR (CD_3CN, 360 MHz): δ = 3.04 (s, 3 H, NCH_3), 3.55−3.75 (m, 16 H, 3 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2), 3.98 (m, 4 H, $N^+CH_2CH_2$), 4.36 (m, 4 H, CO_2CH_2), 4.83 (m, 4 H, N^+CH_2), 6.58 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.73 (d, ^4J = 1.0 Hz, 1 H, ArH, pos. 1), 6.85 (dd, ^3J = 7.8, ^4J = 1.3 Hz, 1 H, ArH, pos. 3), 6.89 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.92 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.06 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 7.89 (d, ^3J = 7.0 Hz, 2 H, PyH), 7.98 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.81 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.87 (d, ^3J = 7.0 Hz, 1 H, PyH). − ^{1}H NMR (CD_2Cl_2, 360 MHz): δ = 3.11 (s, 3 H, NCH_3), 3.60−3.75 (m, 16 H, 3 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2), 4.08 (m, 4 H, $N^+CH_2CH_2$), 4.42 (m, 4 H, CO_2CH_2), 5.12 (m, 4 H, N^+CH_2), 6.69 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.71 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.89 (dd, ^3J not determinable, ^4J = 1.5 Hz, 1 H, ArH, pos. 3), 6.90 (d, ^4J = 1.9 Hz, 1 H, ArH, pos. 6), 6.95 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 7.13 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.06 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.17 (d, ^3J = 6.9 Hz, 2 H, PyH), 9.28 (d, ^3J = 6.9 Hz, 2 H, PyH), 9.38 (d, ^3J = 6.9 Hz, 2 H, PyH). − IR (KBr): $\tilde{\nu}$ = 1730, 1712 ν(C=O). − MS (FAB): *m/z* = 715 [M^+ − 2 I]. − $C_{39}H_{45}I_2O_8N_3S{\cdot}H_2O$ (987.7): calcd. C 47.43, H 4.80 N 4.25, S 3.25; found C 47.28, H 4.59, N 4.37, S 3.29.

Compound 4b: A solution of [11.11]cyclophanium diiodide **4a** (50 mg, 0.051 mmol) in 100 mL of water was shaken with silver oxide (100 mg, 0.71 mmol), with ice cooling. The suspension containing the precipitated silver iodide was immediately filtered into a solution of 48% tetrafluoroboric acid (15 µL, 0.08 mmol). The violet solution was lyophilized and the crude material crystallized from acetonitrile, to give **4b** (24 mg, 53%) as violet microcrystals, m.p. 205 °C. − ^{1}H NMR (360 MHz, CD_3CN): δ = 3.02 (s, 3 H, NCH_3), 3.50−3.80 (m, 16 H, 2 × CH_2CH_2O + 2 × CH_2CH_2OCO + 7′-CH_2 + 2′-CH_2), 3.95 (m, 4 H 2 $N^+CH_2CH_2$), 4.37 (m, 4 H, 2 CO_2CH_2), 4.71 (m, 4 H, 2 N^+CH_2), 6.50 ("d", br., 1 H, ArH, pos. 9), 6.64 ("s", br. 1 H, ArH, pos. 1), 6.83 ("s", br. 2 H, ArH, pos. 3 + 4), 6.90 ("s", br. 1 H, ArH, pos. 6), 7.03 ("d", br. 1 H, ArH, pos. 8), 7.83 (d, ^3J = 6.9 Hz, 2 H, PyH), 7.91 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.69 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.74 (d, ^3J = 7.0 Hz, 2 H, PyH). − MS (FAB): *m/z* (%) = 715 (100) [M^+ − 2 BF_4], 802 (20) [M^+ − BF_4]. − HRMS calcd. for $C_{39}H_{50}O_8N_3F_4SB$ [M − BF_4] 802.2902; found 802.2929.

Compound 4c: Sodium perchlorate (24.7 mg, 0.202 mmol) was added to a solution of [11.11]cyclophanium diiodide **4a** (100 mg, 0.101 mmol) in 100 mL of water. The reaction mixture was kept in the refrigerator overnight. The deposited precipitate was filtered off and washed with a small amount of cold water to remove the remaining sodium iodide. The crude material was crystallized from acetonitrile and dried in vacuo to give **4c** (43.4 mg, 47%) as violet microcrystals, m.p. 238−240 °C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.10 (s, 3 H, NH_3), 3.20−3.60 (m, 14 H, 2 × CH_2CH_2O + 7′- CH_2 +2 × CH_2CH_2OCO), 3.65 (s, 2 H, 2′-CH_2), 3.88 ("t", 2 H, NCH_2CH_2), 3.91 ("t", 2 H, NCH_2CH_2), 4.20 (m, 4 H, CO_2CH_2), 4.78 ("t", 2 H, N^+CH_2), 4.82 ("t", 2 H, N^+CH_2), 6.69 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.75 (d, ^4J = 1.3 Hz, 1 H, ArH, pos. 1), 6.81 (dd, ^3J = 7.8, ^4J = 1.3 Hz, 1 H, ArH, pos. 3), 6.93 (d, $^4J \approx$ 2.6 Hz, 1 H, ArH, pos. 6), 6.94 (d, $^3J \approx$ 7.6 Hz, 1 H, ArH, pos. 4), 7.02 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 8.35 (d, ^3J = 6.6 Hz, 2 H, PyH), 8.39 (d, ^3J = 6.6 Hz, 2 H, PyH), 9.11 ("d", 4 H, PyH); in CD_3CN (360 MHz): δ = 3.02 (s, 3 H, NCH_3), 3.55−3.75 (m, 16 H, 2 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 3.94 (m, 4 H, 2$N^+CH_2CH_2$), 4.36 (m, 4 H, 2 CO_2CH_2), 4.71 (m, 4 H, 2N^+CH_2), 6.51 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.65 ("s", 1 H, ArH, pos. 1), 6.83 ("AB", J = 7.5 Hz, 2 H, ArH, pos. 3 + pos. 4), 6.90 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.04 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 7.85 (d, ^3J = 6.9 Hz, 2 H, PyH), 7.93 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.70 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.76 (d, ^3J = 7.0 Hz, 2 H, PyH). − MS (FAB): *m/z* (%) = 715 (100) [M^+ − 2 ClO_4], 814 (17) [M − ClO_4]. − HRMS calcd. for $C_{39}H_{45}O_{12}N_3ClS$ [M − ClO_4] 814.2412; found 814.2438.

Compound 4d: The preparation was analogous to that of **4c**, starting from [11.11]cyclophanium diiodide **4a** and potassium hexafluorophosphate in water. The precipitated **4d** was filtered off, dried at 50 °C in vacuo and recrystallized from acetonitrile, m.p. 196 °C (decomp.). − ^{1}H NMR (360 MHz, D_2O, only characteristic signals given): δ = 3.07 (s, 3 H, NCH_3), 3.82 (m, 4 H, NCH_2CH_2), 4.05 (m, 4 H, CO_2CH_2), 4.42 (m, 4 H, N^+CH_2), 6.65 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.73 ("d", X part of ABX, 1 H, ArH, pos. 1), 6.93 (AB part of ABX, J_{AB} = 7.8 Hz, J_{BX} = 1.3 Hz, ν_B = 6.92, ν_A = 6.94, 2 H, ArH, pos. 3 and pos. 4), 7.01 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.15 (dd, ^3J = 8.4, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 7.97 (d, ^4J = 6.9 Hz, 2 H, PyH), 8.05 (d, ^4J = 6.9 Hz, 2 H, PyH), 8.86 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.92 (d, ^4J = 6.9 Hz, 2 H, PyH). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.10 (s, 3 H, NCH_3), 3.40−3.70 (m, 16 H, 2 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 3.88 ("t", 2 H, $N^+CH_2CH_2$), 4.20 (m, 4 H, 2CO_2CH_2), 4.78 ("t", 2 H, N^+CH_2), 4.82 ("t", 2 H, N^+CH_2), 6.69 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.75 (d, ^4J = 1.3 Hz, 1 H, ArH, pos. 1), 6.81 (dd, ^3J = 7.9, ^4J = 1.3 Hz, 1 H, ArH, pos. 3), 6.94 (d, ^4J = 2.5 Hz, 1 H, ArH, pos. 6), 6.94 (d, ^3J = 7.5 Hz, 1 H, ArH, pos. 4), 7.02 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.36 (d, ^4J = 6.6 Hz, 2 H, PyH), 8.39 (d, ^4J = 6.8 Hz, 2 H, PyH), 9.11 (d, ^4J = 5.8 Hz, 4 H, PyH); in CD_3CN (360, MHz): δ = 3.02 (s, 3 H, NCH_3), 3.55−3.75 (m, 16 H, 2 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 3.94 (m, 4 H, 2$N^+CH_2CH_2$), 4.36 (m, 4 H, 2CO_2CH_2), 4.70 (m, 4 H, 2 × N^+CH_2), 6.49 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.64 (X part of ABX, not resolved, 1 H, ArH, pos. 1), 6.83 (AB part of ABX, J_{AB} = 7.9 Hz, J_{AX} = 1.4 Hz, ν_B = 6.82, ν_A = 6.84, 2 H, ArH pos. 4 + pos. 3), 6.90 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.04 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 7.84 (d, ^3J = 7.0 Hz, 2 H, PyH), 7.92 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.69 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.74 (d, ^3J = 7.1 Hz, 2 H, PyH). − IR (KBr): $\tilde{\nu}$ = 1732 cm^{-1} (C=O). − MS (FAB): *m/z* (%) = 715 (100) [M − 2 PF_6], 860 (24) [M^+ − PF_6], 1005 (0.4) [M^+]. − $C_{39}H_{45}O_8N_3S{\cdot}2PF_6{\cdot}H_2O$ (1023.8): calcd. C 45.75, H 4.63, N 4.10, S 3.13; found C 45.65, H 4.44, N 3.79, S 3.19.

Compound 5a: The preparation was according to the general procedure described above, starting from **14** and **10**. The reaction time was 4 d. The crude material was dissolved in 30 mL of water and purified by chromatography on BIORAD P-2 Gel (fine) with water. The product was recognizable on the column as a grey blue zone. The fraction was frozen and the solvent removed by lyophilization. The residue was recrystallized from methanol to give **5a** (200 mg, 17%) as black-red crystals, m.p. 75 °C (slow sintering). − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.16 (s, 3 H, NCH_3), 3.30−3.65 (m, 24 H, 4 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 3.95 (m, 4 H, 2 × $N^+CH_2CH_2$), 4.15 (m, 4 H, 2 × CO_2CH_2), 4.86 (m, 4 H, 2 × N^+CH_2), 6.74 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.77 ("d", 1 H, ArH, pos. 1), 6.79 (dd, ^3J = 7.7, ^4J = 1.5 Hz, ArH, pos. 3), 6.93 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 6.95 (d, ^4J =

1.9 Hz, 1 H, ArH, pos. 6), 7.04 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.50 (m, 4 H, PyH), 9.21 (m, 4 H, PyH). − ^{1}H NMR (CD_3CN,360 MHz, only characteristic signals given): δ = 3.10 (s, 3 H, NCH_3), 4.00 (m, 4 H, $N^+CH_2CH_2$), 4.33 (m, 4 H, CO_2CH_2), 4.75 (m, 4 H, N^+CH_2), 6.51 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.74 (d, X part of ABX, not resolved, 1 H, ArH, pos. 1), 6.77 (AB part of ABX, J_{AB} = 7.8 Hz, J_{AX} = 1.6 Hz, ν_B = 6.75, ν_A 6.79, 2 H, ArH, pos. 4 and pos. 3), 6.98 (d, ^3J = 1.9 Hz, 1 H, ArH, pos. 6), 7.01 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 7.93 (d, ^3J = 6.9 Hz, 2 H, PyH), 7.96 (d, ^3J = 6.5 Hz, 2 H, PyH), 8.88 (d, ^3J = 6.6 Hz, 2 H, PyH), 8.91 (d, ^3J = 7.0 Hz, 2 H, PyH). − CD_2Cl_2 (360 MHz): δ = 3.16 (s, 3 H, NCH_3), 3.55 −3.85 (m, 24 H, 4 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 4.13 (m, 4 H, $N^+CH_2CH_2$), 4.40 (m, 4 H, 2 × CO_2CH_2), 5.08 (m, 4 H, N^+CH_2), 6.54 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.76 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.78 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 6.86 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 7.00 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.15 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 8.10 (m, 4 H, PyH), 9.37 (m, 4 H, PyH). − IR (KBr): $\tilde{\nu}$ = 1726 cm^{-1} (νC=O). − MS(FAB): *m*/*z* (%) = 803 (100) [M^+ − 2 I], 402 (16). − $C_{43}H_{53}I_2N_3O_{10}S$·0.5 H_2O (1066.8): calcd. C 48.41, H 5.10, N 3.94, S 3.01; found C 48.58, H 5.14, N 4.21, S 2.97.

Compound 5b: A column filled with DOWEX 1 × 8 (Cl^- form) was rinsed with a 5% solution of sodium tetrafluoroborate until chloride was no longer detectable with $AgNO_3$. The column was then rinsed with water to remove the remaining sodium tetrafluoroborate. The [14.14]cyclophanium diiodide **5a** (100 mg) in 30 mL of water (brown solution) was layered on the column, and slowly (1 drop/s) eluted with water. The violet fraction containing the product was frozen and lyophilized to give **5b** (76 mg, 83%) as a dark violet solid, m.p. 79−80 °C. − ^{1}H NMR (360 MHz, CD_3CN, only characteristic signals given): δ = 3.02 (s, 3 H, NCH_3), 3.93 (m, 4 H, 2 × $N^+CH_2CH_2$), 4.37 (m, 4 H, 2 × CO_2CH_2), 4.71 (m, 4 H, 2 × N^+CH_2), 6.48 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.64 (d, X part of ABX, ^4J = 1.2 Hz, 1 H, ArH, pos. 1), 6.83 (AB part of ABX, J_{AB} = 7.8 Hz, J_{AX} = 1.4 Hz, ν_B = 6.82, ν_A = 6.84, pos. 4 + pos. 3), 6.89 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.04 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 7.83 (d, ^3J = 6.9 Hz, 2 H, PyH), 7.91 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.69 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.74 (d, ^3J = 7.0 Hz, 2 H, PyH). − MS (FAB): *m*/*z* (%) = 890 (32) [M^+ − BF_4], 803 (100) [M^+ − 2 BF_4], 402 (30). − HRMS calcd. for $C_{43}H_{60}BF_4N_3O_{10}S$ [M^+ − BF_4] 890.3481; found 890.3505.

