Synthesis of Crown-Ester–Bipyridines and Crown-Ester–Viologens

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Abstract: Six novel 4,4′-bipyridine-crown-esters, derived from [4,4′]bipyridinyl-3,3′-dicarboxylic acid, [4,4′]bipyridinyl-2,2′-dicarboxylic acid and [4,4′]bipyridinyl-2,2′,6,6′-tetra-carboxylic acid were synthesized employing a procedure closely related to the 'cesium carbonate method'. The 4,4′-bipyridine-crown-esters differ in their substitution positions of the aromatic bipyridine-units, as well as in the geometric extensions of their crown-ester moieties. Addition of 1,3-propane sultone to the 4,4′-bipyridine-crown-esters resulted in five novel propanesultonated 4,4′-bipyridine-crown-ester viologens.

Key words: alkylations, bipyridines, esters, nickel(0), viologens

Since the first bipyridine-crown-ethers were synthesized in 1980 by Rebek[2] and Newkome,[3] a variety of these fascinating compounds were prepared. Besides their original use as organic catalysts,[4] heterocyclic crown-ethers were successfully employed as building blocks for supramolecular organic structures.[5] Bipyridine ring systems serve as versatile chelating agents, because of their ability to form strong ligand fields and therefore, to form kinetically stable complexes with many d-block and f-block metal cations.[6] Crown-ether and crown-ester moieties, derived from bipyridines, can bind various organic and inorganic substrates.[7] Furthermore, crown-ethers can serve as covalent[8] or mechanical[9] connectors in supramolecular devices. Besides their ability to allocate various substrates in the direct proximity of metal complex centers with the ability to undergo (photoinduced) electron-transfer reactions, heterocyclic crown-ethers and -esters often experience characteristic changes in their conformation, especially the dihedral angle between the aromatic rings during the binding of a substrate.[10] If the 2,2-bipyridyl-type of metal complex is fluorescent, then the conformational changes cause remarkable changes in the photophysical properties of these metal complexes, and thus offer the opportunity for the design of luminescence sensors.[11] Another approach to use fluorescence as an analytical tool consists in the binding of rare earth cations within calixcrowns to form highly luminescent devices which can be used as efficient labels for bioaffinity assays.[12] In this work, we have directed our attention toward the synthesis of crown-ester -modified 4,4′-bipyridyl-derivatives, which can serve as versatile electron relays. Di- and tetramethylated 4,4′-bipyridinium salts possess excellent electron transfer abilities.[13] We have chosen to prepare stable 4,4′-bipyridinium salts by reacting the crown-ester-4,4′-bipyridines with propansultone.[14] We followed a synthetic strategy which was first successfully applied for the synthesis of crown-ester-substituted 2,2′-bipyridines and podands.[15] The cesium carbonate method, which permits the template-directed preparation of crown-esters was applied.[16] The variation of the geometric extension of the crown-esters allows the tailoring of the dihedral angle between the connected aromatic rings and, consequently, also their redox potentials (first reduction wave).[17] Our experimental strategy makes use of the steric forces, which the supramolecular building blocks imply on the 4,4′-bipyridinium system, in a somewhat unusual manner. In contrast, the binding of possible guests within these crown-ester host systems is of lesser interest to our research.

Preparation of Dimethyl- and Tetramethyl-4,4′-bipyridines

The synthesis of crown-ester-modified 4,4′-bipyridines started from the analogous dimethyl- and tetramethyl-4,4′-bipyridines: 2,2′-dimethyl-4,4′-bipyridine (**1**), 3,3′-dimethyl-4,4′-bipyridine (**2**) and 2,2′,6,6′-tetramethyl-4,4′-bipyridine (**3**) were prepared according to three different synthetic pathways (Scheme 1):

A) The reductive coupling of bromomethyl-pyridines using nickel(0)-tetrakis-triphenyl-phosphane in anhydrous DMF as reactive reagent.[18]

B) A further development of the pioneering work of Hünig and Wehner permitted the dimerization of 2-picoline, 3-picoline and 2,6-lutidine in toluene by reduction with elementary sodium and subsequent oxidation by SO_2.[19]

C) A variation of method **B**) with further increased yields was developed using dioxane as solvent and $Na_2S_2O_5$ as oxidizing agent.

As it follows from Table 1, in which the obtained yields are summarized, method **A** and **C** lead to the best results. In general, method **B** and **C** are especially suitable for the preparation of methyl-substituted 4,4′-bipyridines in high

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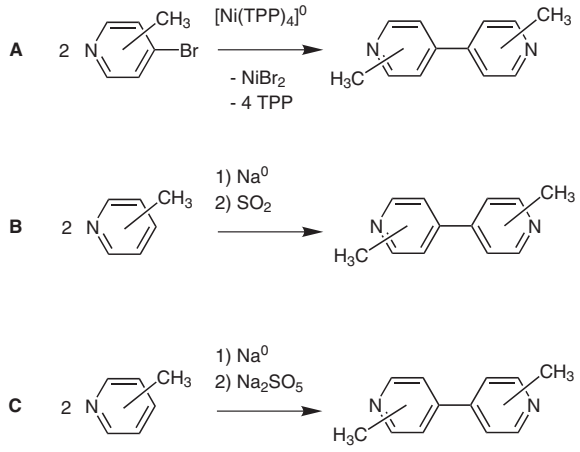