Compound 5c: Sodium perchlorate (24.7 mg, 0.202 mmol) was added to a solution of [14.14]cyclophanium diiodide **5a** (107.7 mg, 0.101 mmol) in 30 mL of water. The reaction mixture was stored overnight in the refrigerator. The precipitate was filtered off and washed with a small amount of cold water to remove the remaining sodium iodide. The crude material was recrystallized from acetonitrile and dried in vacuo to yield **5c** (43.6 mg, 43%) as a microcrystalline product, m.p. 112−113 °C. − ^{1}H NMR (360 MHz, [D_6]DMSO, only characteristic signals given): δ = 3.16 (s, 3 H, NCH_3), 3.62 (s, 2 H, 2′-CH_2), 3.96 (m, 4 H, $N^+CH_2CH_2$), 4.16 (m, 4 H, 2 × CO_2CH_2), 4.84 (m, 4 H, 2 × N^+CH_2), 6.73 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.77 (d, ^4J = 1.9 Hz, 1 H, ArH, pos. 1), 6.80 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 6.93 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 6.96 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.03 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.48 (m, 4 H, PyH), 9.19 (d, ^3J = 6.8 Hz, 2 H, PyH), 9.21 (d, ^3J = 6.8 Hz, 2 H, PyH). − ^{1}H NMR (CD_3CN, only characteristic signals given): δ = 3.09 (s, 3 H, NCH_3), 3.99 (m, 4 H, $N^+CH_2CH_2$), 4.33 (m, 4 H, CO_2CH_2), 4.71 (m, 4 H, N^+CH_2), 6.47 (d, ^3J = 8.2 Hz, 1 H, ArH, pos. 9), 6.70 (d, X part of ABX, J_{XA} = 1.5 Hz, 1 H, ArH, pos. 1), 6.75 (AB part of ABX, J_{AB} = 7.8 Hz, J_{AX} = 1.6 Hz, ν_B = 6.73, ν_A = 6.75, pos. 4 + pos. 3), 6.97 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.00 (dd, ^3J = 8.2, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 7.88 (d, ^3J = 6.7 Hz, 2 H, PyH), 7.91 (d, ^3J = 6.8 Hz, 2 H, PyH), 8.77 (d, ^3J = 6.8 Hz, 2 H, PyH), 8.82 (d, ^3J = 6.8 Hz, 2 H, PyH). − MS (FAB): *m*/*z* (%) = 902 (18) [M^+ − ClO_4], 803 (100) [M^+ − 2 ClO_4]. − HRMS calcd. for $C_{43}H_{60}N_3ClS$ [M^+ − ClO_4] 902.2937; found 902.2940.

Compound 6a: The reaction time after the dropwise addition of the cyclization components **15** and **10** was 6 d. The crude material was chromatographed twice on BIORAD P2-Gel, using water as eluent. The fraction containing the product, recognizable on the column as a broad grey-blue zone, was frozen and the solvent removed in a lyophilisator to give **6a** (138 mg, 10%) as a red-brown powder, m.p. 65° (slow sintering). − ^{1}H NMR (360 MHz, CD_3CN): δ = 3.13 (s, 3 H, NCH_3), 3.40−3.70 (m, 32 H, 6 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 3.99 (m, 4 H, $N^+CH_2CH_2$), 4.26 (m, 4 H, CO_2CH_2), 4.74 (m, 4 H, N^+CH_2), 6.65 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.72 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.82 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 6.86 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 6.94 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.07 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.15 ("t", 4 H, PyH), 8.86 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.91 (d, ^3J = 7.0 Hz, 2 H, PyH); in CD_2Cl_2: δ = 3.18 (s, 3 H, NCH_3), 3.50−3.75 (m, 32 H, 6 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 4.12 (m, 4 H, $N^+CH_2CH_2$), 4.36 (m, 4 H, CO_2CH_2), 5.05 (m, 4 H, N^+CH_2), 6.66 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.77 ("d", not resolved, X part of ABX, 1 H, ArH, pos. 1), 6.85 (AB part of ABX, J_{AB} = 7.7 Hz, J_{BX} = 1.4 Hz, ν_A = 6.87, ν_B = 6.84, pos. 4 and pos. 3), 6.97 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.11 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 8.24 (m, 4 H, PyH), 9.32 (d, ^3J = 6.9 Hz, 2 H, PyH), 9.37 (d, ^3J = 6.9 Hz, 2 H, PyH). − If the crude material was chromatographed on P2-Gel using an aqueous buffer of 0.11 mol/L acetic acid and 0.1 mol/L triethylamine as eluent, with subsequent ion exchange on DOWEX 1 × 8 (I^- form) to transform the compound into the iodide form again, the amorphous red-brown cyclophane contained encapsulated triethylammonium iodide. Yield 250 mg (13%), m.p. 70 °C (sintering). − ^{1}H NMR (360 MHz, [D_6]DMSO): δ = 3.22 (s, 3 H, NCH_3), 3.40−3.55 (m, 30 H, 6 × CH_2CH_2O + 7′-CH_2 + 2 × CH_2CH_2OCO), 3.63 (s, 2 H, 2′-CH_2), 3.97 (m, 4 H, NCH_2CH_2), 4.14 (m, 4 H, CO_2CH_2), 4.86 (m, 4 H, NCH_2), 6.82 (m, 3 H, ArH, pos. 1 + pos. 9 +pos. 3), 6.99 (m, 2H ArH, pos. 6 + pos. 4), 7.07 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.64 (m, 4 H, PyH), 9.25 (m, 4 H, PyH); triethylammonium iodide: δ = 1.17 (t, ^3J = 7.3 Hz, 3 H), 3.07 (q, ^3J = 7.2 Hz, 2 H); in CD_2Cl_2: δ = 3.23 (s, 3 H, NCH_3), 3.50−3.75 (m, 32 H, 6 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × CH_2CH_2OCO), 4.10 (m, 4 H, $N^+CH_2CH_2$), 4.37 (m, 4 H, CO_2CH_2). 5.02 (m, 4 H, $N^+CH_2CH_2$), 6.73 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.80 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.86 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 6.93 (^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.99 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.12 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.35 (m, 4 H, PyH), 9.31 (d, ^3J = 6.3 Hz, 2 H, PyH), 9.35 (d, ^3J = 6.5 Hz, 2 H, PyH); triethylammonium iodide: δ = 1.43 (t, ^3J = 7.3 Hz), 3.13 (q, ^3J = 7.3 Hz). − IR (KBr): $\tilde{\nu}$ = 1724 cm^{-1} (C=O). − MS (FAB): *m*/*z* = 871 (100%) [M − 2 I]. − $C_{47}H_{31}I_2N_3O_{18}S$·1.2$Et_3NHI$ (1420.8): calcd. C 45.82, H 5.69, N 4.11, S 2.26; found C 45.88, H 5.68, N 4.22, S 2.61.

Compound 6b: A column filled with DOWEX 1 × 8 (Cl^- form) was rinsed with a 5% solution of sodium tetrafluoroborate until

chloride could no longer be detected ($AgNO_3$ test). After the column had been washed with 2 L of water to remove sodium tetrafluoroborate, the cyclophanium diiodide **6a** (56 mg, 0.049 mmol) was applied to the column and eluted slowly with water (1 drop/s) to afford a violet product fraction, which was frozen and lyophilized. Compound **6b** was obtained as a faint pink powder, which changed into a dark violet solid on action of moisture. Yield (38.7 mg, 74%), m.p. 80 °C (gradual sintering). −^{1}H NMR (360 MHz, CD_3CN): δ = 3.13 (s, 3 H, NCH_3), 3.30−3.65 (m, 32 H, 6 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × C*H*$_2$ CH_2 OCO), 3.97 (m, 4 H, $N^+CH_2CH_2$), 4.24 (m, 4 H, CO_2CH_2), 4.70 (m, 4 H, N^+CH_2), 6.64 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.70 (d, X part of ABX, J_{XB} = 1.4 Hz, 1 H, ArH, pos. 1), 6.84 (AB part of ABX, J_{AB} = 7.8 Hz, J_{BX} = 1.5 Hz, ν_A = 6.86, ν_B = 6.81, 2 H, ArH, pos. 4 and pos. 3), 6.93 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.06 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.12 (d, ^3J = 7.2 Hz, 2 H, PyH), 8.14 (d, ^3J = 7.2 Hz, 2 H, PyH), 8.81 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.86 (d, ^3J = 6.9 Hz, 2 H, PyH). − ^{1}H NMR (CD_2Cl_2): δ = 3.15 (s, 3 H, NCH_3), 3.45−3.75 (m, 32 H, 6 × CH_2CH_2O + 7′-CH_2 + 2′-CH_2 + 2 × C*H*$_2$$CH_2$OCO), 4.02 (m, 4 H, $N^+CH_2CH_2$), 4.28 (m, 4 H, CO_2CH_2), 4.81 (m, 4 H, N^+CH_2), 6.61 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.68 (d, X part of ABX, J_{XB} = 1.0 Hz, 1 H, ArH, pos. 1), 6.84 (AB part of ABX, J_{AB} = 7.7 Hz, J_{BX} = 1.2 Hz, ν_A = 6.87, ν_B = 6.82, 2 H, ArH, pos. 4 and pos. 3), 6.93 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.06 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.25 (m, 4 H, PyH), 9.00 (d, ^3J = 7.0 Hz, 2 H, PyH), 9.02 (d, ^3J = 7.0 Hz, 2 H, PyH). − MS (FAB): *m*/*z* (%) = 978 (12) [M − BF_4], 891 (100) [M − 2 BF_4]. − HRMS calcd. for $C_{47}H_{61}BF_4N_3O_{12}S$ [M − BF_4] 978.4005; found 978.4039.

Compound 6c: The preparation was analogous to that of compound **6b**, with a 5% solution of sodium perchlorate and starting from the [17.17]cyclophanium diiodide **6a** (40 mg, 0.035 mmol), yielding **6c** as a waxy dark violet solid (30.9 mg, 81%), m.p. 90 °C (sintering). − ^{1}H NMR (360 MHz, [D_6]DMSO, only characteristic signals given): δ = 3.21 (s, 3 H, NCH_3), 3.96 (m, 4 H, $N^+CH_2CH_2$), 4.14 (m, 4 H, CO_2CH_2), 4.85 (m, 4 H, N^+CH_2), 6.80 (m, 3 H, ArH, pos. 1 + 3 + 9), 6.98 (m, 2 H, ArH, pos. 4 + 6), 7.06 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.62 (2 d, ^3J = 7.0 Hz, 4 H, PyH), 9.23 (d, ^3J = 6.8 Hz, 2 H, PyH), 9.24 (d, ^3J = 6.8 Hz, 2 H, PyH). − MS (FAB): *m*/*z* (%) = 990 (26) [M^+ − ClO_4], 891 (100) [M^+ − 2 ClO_4], 697 (28). − HRMS calcd. for $C_{47}H_{61}N_3ClS$ [M − ClO_4] 990.3461, found 990.3492.

Compound 7a: The reaction time after the addition of the cyclization components **16** and **10** was 7 d. The crude material was purified by twofold chromatography on P2-Gel, using an aqueous buffer of 0.11 mol/L acetic acid and 0.1 mol/L triethylamine as eluent. Ion exchange on DOWEX 1 × 8 (I^- form) retransformed the compound into the iodide. After drying in the lyophilisator, **7a** (145 mg, 9%) was obtained as a brown powder containing encapsulated triethylamine, m.p. 60 °C (sintering). − ^{1}H NMR (360 MHz, [D_6]DMSO): δ = 3.24 (s, 3 H, NCH_3), 3.41 (m, 29 H, CH_2O), 3.55 (m, 9 H, CH_2), 3.64 (s, 2 H, 2′-CH_2), 3.98 (m, 4 H, $N^+CH_2CH_2$), 4.12 (m, 4 H, CO_2CH_2), 4.89 (m, 4 H, N^+CH_2), 6.81−6.84 (m, 2 H, pos. 1 and 3), 6.84 (d, ^3J = 8.5 Hz, 1 H, ArH, pos. 9), 7.01 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.02 (d, ^3J = 8.2 Hz, 1 H, ArH, pos. 4), 7.07 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.71 (d, ^3J = 6.6 Hz, 4 H, PyH), 9.30 (m, 4 H, PyH); triethylammonium iodide: δ = 1.18 (t, ^3J = 7.3 Hz, 3 H) and δ = 3.08 (q, ^3J = 7.3 Hz, 2 H); in D_2O: δ = 3.24 (s, 3 H, NCH_3), 3.55−3.90 (m, 40 H, 18 CH_2O + 7′-CH_2 and 2′-CH_2), 4.18 (m, 4 H, $N^+CH_2CH_2$), 4.42 (m, 4 H, CO_2CH_2), 4.98 (m, 4 H, N^+CH_2), 6.80 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.89 (s, 1H. ArH, pos. 1), 6.96 (m, 2 H, ArH, pos. 3 and 4), 7.08 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.23 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.38 (d, ^3J = 6.1 Hz, 4 H, PyH), 9.11 (m, 4 H, PyH); triethylammonium iodide: δ = 1.40 (t, ^3J = 7.3 Hz), and δ = 3.32 (q, ^3J = 7.3 Hz). −^{1}H NMR (CD_2Cl_2): δ = 3.28 (s, 3 H, NCH_3), 3.50−3.60 (m, 30 H, 15 CH_2O) 3.64−3.69 (m, 10 H, 3 CH_2O + 7′-CH_2 + 2′-CH_2), 4.07 (m, 4 H, $N^+CH_2CH_2$), 4.27 (m, 4 H, CO_2CH_2), 5.00 (m, 4 H, N^+CH_2), 6.79 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.79 (d, ^3J = 8.2 Hz, 1 H, ArH, pos. 9), 6.86 (dd, ^3J = 7.9, ^4J = 1.5 Hz, 1 H, ArH, pos. 3), 6.98 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 4), 7.00 (d, ^4J = 2.5 Hz, 1 H, ArH, pos. 6), 7.12 (dd, ^3J = 8.2, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.53 (d, ^3J = 5.2 Hz, 4 H, PyH), 9.32 (m, 4 H, PyH); triethylammonium iodide: δ = 1.43 (t, ^3J = 7.3 Hz) and δ = 3.15 (q, ^3J = 7.3 Hz). − IR (KBr): $\tilde{\nu}$ = 1728 cm^{-1} (C=O). − MS (FAB): *m*/*z* (%) = 980 (100) [MH − 2 I], 1107 (7) [MH − I]. $C_{51}H_{69}I_2N_3O_{14}S$ (M^+, 1233). − $C_{51}H_{69}I_2N_3O_{14}S$·1.8$(C_2H_5)_3NHI$ (1646.4): calcd. C 45.09, H 5.99, N 4.09, S 1.95; found C 45.33, H 6.17, N 4.39, S 2.23. − To free the product from triethylammonium iodide, the crude material was chromatographed twice on BIORAD P2-Gel, using water as eluent. The product fraction appearing on the column as a broad grey-blue zone was frozen and the solvent removed in the lyophilisator to give **7a** (113 mg, 8%) as a dark brown powder, m.p. 55 °C (slow sintering). − ^{1}H NMR (360 MHz, [D_6]DMSO, only characteristic signals given): δ = 3.23 (s, 3 H, NCH_3), 3.96 (m, 4 H, $N^+CH_2CH_2$), 4.12 (m, 4 H, CO_2CH_2), 4.86 (m, N^+CH_2), 6.81−6.85 (m, 3 H, ArH, pos. 1 and 3 and 9), 7.00 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 6), 7.02 (d, ^3J = 8.1 Hz, 1 H, ArH, pos. 4), 7.08 (dd, ^3J = 8.3, ^4J = 1.9 Hz, 1 H, ArH, pos. 8), 8.68 (d, ^3J = 6.0 Hz, 4 H, PyH), 9.27 (m, 4 H, PyH). − ^{1}H NMR (D_2O, only characteristic signals given): δ = 3.12 (s, 3 H, NH_3), 4.07 (m, 4 H, $N^+CH_2CH_2$), 4.33 (m, 4 H, CO_2CH_2), 4.87 (m, 4 H, N^+CH_2), 6.66 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.78 (d, X part of ABX, J_{XA} = 1.4 Hz, 1 H, ArH, pos. 1), 6.84 (AB part of ABX, J_{AB} = 8.0 Hz, J_{AX} = 1.4 Hz, ν_A = 6.86, ν_B = 6.82, 2 H, ArH, pos. 3 and pos. 4), 6.98 (d, ^4J = 1.9 Hz, 1 H, ArH, pos. 6), 7.12 (dd, ^3J = 8.6, ^4J = 2.2 Hz, 1 H, ArH, pos. 8), 8.22 (m, 4 H, PyH), 8.99 (m, 4 H, PyH). − ^{1}H NMR (CD_3CN, only characteristic signals given): δ = 3.16 (s, 3 H, NCH_3), 3.94 (m, 4 H, $N^+CH_2CH_2$), 4.22 (m, 4 H, CO_2CH_2), 4.73 (m, N^+CH_2), 6.69 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.74 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.81 (dd, ^3J = 7.8 Hz, 1 H, ArH, pos. 3), 6.88 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.93 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 7.06 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.22 (m, 4 H, PyH), 8.88 (m, 4 H, PyH). −^{1}H NMR (CD_2Cl_2): δ = 3.24 (s, 3 H, NH_3), 3.50−3.80 (m, 40 H, 18 CH_2O +7′-CH_2 + 2′-CH_2), 4.06 (m, 4 H, $N^+CH_2CH_2$), 4.31 (m, 4 H, CO_2CH_2), 5.04 (m, 4 H, N^+CH_2), 6.76 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.82 ("d", 1 H, ArH, pos. 1), 6.86 (dd, ^3J = 7.8 Hz, ^4J not determinable, 1 H, ArH, pos. 3), 6.98 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 7.00 (d, ^4J = 1.8 Hz, 1 H, ArH, pos. 6), 7.11 (dd, ^3J = 8.3, ^4J = 1.8 Hz, 1 H, ArH, pos. 8), 8.58 (d, ^3J = 6.5 Hz, 4 H, PyH), 9.29 (d, ^3J = 6.1 Hz, 4 H, PyH).

Compound 7b: A DOWEX 1 × 8 (I^- form) column was rinsed with a 5% solution of sodium tetrafluoroborate until the silver nitrate test for chloride was negative. The column was then rinsed with 2 L of water to remove the remaining sodium tetrafluoroborate and subsequently loaded with [20.20]cyclophanium diiodide **7a** (50 mg, 0.041 mmol), dissolved in 30 mL of water (brown solution). Slow elution (1 drop/s) afforded **7b** as a violet product fraction, which was lyophilized to give a faint pink powder, which transformed into a waxy dark violet solid on action of moisture. Yield 38 mg, sintering from 60 °C. − ^{1}H NMR (360 MHz, CD_3CN, only characteristic signals given): δ = 3.19 (s, 3 H, NCH_3), 3.93 (m, 4 H, $N^+CH_2CH_2$), 4.20 (m, 4 H, CO_2CH_2), 4.70 (m, 4 H, N^+CH_2), 6.72

(d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.74 (d, ^4J = 1.7 Hz, 1 H, ArH, pos. 1), 6.82 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.92 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.95 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.07 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 8.23 (m, 4 H, PyH), 8.84 (m, 4 H, PyH). − ^{1}H NMR (CD_2Cl_2, only characteristic signals given): δ = 3.17 (s, 3 H, NCH_3), 4.00 (m, 4 H, $N^+CH_2CH_2$), 4.30 (m, 4 H, CO_2CH_2), 4.75 (m, 4 H, N^+CH_2), 6.64 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.68 (d, X part of ABX, J_{XB} = 1.3 Hz, 1 H, ArH, pos. 1), 6.84 (AB part of ABX, J_{AB} = 7.8 Hz, J_{BX} = 1.3 Hz, ν_A = 6.86, ν_B = 6.82, 2 H, ArH, pos. 4 and pos. 3), 6.94 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.07 (dd, ^3J = 8.2, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 8.23 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.26 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.90 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.92 (d, ^3J = 7.0 Hz, 2 H, PyH). − MS (FAB): *m/z* (%) = 1066.5 (18) [$M^+ - BF_4$], 979.5 (100) [$M^+ - 2\ BF_4$], 891 (16), 490 (49). − HRMS: calcd. for $C_{51}H_{69}BF_4N_3O_{14}S$ [$M^+ - BF_4$] 1066.4529; found 1066.4565.

Compound 7c: The preparation was analogous to that of **7b**, starting from the [20.20]cyclophanium diiodide **7a** and using sodium perchlorate instead of sodium tetrafluoroborate. The fraction of the eluate containing **7c** was violet. After freezing of this fraction and removal of the solvent in the lyophilisator, a faint pink powder was obtained. This turned waxy and dark violet on action of traces of moisture. Yield 35.3 mg (73%), sintering from 68 °C. − ^{1}H NMR (360 MHz, CD_3CN): δ = 3.19 (s, 3 H, NCH_3), 3.35−3.65 (m, 40 H, 18 CH_2O + 7′-CH_2+ 2′-CH_2), 3.94 (m, 4 H, $N^+CH_2CH_2$), 4.20 (m, 4 H, CO_2CH_2), 4.68 (m, 4 H, N^+CH_2), 6.72 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.74 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.82 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 6.92 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.95 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.07 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 8.21 (m, 4 H, PyH), 8.80 (d, ^3J = 7.0 Hz, 2 H, PyH), 8.82 (d, ^3J = 7.1 Hz, 2 H, PyH). − $C_{51}H_{69}O_{22}N_3Cl_2S$ (1179.1). − MS (FAB): *m/z* (%) = 1078 (34) [$M^+ - ClO_4$], 980 (100) [$M^+ - 2\ ClO_4$], 490 (42). − HRMS calcd. for $C_{51}H_{69}ClN_3O_{18}S$ [$M^+ - ClO_4$] 1078.3942; found 1078.3964.

7a·Bis(barium diiodide): A saturated solution of barium diiodide in acetone was added to a solution of **7a** (25 mg, 0.015 mmol) in 10 mL of acetone until precipitation had finished. The precipitate was filtered off and dried at 40 °C in vacuo to give **7a** (6.7 mg, 22%) as a red brown powder. − ^{1}H NMR (360 MHz, CD_3CN): δ = 3.22 (s, 3 H, NCH_3), 3.50−3.80 (m, 40 H, 18 CH_2O + 7′-CH_2 + 2′-CH_2), 4.05 ("t", 2 H, $N^+CH_2CH_2$), 4.09 ("t", 2 H, $N^+CH_2CH_2$), 4.46 (m, 4 H, CO_2CH_2), 4.64 (t, ^3J = 4.6 Hz, 2 H, N^+CH_2), 4.70 (t, ^3J = 4.7 Hz, 2 H, N^+CH_2), 6.77 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.80 ("d", 1 H, ArH, pos. 1), 6.88 (dd, ^3J = 7.9 Hz, ^4J ill-defined, 1 H, ArH, pos. 3), 6.97 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 6.98 (s, 1 H, ArH, pos. 6), 7.11 (dd, ^3J = 8.3, ^4J = 1.9 Hz, 1 H, ArH, pos. 8), 8.26 (d, ^3J = 6.8 Hz, 2 H, PyH), 8.30 (d, ^3J = 6.8 Hz, 2 H, PyH), 8.89 (d, ^3J = 6.7 Hz, 2 H, PyH), 8.94 (d, ^3J = 6.7 Hz, 2 H, PyH). − IR (KBr): $\tilde{\nu}$ = 1699 cm^{-1} (C=O). − MS (FAB): *m/z* (%) = 1891 (24) [$MH^+ - I$], 1764 (89) [$MH^+ - 2\ I$], 1637 (30) [$MH^+ - 3\ I$], 1372 (27) [$MH^+ - BaI_4$], 980 (100) [$MH^+ - Ba_2I_6$] if $M^+ = C_{51}H_{69}Ba_2I_6N_3O_{14}S$. − MS (FAB) of a mixture of **7a** (triethylammonium adduct) and $Ba(SCN)_2$: *m/z* (%) = 980 (100) [$C_{51}H_{70}N_3O_{14}S$], 1234 (3) [$C_{51}H_{70}N_3O_{14}SI_2$], 1303 (5) [$C_{51}H_{70}N_3O_{14}SBa(SCN)I$], 1430 (5) [$C_{51}H_{70}N_3O_{14}SBa_2(SCN)_3$], 1488 (5) [$C_{51}H_{70}N_3O_{14}SBa_2(SCN)_4$], 1499 (5) [$C_{51}H_{70}N_3O_{14}SBa_2(SCN)_2I$], 1543 (10) [$C_{51}H_{69}N_3O_{14}SBa_2(SCN)_2(CF_3CO_2H)I$], 1557 (10) [$C_{51}H_{70}N_3O_{14}SBa(SCN)I_3$], 1612 (10) [$C_{51}H_{69}N_3O_{14}SBa_2(SCN)_2(CF_3CO_2H)I$], 1626 (5) [$C_{51}H_{70}N_3O_{14}SBa_2(SCN)_2I_2$]. − $C_{51}H_{69}I_2N_3O_{14}S{\cdot}2BaI_2$ (2016.3): calcd. C 30.38, H 3.45, N 2.08, S 1.59; found C 28.65, H 3.44, N 2.04, S 1.29.

Compound 8a: A solution of 2,7-bis(3-iodopropyl)-*N*-methylphenothiazine (**30**) (180 mg, 0.33 mmol) in 30 mL of trichloromethane, and a solution of 4,4′-bipyridine (**10**) (51.2 mg, 0.33 mmol) were added to 30 mL of refluxing nitromethane using a two-channel syringe pump (0.5 mL/h). The solution was heated under reflux for a further 24 h. The solvent was evaporated in vacuo and the residue was treated with petroleum ether to remove starting materials. The remaining solid was extracted several times with hot methanol. The combined methanol solution was cooled to room temperature and filtered, and the solvent was removed in vacuo. The crude material was crystallized first from methanol, then from water to afford the title compound **8a** as a black solid (20 mg, 9.1%) with m.p. 290 °C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 2.50−2.70 (m, 4 H, $CH_2CH_2CH_2$), 2.80−2.95 (m, 4 H, Ar−CH_2), 3.05 (s, 3 H, NCH_3), 4.85 (m, 4 H, N^+CH_2), 6.22 (s, 1 H, ArH, pos. 1), 6.52 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.62 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 6), 6.72 (d, ^3J = 7.9 Hz, 1 H, ArH, pos. 3), 6.81 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 6.84 (dd, ^3J = 8.3, ^4J = 1.5 Hz, 1 H, ArH, pos. 8), 8.23 (m, 1 H, PyH), 8.28 (m, 2 H, PyH), 8.34 (m, 1 H, PyH), 9.07 (d, ^3J = 6.2 Hz, 1 H, PyH), 9.24 (d, ^3J = 6.3 Hz, 1 H, PyH), 9.29 (d, ^3J = 6.0 Hz, 1 H, PyH), 9.38 (d, ^3J = 6.4 Hz, 1 H, PyH). −^{1}H NMR (CD_3CN): δ = 2.50−2.70 (m, 4 H, $CH_2CH_2CH_2$), 2.90−3.05 (m, 4 H, $ArCH_2$), 3.10 (s, 3 H, NCH_3), 4.85 (m, 4 H, N^+CH_2), 6.24 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.57 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.66 (d, ^4J = 1.9 Hz, 1 H, ArH, pos. 6), 6.76 (dd, ^3J = 7.8, ^4J = 1.4 Hz, 1 H, ArH, pos. 3), 6.85 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.87 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 7.89 (m, 1 H, PyH), 8.06 (m, 2 H, PyH), 8.16 (m, 1 H, PyH), 8.73 ("d", 1 H, PyH), 8.90 ("d", 1 H, PyH), 8.98 ("d", 1 H, PyH), 9.16 ("d", 1 H, PyH). − $C_{29}H_{29}I_2N_3S$ (705.4). − MS (FAB): *m/z* (%) = 578 (7) [$M^+ - I$], 451 (100) [$M^+ - 2\ I$]. − HRMS calcd. for $C_{29}H_{29}IN_3S$ [$M^+ - I$] 578.1127; found 578.1146.

Compound 8b: A column filled with DOWEX-50 1 × 8 (Cl^- form) was rinsed with aqueous sodium tetrafluoroborate until chloride was no longer detectable. To remove excess sodium tetrafluoroborate, it was washed with 2 L of water. A solution of **8a** (42 mg, 0.06 mol) in 50 mL of water was then loaded onto the column. Elution with water, evaporation of the solvent in a rotary evaporator and crystallization of the residue from water gave **8b** (30 mg, 80%) as green crystals, m.p. > 300 °C. − ^{1}H NMR (500 MHz, CD_3CN): δ = 2.50−2.70 (m, 4 H, $CH_2CH_2CH_2$), 2.90−3.10 (m, 4 H, $ArCH_2$), 4.85 (m, 4 H, N^+CH_2), 6.22 (d, ^4J = 1.7 Hz, 1 H, ArH, pos. 1), 6.56 (d, ^3J = 8.6 Hz, 1 H, ArH, pos. 9), 6.67 (d, ^4J = 1.7 Hz, 1 H, ArH, pos. 6), 6.78 (dd, ^3J = 7.7, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.88 (dd, ^3J = 8.6, ^4J = 1.7 Hz, 1 H, ArH, pos. 8), 6.89 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 7.85 (m, 1 H, PyH), 8.00, (m, 3 H, PyH), 8.65 ("d", 1 H, PyH), 8.81 ("d", 1 H, PyH), 8.88 ("d", 1 H, PyH), 8.97 ("d", 1 H, PyH). − MS (FAB): *m/z* (%) = 538 (16) [$M^+ - BF_4$], 451 (100) [$M^+ - 2\ BF_4$]. − HRMS calcd. for $C_{29}H_{29}BF_4N_3S$ [$M^+ - BF_4$] 538.2111; found 538.2108.