Scheme 1 Three methods for the synthesis of dimethyl- and tetramethyl-4,4′-bipyridines

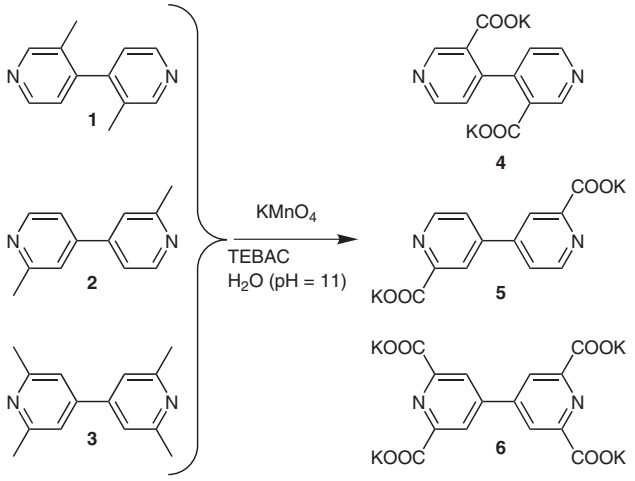
amounts (up to more than 25 g per reaction), as they are needed as starting materials for the preparation of crown-ester-substituted bipyridines.

Table 1 Synthesis of 2,2′-Dimethyl-4,4′-bipyridine (**1**), 3,3′-Dimethyl-4,4′-bipyridine (**2**) and 2,2′,6,6′-Tetramethyl-4,4′-bipyridine (**3**) by Three Different Methods

Entry	Compound	Method	Yield (%)	Physical properties in agreement with
1	1	**A**	67	ref.[22]
2	1	**B**	34	ref.[22]
3	1	**C**	25	ref.[22]
4	2	**A**	62	ref.[4]
5	2	**B**	31	ref.[4]
6	2	**C**	22	ref.[4]

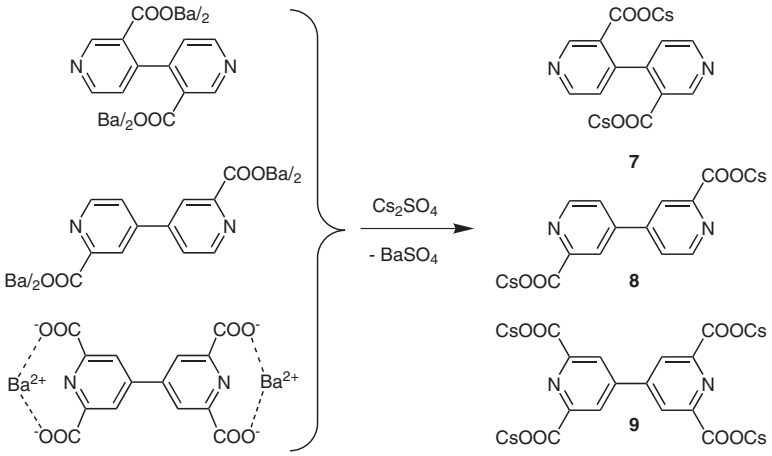
Oxidation of Dimethyl- and Tetramethyl-4,4′-bipyridines

The methyl groups of the starting materials **1**, **2** and **3** were oxidized to dipotassium dicarboxylates and tetrapotassium tetracarboxylates employing $KMnO_4$[20] as oxidizer in aqueous solution (Scheme 2) and a phase transfer catalyst (triethyl-benzyl-ammonium-chloride, TEBAC). The authors are aware that oxidation with potassium dichromate in sulfuric acid[19] leads usually to superior reaction yields. However, compound **5** suffers decarboxylation in acidic medium.



Scheme 2 Oxidation of dimethyl- and tetramethyl-4,4′-bipyridines by $KMnO_4$ in basic solution using a phase transfer catalyst

For the synthesis of crown-esters, the synthesis of cesium salts from potassium salts must be achieved in high yields. For this purpose, the precipitation of the dicarboxylates **4**, **5** and the tetracarboxylate **6** was attained using barium hydroxide ($Ba(OH)_2$). The barium(II)-salts were then reacted in aqueous solution with stoichiometric amounts of Cs_2SO_4 resulting in the formation of solid $BaSO_4$ and the dicesium salts **7**, **8** and the tetracesium salt **9** (Scheme 3).



Scheme 3 Salt conversion and preparation of 4,4′-bipyridine dicesium- and tetracesium salts **7**–**9** from their corresponding barium(II) salts