Compound 9a: A solution of 2,7-bis(4-iodobutyl)-*N*-methylphenothiazine (**31**) (190 mg, 0.33 mmol) in 30 mL of trichloromethane, and a solution of 4,4′-bipyridine (**10**) (51.2 mg, 0.33 mmol) in 30 mL of nitromethane were added simultaneously whilst stirring to 30 mL of refluxing nitromethane, using a two-channel syringe pump (0.4 mL/h). The solution was heated under reflux for a further 24 h. The solvents were removed in vacuo and the residue treated with boiling petroleum ether to separate unconverted cyclization components. The remaining solid product was recrystallized several times from acetonitrile until a green powder was obtained and was then recrystallized from methanol to afford **9a** (16 mg, 6.65%) as very fine, light green needles, m.p. 256−257 °C.

− ^{1}H NMR (500 MHz, [D$_4$]methanol): δ = 1.35−1.55 (m, 2 H, $N^+CH_2CH_2$), 2.00−2.15 (m, 2 H, $N^+CH_2CH_2$), 2.15−2.30 (m, 4 H, Ar CH_2CH_2), 2.30−2.40 (m, 2 H, $ArCH_2$), 2.45−2.70 (m, 2 H, $ArCH_2$), 4.40−4.55 (m, 2 H, N^+CH_2), 4.65−4.75 (m, 2 H, N^+CH_2), 6.05 (d, ^4J = 1.3 Hz, 1 H, ArH, pos. 1), 6.34 (d, ^3J = 2.0 Hz, 1 H, ArH, pos. 6), 6.48 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.57 (dd, ^3J = 7.6, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.73 (d, ^3J = 7.6 Hz, 1 H, ArH, pos. 4), 6.79 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.55 (d, ^3J = 6.3 Hz, 4 H, PyH), 8.99 (d, ^3J = 6.7 Hz, 2 H, PyH), 9.01 (d, ^3J = 6.7 Hz, 2 H, PyH). −^{1}H NMR (CD_3CN, 360 MHz, only characteristic signals given): δ = 4.37 (m, 2 H, N^+CH_2), 4.62 (m, 2 H, N^+CH_2), 6.03 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.36 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 6.45 (d, ^3J = 8.2 Hz, 1 H, ArH, pos. 9), 6.55 (dd, ^3J = 7.6, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.75 (d, ^3J = 7.6 Hz, 1 H, ArH, pos. 4), 6.76 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 8.29 (d, ^3J = 6.8 Hz, 2 H, PyH), 8.30 (d, ^3J = 6.8 Hz, 2 H, PyH), 8.68 (d, ^3J = 6.9 Hz, 2 H, PyH), 8.71 (d, ^3J = 6.9 Hz, 2 H, PyH). − MS (FAB): *m/z* (%) = 606 (2.5) [M$^+$ − I], 479 (100) [M$^+$ − 2 I]. − HRMS calcd. for $C_{31}H_{33}IN_3S$ [M$^+$ − I] 606.1440; found 606.1405.

Compound 9b: A solution of the cyclophanium diiodide **9a** (15 mg, 0.02 mmol) in a water/methanol mixture (3:1) was loaded onto a DOWEX-50 1 × 8 (BF_4^- form) column prepared as described for **8b**. After elution with methanol/water (3:1), the solvents were removed in vacuo and the residue crystallized from water to give **9b** (9.4 mg, 70%) as very fine, green needles, sintering from 250 °C. − ^{1}H NMR (500 MHz, [D$_4$]methanol): δ = 1.33−1.55 (m, 2 H, $ArCH_2CH_2$), 2.00−2.15 (m, 2 H, $ArCH_2CH_2$), 2.15−2.30 (m, 4 H, $N^+CH_2CH_2$), 2.30−2.43 (m, 2 H, $ArCH_2$), 2.43−2.70 (m, 2 H, $ArCH_2$), 4.35−4.50 (m, 2 H, N^+CH_2), 4.60−4.73 (m, 2 H, N^+CH_2), 6.03 (d, ^4J = 1.7 Hz, ArH, pos. 1), 6.33 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6), 6.45 (d, ^3J = 8.1 Hz, 1 H, ArH, pos. 9), 6.54 (dd, ^3J = 7.5, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.72 (d, ^3J = 7.5 Hz, 1 H, ArH, pos. 4), 6.76 (dd, ^3J = 8.1, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 8.50 (d, ^3J = 6.4 Hz, 2 H, PyH), 8.51 (d, ^3J = 6.4 Hz, 2 H, PyH), 8.96 (d, ^3J = 6.7 Hz, 2 H, PyH), 8.99 (d, ^3J = 6.7 Hz, 2 H, PyH). − MS (FAB): *m/z* (%) = 566 (8) [M$^+$ − BF_4], 479 (100) [M$^+$ − 2BF_4]. − HRMS calcd. for $C_{31}H_{33}BF_4N_3S$ [M$^+$ − BF_4] 566.2424; found 566.2418.

2,7-Bis(2′-iodoethoxycarbonylmethyl)-*N*-methylphenothiazine (11): Sodium iodide (4 g, 26 mmol) was added to a solution of the dichloride **19** (1.28 g, 2.8 mmol) in 50 mL of butanone, and the mixture was heated under reflux with stirring for 48 h. Precipitated sodium chloride was filtered off, the solvent was removed in vacuo and the residue was chromatographed on silica gel, using cyclohexane/ethyl acetate (1:1) as eluent, to give **11** (470 mg, 26%) as a yellow oil (R_f = 0.6, cyclohexane/ethyl acetate, 1:1). − ^{1}H NMR (360 MHz, [D$_6$]benzene): δ = 2.68 (m, 4 H, CH_2I), 2.76 (s, 3 H, NCH_3), 3.23 (s, 2 H, 7′-CH_2), 3.28 (s, 2 H, 2′-CH_2), 3.92 (m, 4 H, CO_2CH_2), 6.33 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.49 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.65 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 6.90 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 6.94 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.99 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6). − IR (NaCl, film): $\tilde{\nu}$ = 1737 cm^{-1} (νC=O). − MS (EI, T_P = 280 °C): *m/z* (%) = 639 (6), 638 (15), 637 (100) [M$^+$], 438 (15), 425 (11), 239 (16), 238 (11), 194 (16). − $C_{21}H_{21}I_2NO_4S$ (637.3): calcd. C 39.58, H 3.32, N 2.20, S 5.03; found C 40.02, H 3.43, N 2.21, S 5.33.

2,7-Bis(5′-iodo-3′-oxapentyloxycarbonylmethyl)-*N*-methylphenothiazine (12). − Method A: Sodium iodide was added to a boiling solution of the dichloride **20** (2.0 g, 3.6 mmol) in 60 mL of butanone until the solution was saturated. After heating for a further 48 h, the precipitated sodium chloride was filtered off and the solvent removed in vacuo. The remaining crude material was chromatographed on silica gel, using cyclohexane/ethyl acetate (2:1) as eluent, to give **12** (1.63 g, 62%) as a yellow oil, R_f = 0.5. − **Method B:** Methyl trifluoromethanesulfonate (1.34 mL, 2.0 g, 12.2 mmol) was added dropwise at 0 °C to a solution of carbonyldiimidazole (1.0 g, 6.1 mmol) in 10 mL of nitromethane. This solution was added in one portion to a suspension of *N*-methylphenothiazine-2,7-diacetate **17** (1.0 g) in 40 mL of nitromethane. After 1−2 h, diethylene glycol monoiodide (1.9 g, 9 mmol) was added to the clear solution with stirring, and the mixture was stirred for a further 12 h. Nitromethane was then removed in vacuo and exchanged for 150 mL of ethyl acetate. After washing with 5% sodium hydrogen carbonate and removal of the solvent in vacuo, the residue was chromatographed on silica gel, using cyclohexane/ethyl acetate (1:1) as eluent, to yield **12** (1.93 g, 87%) as a yellow oil. A correct elemental analysis could not be obtained − ^{1}H NMR (500 MHz, [D$_6$]benzene): δ = 2.69−2.76 (m, 7 H, CH_2I and NCH_3), 2.73 (s, 3 H, NCH_3), 3.08−3.18 (m, 8 H, CH_2O), 3.27 (s, 2 H, 7′-CH_2), 3.33 (s, 2 H, 2′-CH_2), 3.98 (m, 4 H, CH_2O), 6.32 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.51 (d, ^4J = 1.2 Hz, 1 H, ArH, pos. 1), 6.69 (dd, ^3J = 7.7, ^4J = 1.3 Hz, 1 H, ArH, pos. 3), 6.93 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 6.97 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 7.01 (d, ^4J = 1.9 Hz, 1 H, ArH, pos. 6). − IR (NaCl film): $\tilde{\nu}$ = 1735 cm^{-1} (νC=O). − MS (EI, T_P = 386 °C): *m/z* (%) = 726 (18), 725 (100) [M$^+$].

Diethylene Glycol Monoiodide: A solution of diethylene glycol monochloride (Fluka) (10 g, 40 mmol) in 80 mL of acetone, saturated with sodium iodide, was heated under reflux for 24 h. The solvent was then removed in vacuo and the residue distilled under reduced pressure to yield a dark brown (because of elementary iodine) liquid, which was purified by dissolution in acetone and dropwise addition of a sulfuric sodium sulfite solution until the mixture was decolourised. After removal of the solvents, the residue was redistilled in vacuo to give the product (10.5 g, 61%) as a light yellow oil, b.p. 73−75 °C, 0.03 mbar. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.12 (s, 1 H, OH), 3.25 (t, ^3J = 6.5 Hz, 2 H, CH_2I), 3.59 (m, 2 H, CH_2OH), 3.71 (m, 4 H, CH_2). − MS (EI, T_P = 32 °C): *m/z* (%) = 217 (0.2), 216 (1) [M$^+$] 185 (8), 155 (100), 127 (5), 89 (17). − $C_4H_9IO_2$ (216.0): calcd. C 22.24, H 4.20; found C 22.57, H 4.37.

2,7-Bis(8′-iodo-3′,6′-dioxaoctyloxycarbonylmethyl)-*N*-methylphenothiazine (13): The preparation was analogous to that of **12**, starting from dichloride **21** (8.77 g, 13.7 mmol) in 110 mL of acetone to afford **13** (9.40 g, 84%) as a yellow oil, R_f = 0.4 (silica gel; ethyl acetate/cyclohexane 1:2) or R_f = 0.7 (RP-18 Gel; methanol/10% water). A correct elemental analysis was not obtained; the product was sufficiently pure, however, for synthetic purposes. − ^{1}H NMR (360 MHz, [D$_6$]benzene): δ = 2.73 (s, 3 H, NCH_3), 2.83 (m, 4 H, CH_2I), 3.26 (m, 20 H, CH_2O + 2′-CH_2 and 7′-CH_2), 4.08 (m, 4 H, CO_2CH_2), 6.32 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.53 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.70 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.94 (dd, ^3J = 8.2, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 6.96 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 7.02 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6). − IR (NaCl, film): $\tilde{\nu}$ = 1737 and 1735 cm^{-1} (νC=O). − MS (EI, T_P = 393 °C): *m/z* (%) = 814 (10), 813 (29) [M$^+$], 199 (11), 155 (100), 142 (84), 141 (12), 128 (22), 127 (37), 88 (22).

2,7-Bis(11′-iodo-3′,6′,9′-trioxaundecyloxycarbonylmethyl)-*N*-methylphenothiazine (14): A solution of 3,3′-dimethylcarbonyldiimidazolium bis(triflate) (prepared from 1 g of carbonyldiimidazole as in the preparation of **12**, method B) was added in one portion to a suspension of *N*-methylphenothiazine-2,7-diacetic acid (**17**) (1 g,

3.3 mmol) in 40 mL of nitromethane. The suspension was stirred until the dissolution was complete (1−2 h). Tetraethylene glycol monoiodide (2.73 g, 8.5 mmol) was then added and stirring was continued overnight. After concentration and dissolution in 200 mL of ethyl acetate, the solution was washed with a 5% solution of sodium hydrogen sulfate (50 mL). The organic phase was dried with sodium sulfate, the solvent removed in vacuo and the residue subjected to chromatography on silica gel, with ethyl acetate/cyclohexane (4:1) as eluent, to give **14** (1.25 g, 45%) as a yellow oil, R_f = 0.7. − ^{1}H NMR (360 MHz, [D$_6$]benzene): δ = 2.73 (s, 3 H, NCH$_3$), 2.83 (m, 4 H, CH$_2$I), 3.25−3.38 (m, 28 H, CH$_2$O +2′-CH$_2$ + 7′-CH$_2$), 4.10 (m, 4 H, CO$_2$CH$_2$), 6.32 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.52 (d, ^4J = 1.7 Hz, 1 H, ArH, pos. 1), 6.69 (dd, ^3J = 7.8, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.93 (dd, ^3J ill-defined, ^4J = 2.2 Hz, 1 H, ArH, pos. 8), 6.95 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4), 7.01 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6). − IR (NaCl film): $\tilde{\nu}$ = 1737 cm^{-1} (νC=O). − MS (EI, T_P = 380 °C): *m*/*z* (%) = 901 (100) [M$^+$], 813 (94), 773 (47), 685 (18), 482 (11), 443 (11), 240 (17), 239 (32), 238 (34), 224 (13), 207 (14), 194 (25), 156 (13), 155 (71), 128 (33), 127 (20), 119 (27), 89 (12). − C$_{33}$H$_{45}$I$_2$NO$_{10}$S (901.6): calcd. C 43.96, H 5.03, N 1.55, S 3.56; found C 44.35, H 5.00, N 1.70, S 3.96.

Tetraethylene Glycol Monoiodide: A solution of tetraethylene glycol mono(*p*-toluenesulfonate) (20 g, 57 mmol) in 200 mL of acetone saturated with sodium iodide (about 40 g of NaI, 220 mmol) was heated under reflux for 15 h. Precipitated sodium *p*-toluenesulfonate was filtered off, the solvent was evaporated and the residue was taken up in 200 mL of ethyl acetate. Insoluble salts were filtered off, the filtrate was concentrated in vacuo and the residue was distilled under reduced pressure. The distillate, which was discoloured by elementary iodine, was diluted with 20 mL of acetone, and treated with a sulfuric sodium sulfite solution until the solution was colourless. After removal of the solvent in a rotary evaporator, the residue was redistilled in vacuo to give the monoiodide (13.02 g, 71%) as a colourless oil, b.p. 140−142 °C, 0.02 mbar. − ^{1}H NMR (360 MHz, CDCl$_3$): δ = 2.55 (s, 1 H, OH), 3.23 (t, ^3J = 6.7 Hz, 2 H, CH$_2$I), 3.60 (m, 2 H, *CH*$_2$OH), 3.64 (m, 8 H, CH$_2$O), 3.70 (m, 4 H, CH$_2$O). − MS (EI, T_P = 95 °C): *m*/*z* (%) = 287 (0.1) [M$^+$ − OH], 198 (10), 155 (100), 89 (18). − C$_8$H$_{17}$IO$_4$ (304.1): calcd. C 31.60, H 5.63; found C 31.33, H 5.85.

2,7-Bis(14′-iodo-3′,6′,9′,12′-tetraoxatetradecyloxycarbonylmethyl)-*N*-methylphenothiazine (15): A solution of ditosylate **22** (1.72 g, 1.6 mmol) in 40 mL of acetone, saturated with sodium iodide, was heated under reflux for 12 h. After removal of the solvent in vacuo, the residue was taken up in 150 mL of ethyl acetate and washed with 30 mL of water. The organic phase was filtered, the solvent was removed in vacuo and the residue was subjected to chromatography on silica gel, eluting with ethyl acetate/5% ethanol, to afford **15** (1.3 g, 82%) as a yellow oil, R_f = 0.6. − ^{1}H NMR (360 MHz, [D$_6$]benzene: δ = 2.76 (s, 3 H, NCH$_3$), 2.85 (t, ^3J = 6.3 Hz, 4 H, CH$_2$I), 3.27−3.43 (m, 36 H, CH$_2$O + 7′-CH$_2$ + 2′-CH$_2$), 4.10 (m, 4 H, CO$_2$CH$_2$), 6.33 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.53 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 1), 6.69 (dd, ^3J = 7.8 Hz, ^4J = 2.0, 1 H, ArH, pos. 3), 6.94 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 6.95 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 7.00 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6). − IR (NaCl, film): $\tilde{\nu}$ = 1738, 1733 cm^{-1} (νC=O). − MS (EI, T_P = 409 °C): *m*/*z* (%) = 989 (100) [M$^+$], 902 (44), 901 (90), 862 (84), 813 (12), 774 (18), 293 (14), 240 (17), 239 (21), 238 (20), 194 (16), 169 (25), 167 (21), 156 (14), 155 (80), 149 (83). − C$_{37}$H$_{53}$I$_2$NO$_{12}$S (989.7): calcd. C 44.90, H 5.40, N 1.42, S 3.24; found C 44.89, H 5.37, N 1.43, S 3.48.

2,7-Bis(17′-iodo-3′,6′,9′,12′,15′-pentaoxaheptadecyloxycarbonylmethyl)-*N*-methylphenothiazine (16): The preparation was analogous to that of **15**, starting with ditosylate **23** (1.86 g, 1.6 mmol). After purification, **16** (1.05 g, 61%) was obtained as a yellow oil, R_f (ethyl acetate/5% ethanol) = 0.5. − ^{1}H NMR (360 MHz, [D$_6$]benzene): δ = 2.77 (s, 3 H, NCH$_3$), 2.86 (t, ^3J = 6.7 Hz, 4 H, CH$_2$I), 3.29−3.45 (m, 44 H, CH$_2$O + 7′-CH$_2$ + 2′-CH$_2$), 4.10 (m, 4 H, CO$_2$CH$_2$), 6.35 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.54 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.70 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 6.94 (dd, ^3J = 8.3, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 6.95 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 7.00 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6). − IR (NaCl, film): $\tilde{\nu}$ = 1737 cm^{-1} (νC=O). − MS (EI, T_P = 389): *m*/*z* (%) = 987 (5), 901 (10), 863 (5) [M$^+$ − I − 2 × CH$_2$CH$_2$O], 814 (20), 776 (16), 725 (11), 659 (13), 284 (13), 240 (25), 239 (23), 238 (28). 155 (100). − C$_{41}$H$_{61}$I$_2$NO$_{14}$S (1077.8): calcd. C 45.69, H 5.70, N 1.30, S 2.97; found C 45.74, H 5.81, N 1.42, S 2.90.

***N*-Methylphenothiazin-2,7-diyldi(acetic acid) (17):** A mixture of 2,7-diacetyl-*N*-methylphenothiazine (**27**) (80 g, 270 mmol), morpholine (150 mL, 144 g, 1.65 mol) and sulfur (30 g, 0.93 mol) was heated to 135 °C (oil bath temp.) for 6 h. The morpholine was then removed in vacuo and the residue was taken up in a solution of potassium hydroxide (160 g, 2.8 mol) in 200 mL of water and 600 mL of ethanol and heated under reflux for 5 h. After removal of ethanol in vacuo, the solution was diluted with water to 2 L and filtered. The filtrate was then acidified with 2 N hydrochloric acid to afford, after standing overnight, a precipitate which was filtered off and reprecipitated from a sodium hydrogen carbonate solution with dilute hydrochloric acid. A dark brown solid (86 g, 97%) was obtained; for purification this was recrystallized twice from water to give **17** as slightly yellow platelets. For the preparation of the pure di(acetic acid) **17** the route via the dimethyl ester was favoured. Sodium hydroxide (1 N 150 mL) was added to a suspension of dimethyl ester **18** (15 g, 42 mmol) in 450 mL of methanol and the mixture was stirred at room temperature for 2 h. After removal of methanol in vacuo, the solution was diluted with water to 800 mL and acidified with hydrochloric acid. The mixture was stirred for a further 30 min, and the precipitate was filtered off, washed with water and dried at 70 °C in a drying oven to give **17** (13.9 g, nearly quant.) as a slightly yellow powder, m.p. 172−175 °C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.28 (s, 3 H, NCH$_3$), 3.46 (s, 2 H, CH$_2$), 3.52 (s, 2 H, CH$_2$), 6.86 (m, 3 H, ArH), 7.06 (m, 3 H, ArH), 12.26 (s, 2 H, CO$_2$H). − IR (KBr): $\tilde{\nu}$ = 1701 cm^{-1} (νC=O). − MS (EI, T_P = 312 °C): *m*/*z* (%) = 330 (20), 329 (100) [M$^+$], 315 (28), 314 (44), 285 (26), 284 (30), 270 (23), 269 (17), 238 (14), 224 (20). − C$_{17}$H$_{15}$NO$_4$S (329.4): calcd. C 61.99, H 4.59, N 4.25, S 9.74; found C 61.70, H 4.49, N 4.55, S 9.52.

Dimethyl *N*-Methylphenothiazine-2,7-diyldi(acetate) (18): Conc. sulfuric acid (25 mL) was added to a suspension of crude di(acetic acid) **17** (40 g, 121 mmol) in 600 mL of methanol and the mixture was heated under reflux for 15 h. After removal of the solvent in a rotary evaporator, the residue was taken up in 50 mL of dichloromethane. The solution was washed with 200 mL of water (2 ×), dried with sodium sulfate and concentrated in vacuo to give a pitchy residue, which was treated (3−4 ×) with hot hexane until complete solidification. The black, viscous residue was taken up in dichloromethane and filtered through silica gel. The filtrate was concentrated and the residue crystallized from hexane to afford **18** (21.5 g, 50%) as lemon-yellow, very light platelets, m.p. 75−77 °C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.29 (s, 3 H, NCH$_3$), 3.59 (s, 2 H, CH$_2$CO), 3.60 (s, 3 H, CH$_3$O), 3.61 (s, 3 H, CH$_3$O), 3.65 (s, 2 H, CH$_2$CO), 6.87 (m, 3 H, ArH), 7.08 (m, 3 H, ArH). −

IR (KBr): $\tilde{\nu}$ = 1737 cm^{-1} (νC=O). − MS (EI, T_P = 201 °C): *m/z* (%) = 358 (22), 357 (100) [M^+], 343 (14), 342 (40), 298 (37), 297 (11), 283 (13); 238 (17), 224 (19). − $C_{19}H_{19}NO_4S$ (357.4): calcd. C 63.84, H 5.36, N 3.92, S 8.97; found C 63.86, H 5.38, N 4.14, S 8.76.

General Procedure for the Preparation of Bis(ω-chlorooligoethylene glycol)-Modified *N*-Methylphenothiazines 19−21 : BF_3·OEt_2 (5 drops) was added to a suspension of phenothiazine dimethyl ester **18** (2 g) and the reported amount of the ω-chlorooligoethylene glycol and the mixture was heated to 130 °C for 15 h. The oily product was taken up in 250 mL of ethyl acetate, and the solution was washed with water and dried with sodium sulfate. The solvent was then removed in vacuo.

2,7-Bis(2′-chloroethoxycarbonylmethyl)-*N*-methylphenothiazine (19): 2-Chloroethanol (50 mL) was used. After workup, the crude oil crystallized on drying in vacuo. It was sufficiently pure for synthetic purposes. For characterization it was chromatographed on silica gel using dichloromethane as eluent (R_f = 0.8) to afford **19** (1.68 g, 66%) as yellow, intergrown needles, m.p. 65 °C. − ^{1}H NMR (360 MHz, [D_6]benzene): δ = 2.70 (s, 3 H, NCH_3), 2.98 (t, ^3J = 5.5 Hz, 4 H, CH_2Cl), 3.20 (s, 2 H, 7′-CH_2), 3.25 (s, 2 H, 2′-CH_2), 3.86 (m, 4 H, CO_2CH_2), 6.28 (d, ^3J = 8.4 Hz, 1 H, ArH, pos. 9), 6.47 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.62 (dd, ^3J = 8.1, ^4J = 1.8 Hz, 1 H, ArH, pos. 3), 6.89 (dd, ^3J and ^4J ill-defined, 1 H, ArH, pos. 8), 6.92 (d, ^3J ill-defined, 1 H, ArH, pos. 4), 6.97 (d, ^4J ill-defined, 1 H, ArH, pos. 6). − IR (KBr): $\tilde{\nu}$ = 1733 cm^{-1} (νC=O). − MS (EI, T_P = 235 °C): *m/z* (%) = 457 (14), 456 (13), 455 (68), 453 (100), 440 (13), 405 (22), 393 (17), 391 (43), 376 (16), 348 (19), 346 (49), 333 (33), 284 (36), 238 (33). − $C_{21}H_{21}Cl_2NO_4S$ (454.4): calcd. C 55.51, H 4.66, N 3.08, S 7.06; found C 55.58, H 4.50, N 3.21, S 7.09.

2,7-Bis(5′-chloro-3′-oxapentyloxycarbonylmethyl)-*N*-methylphenothiazine (20): Use of diethylene glycol monochloride (5-chloro-3-oxapentan-1-ol, 30 g) as starting material and chromatography of the oily crude product on silica gel with cyclohexane/ethyl acetate (1:2) yielded **20** (1.8 g, 60%) as a yellow oil (R_f = 0.6). − ^{1}H NMR (360 MHz, [D_6]benzene): δ = 2.70 (s, 3 H, NCH_3), 3.00−3.20 (m, 12 H, 2 CH_2Cl and 4 CH_2O), 3.25 (s, 2 H, 7′-CH_2), 3.31 (s, 2 H, 2′-CH_2), 3.99 (m, 4 H, CO_2CH_2), 6.30 (d, ^3J = 8.2 Hz, 1 H, ArH, pos. 9), 6.49 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.66 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 6.91 (dd, ^3J = 8.2, ^4J = 2.0 Hz, 1 H, ArH, pos. 8), 6.93 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4), 6.98 (d, ^4J = 2.0 Hz, 1 H, ArH, pos. 6). − IR (KBr): $\tilde{\nu}$ = 1737, 1733 cm^{-1} (νC=O). − MS (EI, T_P = 323 °C): *m/z* (%) = 545 (17), 544 (21), 543 (75), 542 (30), 541 (100) [M^+], 390 (18), 238 (12). − HRMS calcd. for $C_{25}H_{29}Cl_2NO_6S$ [M^+] 541.1093; found 541.1184.

2,7-Bis(8′-chloro-3′,6′-dioxaoctyloxycarbonylmethyl)-*N*-methylphenothiazine (21): Triethylene glycol monochloride (8-chloro-3,6-dioxaoctan-1-ol, 9 g) was used. The crude oil was chromatographed on silica gel with cyclohexane/ethyl acetate (1:2) to give **21** (1.59 g, 44%) as a yellow oil (R_f = 0.3), which was sufficiently pure for synthetic purposes. For characterization, the oil was further chromatographed on RP-18 gel with methanol/water (10:1) (R_f = 0.4). − ^{1}H NMR (360 MHz, [D_6]benzene): δ = 2.71 (s, 3 H, NCH_3), 3.25 (m, 24 H, 8 CH_2O, 7′-CH_2, 2′-CH_2, 2 CH_2Cl), 4.06 (m, 4 H, CO_2CH_2), 6.30 (d, ^3J = 8.2 Hz, 1 H, ArH, pos. 9), 6.51 ("s", 1 H, ArH, pos. 1), 6.67 ("d", 1 H, ArH, pos. 3), 6.92 (m, 2 H, ArH, pos. 8 and pos. 4), 6.95 ("s", 1 H, ArH, pos. 6). − IR (NaCl, film): $\tilde{\nu}$ = 1735, 1732 cm^{-1} (νC=O). − MS (EI, T_P = 263 °C): *m/z* (%) = 631 (2), 629 (3)[M^+], 218 (47), 182 (12), 181 (10), 177 (14), 167 (11), 162 (18), 161 (10), 149 (25), 147 (26). − HRMS calcd. for $C_{29}H_{37}Cl_2NO_8S$ [M^+] 629.1616; found 629.1566.

General Procedure for the Syntheses of 22 and 23 by Esterification of 17 with Oligoethylene Glycol *p*-Toluenesulfonates: A solution prepared from carbonyldiimidazole (CDI) (1 g, 6.1 mmol) and methyl trifluoromethylsulfonate (1.34 mL, 2 g, 12.2 mmol) was added at 0 °C in one portion to a suspension of the di(acetic acid) **17** (1 g, 3.03 mmol) in 40 mL of nitromethane. After 1−2 h, the oligoethylene glycol monotosylate (7.5 mmol, 2.94 g of pentaethylene glycol monotoluenesulfonate or 6.60 g of hexaethylene glycol monotoluenesulfonate) was added to the clear solution whilst stirring. Stirring was continued for 12 h. The solvent was evaporated in vacuo, and the residue was taken up in 200 mL of ethyl acetate and washed twice with 50 mL of a 5% solution of sodium hydrogen carbonate. The organic phase was dried by passing through a paper filter. For purification, the crude material was subjected to chromatography on silica gel.

***N*-Methyl-2,7-bis[14′-(*p*-toluenesulfonyl)-3′,6′,9′,12′-tetraoxatetradecyloxycarbonylmethyl]phenothiazine (22):** Yield: 1.94 g (60%) of a yellow oil, R_f (silica gel, ethyl acetate) = 0.4. − ^{1}H NMR (360 MHz, [D_6]benzene): δ = 1.90 (s, 6 H, tosyl CH_3), 2.79 (s, 3 H, NCH_3), 3.25−3.42 (m, 36 H, CH_2), 3.94 (t, ^3J = 4.7 Hz, 4 H, CH_2OTS), 4.11 (m, 4 H, CO_2CH_2), 6.37 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.55 (d, ^4J ill-defined, 1 H, ArH, pos. 1), 6.70 (dd, ^3J = 7.8 Hz, ^4J ill-defined, 1 H, ArH, pos. 3), 6.78 (d, ^3J = 8.1 Hz, 4 H, tosyl H), 6.94 (m, 2 H, ArH, pos. 4 and pos. 8), 6.98 (d, ^4J = 1.9 Hz, 1 H, ArH, pos. 6), 7.74 (d, ^3J = 8.2 Hz, 4 H, tosyl H). − IR (NaCl, film): $\tilde{\nu}$ = 1734 cm^{-1} (νC=O). − MS (EI, T_P = 377 °C): *m/z* (%) = 818 (1) [M − $CH_3C_6H_4SO_2(OCH_2CH_2)_2OH$], 729 (2), 619 (4), 557 (4), 469 (4), 443 (3), 310 (4), 238 (7), 199 (16), 172 (51), 155 (24), 108 (24), 107 (36), 92 (11), 91 (100), 90 (11), 89 (21), 88 (71), 87 (11). − $C_{51}H_{67}NO_{18}S_3$ (1078.3): calcd. C 56.81, H 6.27, N 1.30, S 8.92; found C 56.91, H 6.36, N 1.46, S 8.79.