Synthesis of Crown-esters From 4,4′-Bipyridine Dicesium- and Tetracesium Salts

The thoroughly dehydrated dicesium salts **7**, **8** as well as the tetracesium salt **9** were then further reacted with either dibromo-pentaethylene glycol [1-bromo-2-(2-{2-[2-(2-bromo-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethane, $C_{10}H_{20}Br_2O_4$],[21] or dichloro-tetraethylene glycol [1-chloro-2-{2-[2-(2-chloro-ethoxy)-ethoxy]-ethoxy}-ethane, $C_8H_{16}Cl_2O_3$] or dichloro-triethylene glycol {1-chloro-2-[2-(2-chloro-ethoxy)-ethoxy]-ethane, $C_6H_{12}Cl_2O_2$}. The formation of ester bonds from heterocyclic cesium carboxylates and the employed bromo- or chloro-oligoethylene glycols was performed in anhydrous DMF under dilution conditions according to conditions previously optimized in ref.[15] The formation of intermediate cesium(I)-oligoethylene glycol complexes[16] could explain the high yields of crown-esters which can be obtained by using this method. A characteristic blue color was observed as soon as the reaction mixtures of **10**–**15** reached 55 ± 5 °C and, which remained visible during the following 30–60 minutes. This particular color can be either attributed to the formation of an intermediate cesium(I)-oligoethylene glycol complex or a charge-transfer complex between the electron poor aromatic bipyridines and the chosen dibromo- and dichloro-oligoethylene glycols. After approximately one hour of reaction, cesium bromide (cesium chloride) began slowly to precipitate. The corresponding reaction schemes are summarized in Scheme 4.

Synthesis of Propanesultonated Crown-Ester Viologens

In the last stage of the linear synthesis procedure reported here, the 4,4′-bipyridine crown-esters were transformed into the structurally related propanesultonated viologens by reacting them with 1,3-propane sultone in DMF. The addition of 1,3-propane sultone to the 4,4′-bipyridines **10**–**14** (Scheme 5) was monitored by TLC. The reaction was stopped immediately after the disappearance of the monopropanesultonated reaction products. Otherwise, almost complete decomposition was observed.

Conclusion

The synthesis of zwitterionic crown-ester electron relays having variable crown-ester units attached to their bipyridinium systems offers the advantage of fine-tuning both the binding-properties for cations within the crown-ether moiety and the resulting redox-potentials of the supramolecular electron relays. The yields for each of the five consecutive steps required are either acceptable or very good, so that these compounds can be extensively studied in systems for artificial photosynthesis.

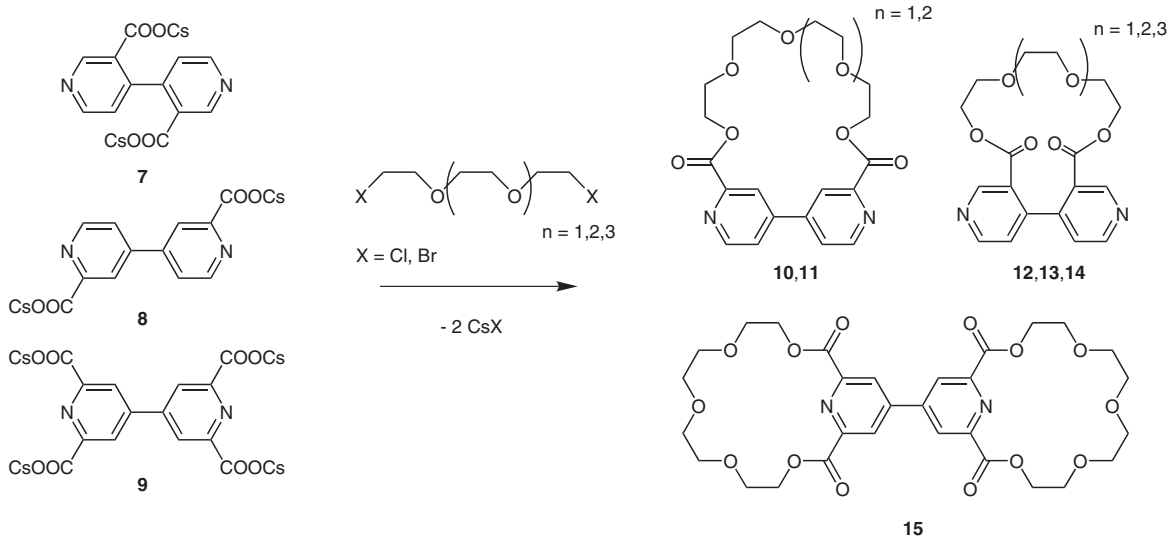
All solvents (ACS-grade) were purchased from Roth. DMF was further purified by azeotropic distillation of DMF–toluene–H_2O (85:10:5), anhydrous and amine-free DMF was collected when reaching 152 °C at the top of a 20 cm vigreux-column.

All bromomethylpyridines were a generous gift from BASF. Dichlorotetraethylene glycol, dichlorotriethylene glycol, pentaethylene glycol and PBr_3 {for the synthesis of dibromo-pentaethylene glycol [1-bromo-2-(2-{2-[2-(2-bromo-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethane, $C_{10}H_{20}Br_2O_4$] according to ref.[21]} were bought from Aldrich.

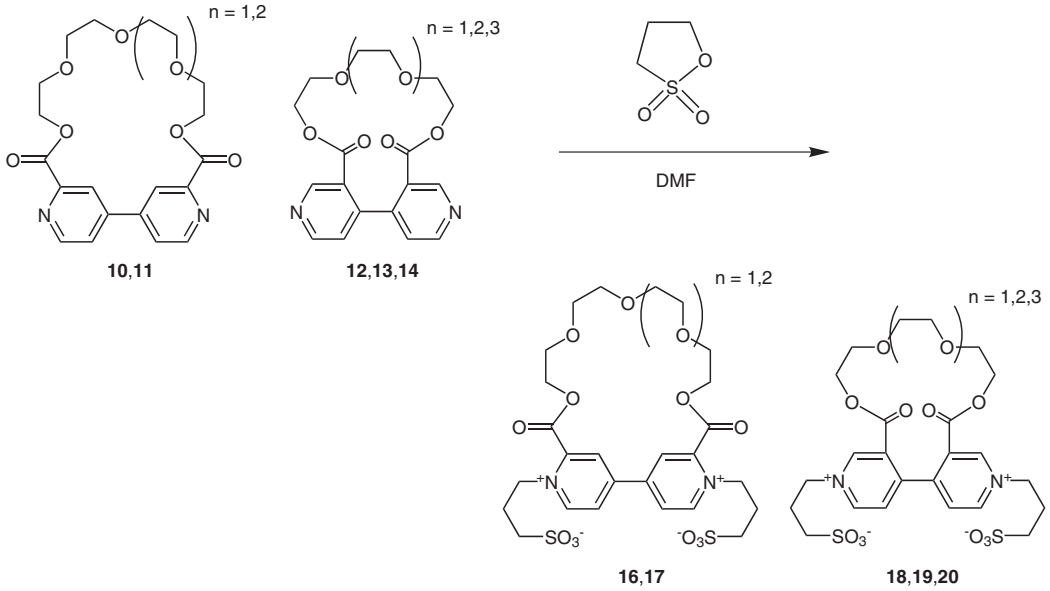
Synthesis of 2,2′-Dimethyl-4,4′-bipyridine (1), 3,3′-Dimethyl-4,4′-bipyridine (2) and 2,2′,6,6′-Tetramethyl-4,4′-bipyridine (3)

Method A

Solution I: Triphenyl-phosphane (30.45 g, 0.116 mol) and $NiCl_2 \cdot 6H_2O$ (6.92 g, 29.1 mmol) were dissolved in anhyd DMF (300 mL). The reaction mixture was stirred for 30 min under a N_2 atmosphere at 50 °C. Elementary zinc (2.0 g, 30.6 mmol) was added to the dark blue solution. The solution turned immediately to a brownish color and after another 30 min slowly to dark green.



Scheme 4 Formation of crown-esters from the 4,4′-bipyridine dicesium- and tetracesium salts **7**–**9** and dichlorotriethylene glycol, dichlorotetraethylene glycol and dibromopentaethylene glycol



Scheme 5 Propanesultonation of the 4,4′-bipyridine crown-esters **10**–**14**

Solution II: 4-Bromo-2-methyl-pyridine (10.0 g, 58.2 mmol), 4-bromo-3-methyl-pyridine (10.0 g, 58.2 mmol) or 4-bromo-2,6-dimethyl-pyridine (10.8 g, 58.2 mmol) was dissolved in anhyd DMF (50 mL) and purged with N_2 for 20 min. Then, solution II was added dropwise to solution I during 10 min. The reaction mixture was allowed to react for 2 h at 50 °C. After completion of the reaction, a brownish color was observed. This reaction mixture was treated with aq NH_3 solution (500 mL, 35% by weight NH_3 in H_2O) and extracted with CH_2Cl_2 (6 × 100 mL). CH_2Cl_2 was removed from the combined organic (lower) phases at 40 °C at normal pressure, DMF and then traces of H_2O were removed in high vacuum. Note that the temperature of the reaction mixture must not exceed 85 °C (decomposition!). After the DMF was completely removed, triphenylphosphane was separated by using descending column chromatography (silica gel, CH_2Cl_2; R_f 0.96). The reaction products were then obtained by increasing the polarity of the mobile phase (silica gel, CH_2Cl_2–MeOH, 98:2); **1**: R_f 0.62; **2** R_f 0.62; **3** R_f 0.62.

Method B

Anhydrous 2-methyl-pyridine, 3-methyl-pyridine or 2,6-dimethyl-pyridine were (50.0 g) mixed with anhyd dioxane (200 mL) and purged with N_2 for 20 min. Sodium (5.0 g) was added in very small amounts. The reaction mixture was then refluxed until the sodium was completely dissolved. A dark green color was observed. After cooling down to r.t., the reaction mixture was treated with SO_2 gas until the dark green color changed to orange (SO_2 was bubbled in the viscous mixture for at least 30 min). Then the reaction mixture was poured on ice (500 g; careful, watch out for unreacted pieces of sodium!) and was then extracted with CH_2Cl_2 (6 × 100 mL). After the removal of CH_2Cl_2 at r.t. and then dioxane in high vacuum, descending column chromatography was performed as described in method A.

Method C

Anhydrous 2-methyl-pyridine, 3-methyl-pyridine or 2,6-dimethyl-pyridine (50.0 g) were mixed with anhyd dioxane (200 mL) and purged with N_2 for 20 min. Sodium (5.00 g) was added in very small amounts. The reaction mixture was then refluxed until the sodium was completely dissolved. A dark green color was observed. The reaction mixture was cooled down to 0 °C and $Na_2S_2O_5$ (10.0 g) was added at once. The reaction mixture was allowed to react overnight and to gradually warm to r.t. Extraction with CH_2Cl_2, removal of the solvent and descending column chromatography were performed as described in methods A and B.