***N*-Methyl-2,7-bis[17′-(*p*-toluenesulfonyl)-3′,6′,9′,12′,15′-pentaoxaheptadecyloxycarbonylmethyl]phenothiazine (23):** Yield 4.5 g (63%) of a yellow oil after chromatography with ethyl acetate/ethanol (95:5), R_f = 0.4 (silica gel, ethyl acetate). A correct elemental analysis could not be obtained. − ^{1}H NMR (360 MHz, [D_6]benzene): δ = 1.83 (s, 6 H, tosyl CH_3), 2.77 (s, 3 H, NCH_3), 3.25−3.46 (m, 44 H, CH_2), 3.95 (m, 4 H, CH_2OTS), 4.12 (m, 4 H, CO_2CH_2), 6.35 (d, ^3J = 8.3 Hz, 1 H, ArH, pos. 9), 6.55 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.72 (m, 5 H, 4 tosyl H + 1 ArH, pos. 3), 6.95 (m, 2 H, ArH, pos. 4 and pos. 8), 7.00 (d, 1.9 Hz, 1 H, ArH, pos. 6), 7.75 (d, ^3J = 8.3 Hz, 4 H, tosyl H). − IR (NaCl, film): $\tilde{\nu}$ = 1737 cm^{-1} (νC=O). − MS (EI, T_P = 359 °C): *m/z* (%) = 729 (3), 641 (6), 293 (6), 239 (10), 238 (15), 207 (9), 199 (16), 181 (6), 172 (10). 91 (64), 89 (18), 88 (100).

General Procedure for the Preparation of Oligoethylene Glycol Monotoluenesulfonates: *p*-Toluenesulfonyl chloride (6.7 g, 35 mmol) in pyridine (12 mL) was added dropwise at 0 °C with stirring to a solution of oligoethylene glycol (88 mmol, 17 g of tetraethylene glycol, 21 g pentaethylene glycol or 25 g hexaethylene glycol) in 50 mL of dichloromethane. Stirring was continued overnight. After shaking twice with 20 mL of 2 N hydrochloric acid, the organic phase was dried by filtering through a paper filter. The solvent was evaporated in a rotary evaporator under vacuum and the remaining colourless oil was subjected to gradient elution chromatography on silica gel with ethyl acetate/cyclohexane (ethyl acetate from 0.33 to 1.0). For characterization the product was chromatographed on RP-18 silica gel with methanol/water (60:40). The procedure could be carried out without problem at larger scales.

11-Hydroxy-3,6,9-trioxaundecyl-1-*p*-toluenesulfonate:[13] Yield 8.2 g (67%) of a colourless oil. In ref.[12] the oil was used directly as crude

material, obtained in 77% yield, but not characterized. R_f (silica gel, ethyl acetate) = 0.65; R_f (RP-18, methanol/water 60:40) = 0.6; gradient chromatography on silica gel with cyclohexane/ethyl acetate from 3:1 to 0:1. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.33 (s, 1 H, OH), 2.43 (s, 3 H, tosyl CH_3), 3.56−3.70 (m, 14 H, CH_2O), 4.15 (t, ^3J = 4.1 Hz, 2 H, CH_2O-tosyl), 7.32 (d, ^3J = 7.9 Hz, 2 H, tosyl H), 7.78 (d, ^3J = 7.9 Hz, 2 H, tosyl H). − IR (NaCl, film): $\tilde{\nu}$ = 3457 cm^{-1} (ν OH), 1357, 1178 cm^{-1} (ν S=O). − MS (EI, T_P = 271 °C): *m/z* (%) = 349 (0.4), 348 (0.8) [M$^+$], 305 (1.7), 273 (2.1), 243 (8), 217 (4), 200 (7.5), 199 (100), 155 (67), 91 (89), 89 (56), 88 (11), 87 (15). − $C_{15}H_{24}O_7S$ (348.4): calcd. C 51.71 H 6.95 S 9.20; found C 51.43, H 7.07, S 9.31.

14-Hydroxy-3,6,9,12-tetraoxatetradecyl-1-*p*-toluenesulfonate: Yield 7.7 g (56%) of a colourless oil. R_f (silica gel, ethyl acetate/ 20 % ethanol) = 0.65. Gradient elution chromatography on silica gel with cyclohexane/ethyl acetate (4:1), pure ethyl acetate and finally ethyl acetate/ethanol (4:1). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, tosyl CH_3), 2.47 (s, 1 H, OH), 3.54−3.67 (m, 18 H, CH_2O), 4.12 (t, ^3J = 4.4 Hz, 2 H, CH_2O-tosyl), 7.30 (d, ^3J = 8.4 Hz, 2 H, tosyl H), 7.76 (d, ^3J = 8.4 Hz, 2 H, tosyl H). − IR (NaCl, film): $\tilde{\nu}$ = 3460 cm^{-1} (νOH), 1357, 1178 cm^{-1} (νS=O). − MS (EI, T_P = 205 °C): *m/z* (%) = 393 (0.3), 392 (0.5) [M$^+$], 317 (1.4), 305 (2), 261 (2), 243 (8), 199 (100), 155 (59), 91 (88), 89 (65), 87 (29). − $C_{17}H_{28}O_8S$ (392.5): calcd. C 52.02, H 7.20, S 8.17; found C 52.14, H 7.38, S 7.95.

17-Hydroxy-3,6,9,12,15-pentaoxaheptadecyl-1-*p*-toluenesulfonate: Yield 8.88 g of a colourless oil, R_f (silica gel, ethyl acetate/20 % ethanol) = 0.5. Gradient elution chromatography on silica gel with cyclohexane/ethyl acetate (4:1), pure ethyl acetate and finally ethyl acetate/ethanol (4:1). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, tosyl CH_3), 2.52 (br. s, 1 H, OH), 3.58−3.72 (m, 23 H, CH_2O), 4.16 (t, ^3J = 4.8 Hz, 2 H, CH_2O-tosyl), 7.33 (d, ^3J = 8.4 Hz, 2 H, tosyl H), 7.80 (d, ^3J = 8.4 Hz, 2 H, tosyl H). − IR (NaCl, film): $\tilde{\nu}$ = 3470 cm^{-1} (νOH), 1355, 1177 cm^{-1}(νS=O). − MS (EI, T_P = 95 °C): *m/z* = 436 (0.1) [M$^+$], 349 (1), 287 (3), 199 (100), 155 (27), 91 (95), 89 (80), 87 (28), 73 (14). − $C_{19}H_{32}O_9S$ (436.5): calcd. C 52.28, H 7.39, S 7.35; found C 52.04, H 7.53, S 7.10.

2-(2-Methyl-1,3-dioxolan-2-yl)-10*H*-phenothiazine (25): Ethylene glycol (100 g, 1.61 mol) and $BF_3{\cdot}OEt_2$ (2 mL) were added to a suspension of 2-acetylphenothiazine (**24**) (Aldrich, 100 g, 415 mmol) in 1 L of benzene. The mixture was refluxed in a Dean−Stark apparatus for 36 h and then washed twice with 500 mL of water. After concentration of the organic phase in a rotary evaporator, the resulting brown oil was crystallized from 600 mL of cyclohexane to give **25** (110 g, 93%) as yellow plates, m.p. 90−91 °C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 1.51 (s, 3 H, CH_3), 3.68 (m, AA′, 2 H, CH_2), 3.95 (m, BB′, 2 H, CH_2), 6.64−6.99 (m, 7 H, ArH), 8.58 (s, 1 H, NH); ($CDCl_3$): δ = 1.63 (s, 3 H, CH_3), 3.75 (m, AA′, 2 H, CH_2), 4.05 (m, BB′, 2 H, CH_2), 5.99 (s, 1 H, NH), 6.50−7.00 (m, 7 H, ArH). − IR (KBr): $\tilde{\nu}$ = 3334 cm^{-1} (νNH). − MS (EI, T_P = 143 °C): *m/z* (%) = 286 (19), 285 (100) [M$^+$], 271 (11), 270 (61), 226 (33), 225 (11), 199 (13), 198 (42), 197 (13), 193 (18), 154 (12). − $C_{16}H_{15}NO_2S$ (285.4): calcd. C 67.34, H 5.30, N 4.91, S 11.24; found C 67.30, H 5.30, N 5.04, S 11.29.

2-Acetyl-*N*-methylphenothiazine (26):[14] A solution of butyllithium in hexane (1.6 M, 300 mL, 480 mmol) was added at −80 °C to a solution of ketal **25** (110 g, 385 mmol) in 650 mL of absolute tetrahydrofuran. The orange colour of the resulting solution changed to deep black, then brown before the bright yellow lithiophenothiazine compound deposited. Methyl iodide (35 mL, 550 mmol) was added dropwise to the stirred suspension, which was allowed to warm slowly to −40 °C. When the clear solution had reached room temperature, 200 mL of 2 N hydrochloric acid was added and stirring was continued for another 3 h. The tetrahydrofuran was removed in vacuo. The residue was dissolved in 500 mL of trichloromethane and washed twice with 200 mL of water. The organic phase was filtered through silica gel. After evaporation of the solvent the residual oil was crystallized from ethanol to give **26** (93 g, 95%) as bright yellow prisms, m.p. 68.5 °C (ref.[14] 70 °C). Because the crystallization of **26** normally takes several weeks, it is recommended that the deep yellow oil be used for further conversions. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.55 (s, 3 H, CH_3CO), 3.39 (s, 3 H, NCH_3), 6.80 (dd, ^3J = 8.0, ^4J = 1.0 Hz, 1 H, ArH, pos. 9), 6.92 (dt, ^3J = 7.5, ^4J = 1.0 Hz, 1 H, ArH, pos. 8), 7.09 (dd, ^3J = 7.5, ^4J = 1.5 Hz, 1 H, ArH, pos. 6), 7.14 (d, ^3J = 8.0 Hz, 1 H, ArH, pos. 4), 7.16 (dt, ^3J = 8.0, ^4J = 1.5 Hz, 1 H, ArH, pos. 7), 7.34 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 7.45 (dd, ^3J = 8.0, ^4J = 1.6 Hz, 1 H, ArH, pos. 3). − IR (KBr). $\tilde{\nu}$ = 1675 cm^{-1} (νC=O). − MS (EI, T_P = 202 °C): *m/z* (%) = 256 (15) [M$^+$ +1], 255 (100) [M$^+$], 240 (65), 213 (18), 197 (21). − The preparation of **26**[14] by treatment of 2-acetylphenothiazine (**24**) (for example, 15 g, 62 mmol) with methyl iodide (for example, 20 mL, 315 mmol) in methanol (65 mL) in a sealed tube at 110 °C (***CAUTION!***) for 24 h is ***very dangerous***. In one case an explosion occurred, probably as a result of a reaction between the hydroiodic acid produced and methyl iodide to give elementary iodine and methane.

2,7-Diacetyl-*N*-methylphenothiazine (27):[15] A solution of 2-acetyl-*N*-methylphenothiazine (**26**) (93 g, 365 mmol) and acetyl chloride (41 g, 522 mmol) in 500 mL of carbon disulfide was added dropwise at room temperature to a suspension of aluminium trichloride (220 g, 1.62 mol) in 500 mL of carbon disulfide. The mixture was then refluxed for 14 h, the solvent was removed by evaporation in vacuo and the residue was hydrolysed with ice. The solid was filtered under suction, dried and recrystallized from ethyl acetate to afford **27** (81.2 g, 75%) as green yellow crystals, m.p. 221 °C (ref.[14] 61%, m.p. 223 °C). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.52 (s, 3 H, CH_3CO), 2.57 (s, 3 H, CH_3CO), 3.44 (s, 3 H, NCH_3), 6.81 (d, ^3J = 8.5 Hz, 1 H, ArH, pos. 9), 7.17 (d, ^3J = 7.9 Hz, 1 H, ArH, pos. 4), 7.39 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 7.51 (dd, ^3J = 7.9, ^4J = 1.6 Hz, 1 H, ArH, pos. 3), 7.68 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.78 (dd, ^3J = 8.5, ^4J = 2.1 Hz, 1 H, ArH, pos. 8). − IR (KBr): $\tilde{\nu}$ = 1673, 1663 cm^{-1} (νC=O). − MS (EI, T_P = 249 °C): *m/z* (%) = 298 (12) [M$^+$ + 1], 297 (100) [M$^+$], 282 (33), 254 (12), 240 (13).

1,1′-Bis(2′′-hydroxyethyl)-4,4′-bipyridinium Bis(trifluoromethanesulfonate) (28): Silver trifluoromethylsulfonate (1.43 g, 5.6 mmol) was added to a stirred suspension of 1,1′-bis(2′′-hydroxyethyl)-4,4′-bipyridinium diiodide (1.4 g, 2.8 mmol) (see below) in 200 mL of nitromethane and stirring was continued for 1 h. The yellow-orange colour of the bipyridinium diiodide disappeared and a yellow precipitate of AgI was formed. The mixture was filtered and the filtrate was concentrated in vacuo to give a colourless powder. After recrystallization from trichloromethane/nitromethane (1:2), compound **28** (1.29 g, 86%) was obtained as a colourless powder with m.p. 168 °C (decomp.). − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.94 (t, ^3J = 4.9 Hz, 4 H, CH_2OH), 4.76 (t, ^3J = 4.8 Hz, 4 H, N^+CH_2), 5.30 (br., 2 H, OH), 8.78 (d, ^3J = 6.9 Hz, 4 H, ArH), 9.30 (d, ^3J = 6.9 Hz, 4 H, ArH). − $C_{16}H_{18}F_6S_2N_2O_8$ (544.4): calcd. C 35.30, H 3.30, N 5.15, S 11.78; found C 35.20, H 3.28, N 5.20, S 11.79.

1,1′-Bis(2′′-hydroxyethyl)-4,4′-bipyridinium Diiodide:[16] A mixture of 4,4′-bipyridine (1.56 g, 10 mmol) and iodoethanol (5.2 g, 2.4 mL, 30 mmol) in 30 mL of nitromethane was refluxed for 2 h.