Dipotassium-4,4′-bipyridinyl-2,2′-dicarboxylate (4), Dipotassium-4,4′-bipyridinyl-3,3′-dicarboxylate (5) and Tetrapotassium-4,4′-bipyridinyl-2,6,2′,6′-tetracarboxylate (6)

Compounds **1**, **2** (5.0 g, 27.0 mmol) or **3** (5.00 g, 23.5 mmol) were dissolved in CH_2Cl_2 (10 mL). In a 2000 mL three-necked flask, the organic phase, bidest. H_2O (800 mL) and TEBAC (11.4 g, 50.0 mmol) were combined. The reaction mixture was heated to 40 °C and CH_2Cl_2 was distilled off. Then, $KMnO_4$ (64.0 g, 0.41 mol) was added at once. The reaction mixture was slowly heated to the boiling temperature and refluxed until its color changed from dark-violet to brown. Residual $KMnO_4$ was reduced by adding EtOH (50 mL). MnO_2 was immediately filtered off. EtOH (100 mL) was added to the light-brown filtrate and then H_2O–EtOH was removed in vacuum until white or lightly yellow precipitates were formed. Further removal of H_2O from the potassium salts **4**, **5** or **6** was achieved in high vacuum. Note that heating above 80 °C should be avoided due to the danger of decomposition!

Dicesium-4,4′-bipyridinyl-2,2′-dicarboxylate (7), Dicesium-4,4′-bipyridinyl-3,3′-dicarboxylate (8) and Tetracesium-4,4′-bipyridinyl-2,6,2′,6′-tetracarboxylate (9)

In a 500 mL three necked flask compound **4**, **5** (3.00 g, 9.40 mmol) or **6** (3.00 g, 6.20 mmol) was suspended in bidest. H_2O (150 mL) and heated to 45 °C, until it was completely dissolved. Then, solid $Ba(OH)_2$ (1.61 g, 9.40 mmol) was added at once [if compound **6** is the starting material, solid $Ba(OH)_2$ (2.13 g, 12.4 mmol) was needed]. The reaction mixture was continuously stirred for 24 h at 45 °C and then slowly cooled to 2 °C. After 24 h at 2 °C, crystallization was completed and the barium salts were filtered off in the cold. The white barium-salts were further dehydrated in high vacuum, weighed and re-suspended in bidest. H_2O (150 mL). After heating to 60 °C, the stoichiometric amount of Cs_2SO_4 was added at once. The reaction mixture was continuously stirred for 24 h at 60 °C. Then $BaSO_4$ was filtered off from the warm supernatant. From the latter, water was removed in vacuum, until white or lightly yellow precipitates were formed. Further removal of H_2O from the cesium salts **7**, **8** or **9** was achieved in high vacuum. Note that heating above 80 °C should be avoided due to the danger of decomposition!

8,11,14,17,20,23-Hexaoxa-5,26-diaza-tricyclo[23.3.1.10,255]triaconta-1(28),2,4,6(30),25(29),26-hexaene-7,24-dione (10), 8,11,14,17,20,23-Hexaoxa-5,26-diaza-tricyclo[23.3.1.10,255]triaconta-1(28),2,4,6(30),25(29),26-hexaene-7,24-dione (11), 9,12,15,18,21,24-Hexaoxa-5,28-diaza-tricyclo[24.4.0.0^{0,255}]triaconta-1(30),2,4,6,26,28-hexaene-8,25-dione (12), 9,12,15,18,21-Pentaoxa-5,25-diaza-tricyclo[21.4.0.0^{0,255}]heptacosa-1(27),2,4,6,23,25-hexaene-8,22-dione (13), 7,8,10,11,13,14-Hexahydro-6,9,12,15-tetraoxa-3,18-diaza-dibenzo[*a*,*c*]cyclohexadecene-5,16-dione (14) and [19,19′]Bi[3,6,9,12,15-pentaoxa-21-aza-bicyclo[15.3.1]heneicosyl]1(20),17(21), 18,1′(20′), 17′(21′),18′-hexaene-2,16,2′,16′-tetraone (15)

In a 3000 mL three-necked flask, equipped with a syringe-pump and an efficient stirring device, the dicesium salts **7**, **8** or the tetracesium salt **9** were dissolved in DMF (2000 mL) at 25 °C under intensive stirring. Then the suitable oligo-ethylene glycol dibromide ($C_{10}H_{20}Br_2O_4$) or dichloride ($C_8H_{16}Cl_2O_3$; $C_6H_{12}Cl_2O_2$), dissolved in DMF (500 mL), was added dropwise within 30 min at 25 °C. The reaction mixture was then slowly (during 2 h) heated to 55 °C and allowed to react for 96 h under gentle stirring. Immediately after the reaction temperature was reached, a characteristic blue color of the reaction mixture formed, which disappeared, depending on the actual reaction, within several minutes to yield a slight and constantly increasing yellow color. After 96 h, the formed white precipitate (CsBr or CsCl) was filtered off and then the DMF was removed in high vacuum. Note that an increase of the temperature of the reaction mixture beyond 70 °C led to partial decomposition, as TLC indicated. After the removal of DMF, the dark-brown oils or brown precipitates were dried in an N_2 stream in order to remove residual traces of DMF. The reaction mixture was dissolved in as little CH_2Cl_2 as possible and then purified employing descending column chromatography (aluminum oxide, CH_2Cl_2–MeOH, 98:2); the R_f values of the products were ranging from 0.35–0.45.

5,26-(3-Sulfonatopropyl)-8,11,14,17,20,23-hexaoxa-5,26-diazonia-tricycl[23.3.1.1^{0,255}]triaconta-1(28),2,4,6(30),25(29),26-hexaene-7,24-dione (16), 5,23-Dimethyl-8,11,14,17,20-pentaoxa-5,23-diazonia-tricyclo[20.3.1.1^{0,255}]heptacosa-1(25),2,4,6(27), 22(26),23-hexaene-7,21-dione (17), 5,28-Di(3-Sulfonatopropyl)-9,12,15,18,21,24-hexaoxa-5,28-diazonia-tricyclo[24.4.0.0^{0,255}]triaconta-1(30),2,4,6,26,28-hexaene-8,25-dione (18), 5,25-Di(3-Sulfonatopropyl)-9,12,15,18,21-pentaoxa-5,25-diazonia-tricyclo[21.4.0.0^{0,255}]heptacosa-1(27),2,4,6,23,25-hexaene-8,22-dione (19) and 3,18-Di(3-Sulfonatopropyl)-7,8,10,11,13,14-hexahydro-6,9,12,15-tetraoxa-3,18-diazonia-dibenzo[*a*,*c*]cyclohexa-decene-5,16-dione (20)

In a 100 mL one-necked flask, the crown-ester-bipyridines **10**–**14** were dissolved in anhyd DMF (10 mL) at r.t. The 5-fold molar excess of 1,3-propane sultone, calculated according the number of nitrogen atoms, was added. The mixture was heated to 100 °C. The reaction progress was monitored by using TLC (aluminum oxide, EtOH). Usually, the starting material was consumed after 10 min and after 30 min, the mono-addition products (R_f ca. 0.5) disappeared again. Purging with N_2 increased the obtained yields substantially. After cooling to r.t., anhyd acetone (20 mL) was added. A white precipitate was formed after 5–10 min, whose formation was allowed to complete overnight at 0 °C. The precipitate was filtered off and residual traces of solvent were removed in high vacuum. Then, the precipitate was redissolved in anhyd EtOH and further purified by descending column chromatography (aluminum oxide/EtOH), the R_f values of the mono-propanesultonated products were ranging from 0.85–0.90, whereas the reaction products featured R_f values of 0.25–0.35.

Table 3 Concentrations of the Reactants and Yields Obtained in the Synthesis of Crown-Ester-Modified Bipyridinium Relays

Component	$C_3H_6O_3S$ [g/mmol]	Crown-ester bipyridinium relay Yield (%)
10 0.223/0.50	0.610/5.0	**16** (37)
11 0.200/0.50	0.610/5.0	**17** (42)
12 0.223/0.50	0.610/5.0	**18** (87)
13 0.200/0.50	0.610/5.0	**19** (44)
14 0.180/0.50	0.610/5.0	**20** (42)

Table 2 Concentrations of the Reactants and Yields Obtained in the Synthesis of Crown-Ester-Modified Bipyridines

Component [g/mmol]	$C_{10}H_{20}Br_2O_4$ [g/mmol]	$C_8H_{16}Cl_2O_3$ [g/mmol]	$C_6H_{12}Cl_2O_2$ [g/mmol]	Crown-ester Yield (%)
7 5.00/9.80	3.56/9.80			**10** (12)
7 5.00/9.80		2.26/9.80		**11** (15)
8 5.00/9.80	3.56/9.80			**12** (24)
8 5.00/9.80		2.26/9.80		**13** (43)
8 5.00/9.80			1.83/9.80	**14** (42)

Table 4 Characterization of the Dipotassium-4,4′-bipyridinyl-dicarboxylates (**4** and **5**) and the Tetrapotassium-4,4′-bipyridinyl-tetracarboxylate (**6**) as well as the Dicesium-4,4′-bipyridinyl-dicarboxylates (**7** and **8**) and the Tetrapotassium-4,4′-bipyridinyltetracarboxylate (**9**)

Product[a]	Yield (%)	Mp (°C) (dec.)	FT-IR (KBr, cm^{-1})	^1H NMR (400 MHz, D_2O) δ, *J* (Hz)
4	80	> 350	3102, 2840, 1715 (C=O), 1562, 1445, 820	8.70 (d, *J* = 4.77 Hz, 2 H, ArH), 7.69 (s, 2 H, ArH), 7.58 (d, *J* = 4.77 Hz, 2 H, ArH)
5	90	> 350	3050, 2945, 1710 (C=O), 1480, 1405, 1307, 1220, 1085, 1043, 961, 802, 745	8.37 (s, 2 H, ArH), 8.34 (s, 2 H, ArH), 7.88 (s, 2 H, ArH)[b]
6	44	> 350	3440, 3080, 3065, 2915, 1645 (C=O), 1582, 1490, 1415, 845	7.30 (s, 4 H, ArH)[b]
7	53	> 350	3105, 2835, 1712 (C=O), 1560, 1440, 825	8.72 (d, *J* = 4.72 Hz, 2 H, ArH), 7.70 (s, 2 H, ArH), 7.56 (d, *J* = 4.72 Hz, 2 H, ArH)
8	85	> 350	3065, 2930, 1710 (C=O), 1650, 1560, 1470, 1302, 1277, 1255, 1104, 1048, 970, 803, 760	8.40 (s, 2 H, ArH), 8.32 (s, 2 H, ArH), 7.89 (s, 2 H, ArH)[b]
9	92	> 350	3410, 3070, 3115, 3040, 2905, 1681 (C=O), 1470, 926	7.32 (s, 4 H, ArH)[b]

[a] Satisfactory microanalyses were obtained: C, ± 0.06; H, ± 0.03; N ± 0.04
[b] Broad singlets were obtained due to inferior resolution of the ^1H NMR spectra.