During this time a yellow orange precipitate was formed; this was filtered off under suction and washed first with nitromethane, then with ether. After drying at 60 °C in vacuo, the product (3.74 g, 74%) was obtained as a yellow orange powder, m.p. 252 °C (decomp.). In reference[15] the yield was 71% and the m.p. 250 °C (decomp.). − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 3.95 (br., 4 H, CH_2OH), 4.79 (t, ^3J = 4.8 Hz, 4 H, N$^+$CH$_2$), 5.28 (br., 2 H, OH), 8.82 (d, ^3J = 6.9 Hz, 4 H, ArH), 9.33 (d, ^3J = 6.9 Hz, 4 H, ArH). − IR (KBr): $\tilde{\nu}$ = 3306 cm^{-1} (νOH). − MS (EI, T_P = 333 °C): *m*/*z* (%) = 156 (100) [M$^+$ − 2 × CH$_2$CH$_2$I], 128 (85), 127 (30). − C$_{14}$H$_{18}$I$_2$N$_2$O$_2$ (500.1): calcd. C 33.62, H 3.63, I 50.75, N 5.60; found C 33.76, H 3.60, I 50.70, N 5.72.

2,7-Bis(2′-iodoethyl)-*N*-methylphenothiazine (29): 2,7-Bis(2′-bromoethyl)-*N*-methylphenothiazine (**38**) (2.0 g, 4.68 mmol) was dissolved in 100 mL of acetone, saturated with sodium iodide, and the mixture was refluxed for 18 h. After the mixture had been allowed to cool down to room temperature, the precipitated sodium bromide was filtered off. The solvent was removed in a rotary evaporator at reduced pressure, and the residue was dissolved in 100 mL of trichloromethane and washed with two 100-mL portions of water. After filtration through silica gel, the solvent was distilled off in vacuo. The residue was crystallized at −20 °C from dichloromethane/petroleum ether to give **29** (2.2 g, 90%) as slightly yellow crystals, m.p. 126−127 °C. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.07 (t, ^3J = 7.8 Hz, 2 H, CH$_2$I), 3.13 (t, ^3J = 7.7 Hz, 2 H, CH$_2$I), 3.29 (t, ^3J = 7.6 Hz, 2 H, ArCH$_2$), 3.32 (t, ^3J = 7.7 Hz, 2 H, ArCH$_2$), 3.37 (s, 3 H, NCH$_3$), 6.62 ("d", 1 H, ArH, pos. 1), 6.75 (d, ^3J = 8.1 Hz, 1 H, ArH, pos. 9), 6.76 (dd, not resolved, 1 H, ArH, pos. 3), 6.96 (d, ^4J = 1.8 Hz, 1 H, ArH, pos. 6), 6.99 (dd, ^3J = 8.2, ^4J = 1.7 Hz, 1 H, ArH, pos. 8), 7.07 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − MS (EI, T_P = 278 °C): *m*/*z* (%) = 522 (14), 521 (100) [M$^+$], 394 (15), 266 (12), 134 (17). − C$_{17}$H$_{17}$I$_2$NS (521.2): calcd. C 39.19, H 3.29, I 48.69, N 2.79, S 6.15; found C 39.49, H 3.42, I 48.50, N 2.78, S 5.88.

2,7-Bis(3′-iodopropyl)-*N*-methylphenothiazine (30): 2,7-Bis(3′-bromopropyl)-*N*-methylphenothiazine (**39**) (1.0 g, 3.04 mmol) was dissolved in 20 mL of acetone, saturated with sodium iodide, and the mixture was refluxed for 10 h. The deposited sodium bromide was filtered off and the solvent removed in vacuo. The residue was taken up in dichloromethane, the mixture was filtered and the filtrate was concentrated in a rotary evaporator to give a yellow oil, which after treatment with petroleum ether at −20 °C yielded **30** (900 mg, 54%) as an orange-yellow solid, m.p. 38 °C. − ^{1}H NMR (360 MHz, CDCl$_3$): δ = 2.09 (m, 4 H, CH$_2$CH_2CH$_2$), 2.63 (t, ^3J = 6.0 Hz, 2 H, ArCH$_2$), 2.69 (t, ^3J = 7.0 Hz, 2 H, ArCH$_2$), 3.12−3.20 (m, 4 H, CH$_2$I), 3.36 (s, 3 H, NCH$_3$), 6.64 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.75 (m, 2 H, ArH, pos. 9 and pos. 3), 6.98 (m, 2 H, ArH, pos. 6 and pos. 8), 7.05 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − MS (EI, T_P = 289 °C): *m*/*z* (%) = 550 (30), 549 (100) [M$^+$], 394 (27), 239 (11). − C$_{19}$H$_{21}$I$_2$NS (549.3): calcd. C 41.55, H 3.85, I 46.21, N 2.55, S 5.84; found C 41.29, H 3.93, I 46.03, N 2.60, S 5.94.

2,7-Bis(4′-iodobutyl)-*N*-methylphenothiazine (31): The preparation was analogous to that of **30**, starting from 2,7-bis(4′-bromobutyl)-*N*-methylphenothiazine (**40**) (1.75 g, 3.62 mmol) and 30 mL of acetone, saturated with sodium iodide. After crystallization from petroleum ether at −20 °C, compound **31** (1.44 g, 69%) was obtained as yellow crystals, m.p. 83−84 °C. − ^{1}H NMR (360 MHz, CDCl$_3$): δ = 1.68 (m, 4 H, CH$_2$CH_2CH$_2$CH$_2$), 1.84 (m, 4 H, CH$_2$CH$_2$CH_2CH$_2$), 2.53 (t, ^3J = 7.4 Hz, 2 H, ArCH$_2$), 2.59 (t, ^3J = 7.4 Hz, 2 H, ArCH$_2$), 3.19 (m, 4 H, CH$_2$I), 3.36 (s, 3 H, NCH$_3$), 6.61 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.73 (m, 2 H, ArH, pos. 9 and pos. 3), 6.95 (m, 2 H, ArH, pos. 6 and pos. 8), 7.05 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4). − MS (EI, T_P = 289 °C): *m*/*z* (%) = 578 (16), 577 (100) [M$^+$], 120 (41). − C$_{21}$H$_{25}$I$_2$NS (576.9): calcd. C 43.69, H 4.37, I 43.96, N 2.43, S 5.55; found C 43.62, H 4.46, I 44.00, N 2.52, S 5.36.

2,7-Bis(5′-iodopentyl)-*N*-methylphenothiazine (32): Borane−tetrahydrofuran complex (1 M, 0.6 mL) was slowly added at 0 °C by syringe to a solution of 2,7-bis(pent-4-en-1-yl)-*N*-methylphenothiazine (**43**) (310 mg, 0.89 mmol) in 15 mL of tetrahydrofuran. The reaction mixture was heated to 50 °C for 1 h, then cooled to room temperature. To destroy the excess of borane, 0.6 mL of methanol was added, followed by 1.8 mL of 1 M sodium acetate in methanol. Finally, iodine chloride (192 mg) was added dropwise. The mixture was stirred for 45 min, then poured into 50 mL of water. The excess of iodine chloride was destroyed with sodium thiosulfate. After removal of the tetrahydrofuran in vacuo, the residue was extracted with two 50-mL portions of trichloromethane, then washed with 50 mL of water. The combined organic phases were concentrated and subjected to chromatography on silica gel with cyclohexane/toluene (2:1). The solvent was evaporated under reduced pressure to give **32** (220 mg, 25%) as a yellow oil, R_f = 0.6. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.43 [m, 4 H, (CH$_2$)$_2$CH_2(CH$_2$)$_2$], 1.62 (m, 4 H, ArCH$_2$−CH_2−CH$_2$), 1.84 (m, 4 H, CH_2CH$_2$I), 2.51 (t, ^3J = 7.7 Hz, 2 H, ArCH$_2$), 2.57 (t, ^3J = 7.8 Hz, 2 H, ArCH$_2$), 3.17 (t, ^3J = 7.0 Hz, 2 H, CH$_2$I), 3.19 (t, ^3J = 7.0 Hz, 2 H, CH$_2$I), 3.36 (s, 3 H, NCH$_3$), 6.61 ("d", 1 H, ArH, pos. 1), 6.74 (m, 2 H, ArH, pos. 9 and pos. 3), 6.96 (m, 2 H, ArH, pos. 6 and pos. 8), 7.04 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − MS (EI, T_P = 260 °C): *m*/*z* (%) = 605 (83) [M$^+$], 477 (100) [M − HI], 437 (27) [M − (CH$_2$)$_3$I+1], 349 (23), 294 (45), 252 (50), 224 (54), 194 (44), 180 (18), 127 (63), 91 (17), 55 (30). − HRMS calcd. for C$_{23}$H$_{29}$I$_2$NS [M$^+$] 605.0110; found 605.0099.

2,7-Bis[2′-(methoxycarbonyl)ethyl]-*N*-methylphenothiazine (33): A vigorous stream of hydrogen chloride was passed through a suspension of 2,7-bis(2′-cyanoethyl)-*N*-methylphenothiazine (**41**) (5.5 g, 17.2 mmol) in 800 mL of abs. methanol, with ice cooling and stirring. During this procedure the methanol began to boil and the colour changed from bright yellow to red-brown. After boiling had ceased, hydrogen chloride was bubbled through the solution for a further 3 h at room temperature. The stirring was continued overnight. The mixture was poured onto 1 L of ice and the methanol evaporated under reduced pressure. The aqueous phase was extracted with three 200-mL portions of trichloromethane. The combined organic phases were concentrated and subjected to chromatography on silica gel, with ethyl acetate/cyclohexane (1:2). The product fraction (R_f = 0.39) was crystallized from hexane to yield **33** (3.6 g, 55%) as light yellow crystals, m.p. 78−80 °C. − ^{1}H NMR (360 MHz, CDCl$_3$): δ = 2.61 (m, 4 H, CH$_2$CO), 2.84 (t, ^3J = 7.5 Hz, 2 H, ArCH$_2$), 2.90 (t, ^3J = 7.6 Hz, 2 H, ArCH$_2$), 3.34 (s, 3 H, NCH$_3$), 3.66 (s, 3 H, CH$_3$O), 3.67 (s, 3 H, CH$_3$O), 6.64 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.75 (m, 2 H, ArH), 6.98 (m, 2 H, ArH), 7.03 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − IR (KBr): $\tilde{\nu}$ = 1742 cm^{-1} (νC=O). − MS (EI, T_P = 248 °C): *m*/*z* (%) = 386 (15), 385 (100) [M$^+$], 371 (17), 285 (25). − C$_{21}$H$_{23}$NO$_4$S (385.5): calcd. C 65.43, H 6.01, N 3.63, S 8.32; found C 65.47, H 6.04, N 3.50, S 8.42.

2,7-Bis[3′-(methoxycarbonyl)propyl]-*N*-methylphenothiazine (34): In analogy to a method described in ref.[17] 2,7-bis[3′,3′-bis(methoxycarbonyl)propyl]-*N*-methylphenothiazine (**42**) (3.6 g, 6.81 mmol), tetramethylammonium acetate (18 g) and water (0.4 mL) in 50 mL

of 1,3-dimethylimidazolidin-2-one were heated to 140 °C for 10 h. The solvent was evaporated in vacuo and the residue chromatographed on silica gel with cyclohexane/ethyl acetate (4:1) to yield **34** (2.3 g, 80%) as a yellow oil, R_f = 0.35. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.80 (m, 4 H, $CH_2CH_2CH_2$), 2.30 (t, ^3J = 7.7 Hz, 2 H, CH_2CO_2), 2.32 (t, ^3J = 7.5 Hz, 2 H, CH_2CO_2), 2.55 (t, ^3J = 7.7 Hz, 2 H, $ArCH_2$), 2.60 (t, ^3J = 7.8 Hz, 2 H, $ArCH_2$), 3.35 (s, 3 H, NCH_3), 3.66 (s, 6 H, CO_2CH_3), 6.61 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.74 (m, 2 H, ArH), 6.96 (m, 2 H, ArH), 7.04 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − IR (NaCl, film): $\tilde{\nu}$ = 1742 cm^{-1} (νC=O). − MS (EI, T_P = 297 °C): *m/z* (%) = 414 (17), 413 (100) [M^+], 326 (14). − $C_{23}H_{27}NO_4S$ (413.5): calcd. C 66.80, H 6.58, N 3.39, S 7.75; found C 66.65, H 6.56, N 3.58, S 7.84.

2,7-Bis(2′-hydroxyethyl)-*N*-methylphenothiazine (35): A solution of 2,7-bis[(methoxycarbonyl)methyl]-*N*-methylphenothiazine (**18**) (3.0 g, 8.4 mmol) in 500 mL of tetrahydrofuran was added dropwise with stirring, at room temperature, to a suspension of lithium aluminium hydride (6.0 g, 150 mmol) in 500 mL of tetrahydrofuran. The mixture was stirred at room temperature for a further 2 h and subsequently refluxed for 2 h. After cooling, the excess of $LiAlH_4$ was destroyed by addition of 2 N hydrochloric acid, the tetrahydrofuran was evaporated in vacuo and the residue was taken up in dichloromethane. After washing of the organic phase with water and drying with sodium sulfate, the solvent was removed and the residue was crystallized from methanol/water to give **35** (15 g, 58%) as slightly yellow, fibrous needles, m.p. 127−128 °C. − ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 2.61 (t, ^3J = 6.7 Hz, 2 H, $ArCH_2$), 2.67 (t, ^3J = 7.0 Hz, 2 H, $ArCH_2$), 3.27 (s, NCH_3), 3.52 (m, 2 H, $ArCH_2CH_2$), 3.59 (m, 2 H, $ArCH_2CH_2$), 4.53 (m, 1 H, OH), 4.55 (m, 1 H, OH), 6.81 (m, 3 H, ArH), 7.01 (m, 3 H, ArH). − IR (KBr): $\tilde{\nu}$ = 3242 (br.) (νOH). − MS (EI, T_P = 225 °C): *m/z* = 302 (12), 301 (100) [M^+], 287 (9), 286 (12), 270 (60), 224 (11). − $C_{17}H_{19}NO_2S$ (301.4): calcd. C 67.74, H 6.36, N 4.65, S 10.64; found C 67.97, H 6.42, N 4.64, S 10.78.

2,7-Bis(3′-hydroxypropyl)-*N*-methylphenothiazine (36): The preparation was analogous to that of **35**, starting with lithium aluminium hydride (1.1 g, 28.8 mmol) in 100 mL of abs. tetrahydrofuran and 2,7-bis[2′-(methoxycarbonyl)ethyl]-*N*-methylphenothiazine (**33**) (3.7 g, 9.61 mmol) in 100 mL of abs. tetrahydrofuran. Refluxing time was 8 h. After removal of the tetrahydrofuran in vacuo, the residue was taken up in trichloromethane. Crystallization from methanol/water yielded **36** (2.21, 70%) as light brown crystals, m.p. 119−120 °C. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.85 (m, 4 H, $CH_2CH_2CH_2$), 2.61 (t, ^3J = 8.0 Hz, 2 H, $ArCH_2$), 2.66 (t, ^3J = 8.0 Hz, 2 H, $ArCH_2$), 3.35 (s, 3 H, NCH_3), 3.64 (t, ^3J = 6.4 Hz, 2 H, CH_2OH), 3.66 (t, ^3J = 6.4 Hz, 2 H, CH_2OH), 4.81 (br., 2 H, OH), 6.63 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.75 (m, 2 H, ArH), 6.95 (m, 2 H, ArH), 7.03 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − IR (KBr): $\tilde{\nu}$ = 3305 cm^{-1} (br., νOH). − MS (EI, T_P = 289 °C): *m/z* (%) = 331 (21), 330 (14), 329 (100) [M^+], 299 (10), 284 (11), 254 (11). − $C_{19}H_{23}NO_2S$ (329.2): calcd. C 69.27, H 7.04, N 4.25, S 9.73; found C 68.99, H 7.03, N 4.34, S 9.81.

2,7-Bis(4′-hydroxybutyl)-*N*-methylphenothiazine (37): The preparation was analogous to that of **35**, starting with lithium aluminium hydride (260 mg, 6.86 mmol) in 25 mL of abs. tetrahydrofuran and 2,7-bis[3′-(methoxycarbonyl)propyl]-*N*-methylphenothiazine (**34**) (1.42 g, 3.43 mmol) in 25 mL of abs. tetrahydrofuran. The refluxing time was 12 h. After evaporation of the tetrahydrofuran in vacuo, the residue was taken up in ethyl acetate and filtered through silica gel. Crystallization from cyclohexane/ethyl acetate afforded **37** (1.0 g, 82%) as colourless needles, m.p. 71−72 °C. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.21 (br., 2 H, OH), 1.56−1.68 (m, 8 H, $CH_2CH_2CH_2CH_2$), 2.54 (t, ^3J = 7.4 Hz, 2 H, $ArCH_2$), 2.60 (t, ^3J = 7.6 Hz, 2 H, $ArCH_2$), 3.36 (s, 3 H, NCH_3), 3.65 (m, 4 H, CH_2OH), 6.62 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.74 (m, 2 H, ArH), 6.96 (m, 2 H, ArH), 7.04 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − IR (NaCl, film): $\tilde{\nu}$ = 3419 cm^{-1} (νOH). − MS (EI, T_P = 273 °C): *m/z* (%) = 358 (16), 357 (100) [M^+], 298 (15). − $C_{21}H_{27}NO_2S$ (357.5): calcd. 70.55, H 7.61, N 3.92, S 8.97; found C 70.44, H 7.60, N 4.15, S 8.86.

2,7-Bis(2′-bromoethyl)-*N*-methylphenothiazine (38): Triphenylphosphane (2.1 g, 8 mmol) was added to a solution of 2,7-bis(2′-hydroxyethyl)-*N*-methylphenothiazine (**35**) (1.0 g, 3.32 mmol) and tetrabromomethane (2.65 g, 8 mmol) in 50 mL of absolute tetrahydrofuran and the solution was stirred at 55 °C for 5 h. The deposited triphenylphosphane oxide was filtered off, the solvent was removed in vacuo and the mixture was taken up in cyclohexane/toluene (3:2). After filtration through silica gel, the filtrate was concentrated and the residue was crystallized from dichloromethane/petroleum ether at −20 °C to give **38** (720 mg, 51%) as yellow green needles, m.p. 128−130 °C. Transformations at larger scales were possible without problem. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.05 (t, ^3J = 7.4 Hz, 2 H, $ArCH_2$), 3.11 (t, ^3J = 7.4 Hz, 2 H, $ArCH_2$), 3.36 (s, 3 H, NCH_3), 3.50 (t, ^3J = 7.4 Hz, 2 H, CH_2Br), 3.53 (t, ^3J = 7.4 Hz, 2 H, CH_2Br), 6.63 (d, ^4J = 1.3 Hz, 1 H, ArH, pos. 1), 6.78 (m, 2 H, ArH), 7.00 (m, 3 H, ArH). − MS (EI, T_P = 246 °C): *m/z* (%) = 429 (32), 428 (11), 427 (100) [M^+], 425 (33), 412 (14), 334 (16), 332 (21). − $C_{17}H_{17}Br_2NS$ (427.2): calcd. C 47.79, H 4.01, N 3.28, S 7.51; found C 47.59, H 4.02, N 3.34, S 7.63.

2,7-Bis(3′-bromopropyl)-*N*-methylphenothiazine (39): The preparation was analogous to that of **38**, starting with 2,7-bis(3′-hydroxypropyl)-*N*-methylphenothiazine (**36**) (2.0 g, 6.08 mmol), tetrabromomethane (4.85 g, 14.65 mmol) and triphenylphosphane (3.85 g, 14.65 mmol) in 100 mL of abs. tetrahydrofuran. Stirring was at 55 °C for 24 h. Yield 1.8 g (65%) of colourless crystals, m.p. 55 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.13 (m, 4 H, $CH_2CH_2CH_2$), 2.69 (t, ^3J = 7.0 Hz, 2 H, $ArCH_2$), 2.74 (t, ^3J = 7.2 Hz, 2 H, $ArCH_2$), 3.35−3.43 (m, 7 H, 2 × CH_2Br and NCH_3 at 3.38), 6.65 ("s", 1 H, ArH, pos. 1), 6.74 (m, 2 H, ArH), 6.99 (m, 2 H, ArH), 7.06 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4). − MS (EI, T_P = 289 °C): *m/z* (%) = 457 (53), 456 (22), 455 (100) [M^+], 454 (11), 453 (49), 440 (17), 348 (40), 346 (40). − $C_{19}H_{21}Br_2NS$ (454.8): calcd. C 50.13, H 4.65, Br 35.10, N 3.08, S 7.04; found C 50.14, H 4.75, Br 35.25, N 3.18, S 7.25.

2,7-Bis(4′-bromobutyl)-*N*-methylphenothiazine (40): The preparation was analogous to that of **39**, starting with 2,7-bis(4′-hydroxybutyl)-*N*-methylphenothiazine (**37**) (2.0 g, 5.6 mmol), tetrabromomethane (4.5 g, 13.6 mmol) and triphenylphosphane (3.6 g, 13.6 mmol) in 80 mL of abs. tetrahydrofuran. Yield 1.81 g (67%) of yellow needles, m.p. 71 °C. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.74 (m, 4 H, $CH_2CH_2CH_2CH_2$), 1.88 (m, 4 H, $CH_2CH_2CH_2CH_2$), 2.54 (t, ^3J = 7.4 Hz, 2 H, $ArCH_2$), 2.60 (t, ^3J = 7.6 Hz, 2 H, $ArCH_2$), 3.36 (s, 3 H, NCH_3), 3.42 (m, 4 H, CH_2Br), 6.61 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.75 (m, 2 H, ArH), 6.99 (m, 2 H, ArH), 7.06 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − MS (EI, T_P = 361 °C): *m/z* (%) = 485 (35), 484 (18), 483 (100) [M^+], 482 (10), 481 (36), 362 (15), 360 (15), 224 (40), 119 (14). − $C_{21}H_{25}Br_2NS$ (483.3): calcd. C 52.19, H 5.21, Br 33.07, N 2.90, S 6.63; found C 52.00, H 5.22, Br 33.28, N 3.00, S 6.62.

2,7-Bis(2′-cyanoethyl)-*N*-methylphenothiazine (41): In analogy to the method described in ref.[18] a solution of 2,7-bis(2′-bromoethyl)-*N*-methylphenothiazine (**38**) (2.0 g, 4.68 mmol) and sodium cyanide (514 mg, 14.7 mmol) in 10 mL of abs. dimethyl sulfoxide

was heated to 70 °C for 24 h. After removal of the solvent in vacuo, the residue was taken up in dichloromethane and precipitated with petroleum ether at −20 °C to afford **41** (915 mg, 87%) as a yellow solid, m.p. 149 °C. − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.56 (t, ^3J = 7.4 Hz, 2 H, CH_2CN), 2.60 (t, ^3J = 7.2 Hz, 2 H, CH_2CN), 2.85 (t, ^3J = 7.3 Hz, 2 H, $ArCH_2$), 2.90 (t, ^3J = 7.3 Hz, 2 H, $ArCH_2$), 3.37 (s, 3 H, NCH_3), 6.67 (d, ^4J = 1.6 Hz, 1 H, ArH, pos. 1), 6.78 (m, 2 H, ArH, pos. 9 and pos. 3), 6.99 (d, ^4J = 2.1 Hz, 1 H, ArH, pos. 6), 7.04 (dd, ^3J = 8.1, ^4J = 2.1 Hz, 1 H, ArH, pos. 8), 7.08 (d, ^3J = 7.8 Hz, 1 H, ArH, pos. 4). − IR (KBr): $\tilde{\nu}$ = 2243 cm^{-1} (νC≡N). − MS (EI, T_P = 218 °C): *m/z* (%) = 319 (47) [M^+], 292 (23) [M − HCN], 279 (44), 278 (53), 277 (100) [M − HCN − CH_3], 201 (16), 199 (13), 183 (11), 119 (14), 77 (19). − $C_{19}H_{17}N_3S$ (319.3): calcd. C 71.44, H 5.36, N 13.15, S 10.04; found C 71.18, H 5.52, N 12.96, S 9.98.

2,7-Bis[3′,3′-bis(methoxycarbonyl)propyl]-*N*-methylphenothiazine (42): In analogy to the method described in ref.[19] a 0.5 M methanolic sodium methoxide solution (50 mL) was added dropwise by syringe pump (0.5 mL/h), under reflux, to a solution of 2,7-bis(2′-iodoethyl)-*N*-methylphenothiazine (**29**) (4.97 g, 9.53 mmol) and dimethyl malonate (3.8 g, 28.6 mmol) in 100 mL of abs. tetrahydrofuran. The solution was heated for a further 2 d, then cooled and filtered. The solvent was removed in vacuo, and the residue was taken up in ethyl acetate and filtered through silica gel. After evaporation of the solvent in a rotary evaporator under reduced pressure, compound **42** (3.7 g, 74%) was obtained as a yellow oil; R_f = 0.51 (cyclohexane/ethyl acetate 1:1). − ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.19 (m, 4 H, CH_2CH), 2.55 (t, ^3J = 7.2 Hz, 2 H, $ArCH_2$), 2.60 (t, ^3J = 7.2 Hz, 2 H, $ArCH_2$), 3.35 (s, 3 H, NCH_3), 3.38 (m, 2 H, CH_2CH), 3.73 (s, 12 H, OCH_3), 6.61 (d, ^4J = 1.5 Hz, 1 H, ArH, pos. 1), 6.74 (m, 2 H, ArH), 6.96 (m, 2 H, ArH), 7.04 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − IR (KBr): $\tilde{\nu}$ = 1737 cm^{-1} (νC=O). − MS (EI, T_P = 280 °C): *m/z* (%) = 531 (16), 530 (31), 529 (100) [M^+], 515 (12), 471 (16), 398 (17), 397 (58), 384 (25), 382 (13), 252 (22), 250 (18), 237 (15), 132 (14). − $C_{27}H_{31}NO_8S$ (529.4): calcd. C 61.23, H 5.90, N 2.64, S 6.05; found C 60.97, H 6.13, N 2.63, S 6.18.

***N*-Methyl-2,7-bis(pent-4-en-1-yl)phenothiazine (43):** In analogy to the method described in ref.[20] [1,2-bis(diphenylphosphanyl)-ethane]nickel(II) chloride $NiCl_2(dppe)_2$ (132 mg, 0.25 mmol) was added to a solution of 2,7-bis(2′-iodoethyl)-*N*-methylphenothiazine (**29**) (1.0 g, 1.92 mmol) in 15 mL of anhydrous tetrahydrofuran followed at −78 °C over 30 min by a 1 M solution of allylmagnesium bromide (4.8 mL) in tetrahydrofuran. The mixture was allowed to warm to room temperature whilst stirring over 2 h, and was then refluxed for a further 2 h. After it had cooled to room temperature, hydrochloric acid (2 N, 10 mL) was added. The solvent was removed in vacuo and the residue was shaken with trichloromethane/water. The organic phase was concentrated and the residue chromatographed on silica gel with cyclohexane/toluene (10:1) to give **43** (337 mg, 51%) as a slightly yellow oil, R_f = 0.32. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.64−1.73 (m, 4 H, $ArCH_2CH_2$), 2.05−2.11 (m, 4 H, $CH_2CH=CH_2$), 2.52 (t, ^3J = 7.6 Hz, $ArCH_2$), 2.58 (t, ^3J = 7.8 Hz, 2 H, $ArCH_2$), 3.36 (s, 3 H, NCH_3), 4.96−5.05 (m, 4 H, $CH=CH_2$), 5.79−5.86 (m, 2 H, $CH=CH_2$), 6.62 (d, ^4J = 1.1 Hz, 1 H, ArH, pos. 1), 6.73 (m, 2 H, ArH), 6.95 (m, 2 H, ArH), 7.04 (d, ^3J = 7.6 Hz, 1 H, ArH, pos. 4). − IR (NaCl, film): $\tilde{\nu}$ = 1640 cm^{-1} ($\nu CH=CH_2$). − MS (EI): *m/z* (%) = 349 (100) [M^+], 334 (10), 309 (12), 294 (34), 262 (10). − $C_{23}H_{27}NS$ (349.5): calcd. C 79.03, H 7.79, N 4.01, S 9.17; found C 79.15, H 7.80, N 4.09, S 9.03.

2,7-Diethyl-*N*-methylphenothiazine (44): Lithium aluminium hydride (800 mg, 21.0 mmol) was added to a solution of 2,7-bis(2′-bromoethyl)-*N*-methylphenothiazine (**38**) (1.12 g, 2.75 mmol) in 50 mL of anhydrous tetrahydrofuran, and the mixture was heated under reflux for 10 h. After the mixture had cooled to room temperature, hydrochloric acid (2 N, 10 mL) was added dropwise, and the solvent was removed in vacuo. The residue was taken up in dichloromethane. After filtration and evaporation of the solvent under reduced pressure in a rotary evaporator, compound **44** (700 mg, 95%) was obtained as a yellow oil; R_f = 0.67 (cyclohexane/ethyl acetate, 1:1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.22 (t, ^3J = 7.6 Hz, 3 H, CH_2CH_3), 2.55 (q, ^3J = 7.6 Hz, 2 H, $ArCH_2$), 2.60 (q, ^3J = 7.6 Hz, 2 H, $ArCH_2$), 3.37 (s, 3 H, NCH_3), 6.64 (d, ^4J = 1.4 Hz, 1 H, ArH, pos. 1), 6.73 (d, ^3J = 8.0 Hz, 1 H, ArH, pos. 9), 6.77 (dd, ^3J = 7.7, ^4J = 1.7 Hz, 1 H, ArH, pos. 3), 6.98 (m, 2 H, ArH, pos. 8 and pos. 6), 7.05 (d, ^3J = 7.7 Hz, 1 H, ArH, pos. 4). − MS (EI, T_P = 238 °C): *m/z* (%) = 270 (19), 269 (100) [M^+], 255 (17), 254 (95), 239 (17), 224 (26), 194 (16), 192 (10). − $C_{17}H_{19}NS$ (269.2): calcd. C 75.84, H 7.06, N 5.20, S 11.90; found C 75.88, H 7.34, N 4.98, S 11.66.

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