Table 5 Characterization of the 4,4′-Bipyridinyl-Crown-Esters (**10**–**14**)

Product[a]	FT-IR (KBr, cm^{-1})	^1H NMR (400 MHz, D_2O) δ, *J* (Hz)	^{13}C NMR (400 MHz, D_2O) δ, *J* (Hz)	MS (FAB) *m*/*z* (%)
10	3230, 3035, 2980, 2945, 2260, 1840, 1730 (C=O), 1705 (C=O), 1585, 1430, 1390, 1315, 1280, 1240, 1230, 1110, 1080, 1060, 970, 945, 835, 745, 680	8.91 (s, 2 H, ArH), 8.45 (dd, ^3J = 5.31 Hz, ^4J = 1.12 Hz, 2 H, ArH), 7.79 (dd, *J* = ^3J = 5.31 Hz, ^4J = 1.12 Hz, 2 H, ArH), 4.36 (m, 2 H), 3.53 (m, 4 H), 3.42 (m, 4 H), 3.41 (m, 4 H), 3.26 (m, 4 H), 1.97 (m, 2 H)	159.59 (C=O), 150.14, 146.41, 121.41, 118.77, 71.41, 70.68, 36.40, 31.36, 24.73	447 (0.08) [M + 1], 271 (1.5), 244 (0.8), 157 (2.2), 78 (100), 64 (56)
11	3235, 3035, 2990, 2950, 2255, 1840, 1730 (C=O), 1710 (C=O), 1580, 1440, 1390, 1315, 1280, 1250, 1230, 1100, 1080, 970, 945, 840, 745, 685	8.90 (s, 2 H, ArH),[b] 8.43 (dd, ^3J = 5.25 Hz, ^4J = 1.15 Hz, 2 H, ArH), 7.74 (dd, *J* = ^3J = 5.25 Hz, ^4J = 1.15 Hz, 2 H, ArH), 4.38 (m, 2 H), 3.51 (m, 2 H), 3.42 (m, 2 H), 3.40 (m, 4 H), 3.23 (m, 4 H), 1.95 (m, 2 H)	159.66 (C=O), 150.11, 146.11, 121.61, 119.02, 71.40, 70.63, 36.45, 31.32, 24.70	403 (0.03) [M + 1], 271 (2.7), 244 (1.8), 157 (0.5), 78 (100), 64 (34)
12	3070, 2900, 1745 (C=O), 1650, 1560, 1460, 1390, 1300, 1250, 1120, 1050, 960, 800, 760	9.02 (s, 2 H, ArH),[b] 8.40 (dd, ^3J = 7.92 Hz, ^4J = 1.70 Hz, 2 H, ArH), 7.49 (dd, ^3J = 7.92 Hz, ^4J = 1.70 Hz, 2 H, ArH), 4.20 (m, 4 H), 3.79 (m, 4 H), 3.62 (m, 12 H)	164.03 (C=O), 155.31, 151.05, 138.36, 125.13, 122.50, 70.65, 69.38, 64.07	446 (0.01), 271 (2.5), 244 (1.0), 158 (1.1), 78 (100), 64 (27)
13	3070, 2900, 1745 (C=O), 1650, 1560, 1460, 1390, 1300, 1250, 1050, 950, 800, 760	9.04 (s, 2 H, ArH),[b] 8.40 (dd, ^3J = 7.73 Hz, ^4J = 1.68 Hz, 2 H, ArH), 7.38 (dd, ^3J = 7.73 Hz, ^4J = 1.68 Hz, 2 H, ArH), 4.23 (m, 4 H), 3.76 (m, 4 H), 3.68 (m, 8 H)	162.70 (C=O), 153.04, 148.20, 139.26, 123.12, 121.60, 71.39, 70.62, 70.35, 64.50	403 (0.21) [M + 1], 271 (1.0), 244 (1.0), 157 (0.4), 78 (100), 64 (44)
14	3060, 2900, 1740 (C=O), 1650, 1560, 1450, 1400, 1310, 1250, 1050, 950, 800, 760	8.13 (s, 4 H, ArH),[b] 8.02 (s, 2 H, ArH), 3.58 (m, 4 H), 3.45 (m, 8 H)	162.47 (C=O), 156.37, 150.83, 134.84, 127.36, 122.07, 71.38, 70.67, 42.76	359 (0.03) [M + 1], 271 (2.7), 244 (1.0), 156 (0.7), 78 (100), 64 (21)
15	3420, 3060, 3130, 3025, 2910, 1725 (C=O), 1465, 930	8.75 (m, 2 H, ArH), 8.27 (m, 2 H, ArH), 4.51 (m, 4 H), 3.80 (m, 4 H), 3.57 (m, 8 H), 3.54 (m, 16 H)		649 (0.015) [M + 1], 333 (0.07), 154 (1.0), 77 (100), 63 (21)

[a] Satisfactory microanalyses were obtained: C, ± 0.06; H, ± 0.04; N, ± 0.05.
[b] Broad singlets were obtained due to inferior resolution of the ^1H NMR spectra.

Table 6 Characterization of the 4,4′-Bipyridinium-Crown-Ester Relays (**16**–**20**)

Product[a]	FT-IR (KBr, cm^{-1})	^1H NMR (400 MHz, D_2O) δ, *J* (Hz)	MS (FAB) *m/z* (%)	Mp (°C)
16	3080, 2995, 2945, 1715 (C=O), 1680, 1610, 1590, 1505, 1465, 1445, 1425, 1390, 1060 (OSO_2^-)	8.04 (s, 4 H, ArH), 7.75 (dd, 2 H, ArH), 4.40 (t, 2 H), 4.26 (t, 2 H), 3.50 (mc, 10 H), 3.27 (t, 4 H), 2.86 (td, 4 H, N^+CH_2), 2.47 (t, 4 H, $CH_2OSO_2^-$), 1.77 (td, $^3J_1$ = 6.75 Hz, $^3J_2$ = 7.53 Hz, $^3J_3$ = 7.11 Hz, $^3J_4$ = 7.02 Hz, ^4J = 1.16 Hz, 4 H)	691 (0.011) [M + 1], 271 (0.5), 200 (0.03), 156 (3.2), 78 (100), 64 (16)	202 (dec.)
17	3080, 2995, 2950, 1715 (C=O), 1680, 1610, 1585, 1510, 1465, 1450, 1425, 1390, 1060 (OSO_2^-)	8.04 (s, 4 H, ArH), 7.76 (dd, 2 H, ArH), 4.42 (t, 2 H), 4.28 (t, 2 H), 3.52 (mc, 6 H), 3.25 (t, 4 H), 2.86 (td, 4 H, N^+CH_2), 2.47 (t, 4 H, $CH_2OSO_2^-$), 1.77 (td, $^3J_1$ = 6.77 Hz, $^3J_2$ = 7.51 Hz, $^3J_3$ = 7.08 Hz, $^3J_4$ = 7.05 Hz, ^4J = 1.13 Hz, 4 H)	647 (0.02) [M + 1], 392 (1.4), 157 (0.9), 78 (100), 64 (42)	200 (dec.)
18	3080, 2940, 2860, 1730 (C=O), 1670, 1640, 1600, 1510, 1470, 1445, 1430, 1385, 1060 (OSO_2^-), 728	8.04 (s, 4 H, ArH),[b] 7.76 (s, 2 H, ArH), 4.40 (t, 4 H), 4.26 (t, 2 H), 3.50 (m, 4 H), 3.54 (m, 6 H), 3.27 (t, 4 H), 2.76 (td, 4 H, N^+CH_2), 2.47 (t, 4 H, $CH_2OSO_2^-$), 1.77 (td, $^3J_1$ = 6.86 Hz, $^3J_2$ = 4.77 Hz, $^3J_3$ = 4.12 Hz, $^3J_4$ = 4.08 Hz, ^4J = 1.27 Hz, 4 H)	690 (0.004), 390 (1.6), 158 (1.3), 78 (100), 64 (28)	248 (dec.)
19	3080, 2985, 2935, 1725 (C=O), 1645, 1580, 1505, 1465, 1445, 1430, 1380, 1060 (OSO_2^-), 740	8.04 (s, 4 H, ArH),[b] 7.75 (s, 2 H, ArH), 4.40 (t, 4 H), 4.26 (t, 2 H), 3.65 (m, 2 H), 3.50 (m, 6 H), 3.26 (t, 2 H), 2.78 (td, 4 H, N^+CH_2), 2.47 (t, 4 H, $CH_2OSO_2^-$), 177 (td, $^3J_1$ = 6.84 Hz, $^3J_2$ = 4.81 Hz, $^3J_3$ = 4.12 Hz, $^3J_4$ = 4.02 Hz, ^4J = 1.22 Hz, 4 H)	646 (0.0015), 391 (1.5), 157 (1.6), 78 (100), 64 (54)	217 (dec.)
20	3080, 2990, 2950, 2935, 1715 (C=O), 1680, 1650, 1585, 1510, 1470, 1445, 1430, 1285, 1060 (OSO_2^-)	8.07 (s, 4 H, ArH), 7.77 (s, 2 H, ArH), 4.53 (t, 1 H), 4.29 (t, 1 H), 3.55 (t, 10 H), 2.85 (s, 2 H, $CH_2OSO_2^-$), 2.79 (td, 4 H, N^+CH_2), 2.69 (s, 2 H, $CH_2OSO_2^-$), 1.80 (td, $^3J_1$ = 6.78 Hz, $^3J_2$ = 6.46 Hz, $^3J_3$ = 4.12 Hz, ^4J = 1.26 Hz, 4 H)	603 (0.013) [M + 1], 391 (3.3), 156 (2.0), 78 (100), 64 (26)	253 (dec.)

[a] Satisfactory microanalyses were obtained: C, ± 0.06; H, ± 0.04; N, ± 0.05.
[b] Broad singlets were obtained due to inferior resolution of the ^1H NMR spectra.

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