Synthesis and Structures of Novel Pyridine-Bridged Phanes of 4,4′-Bipyridine[1]

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Dedicated to Professor Peter Böttcher on the occasion of his 60th birthday

Keywords: 4,4′-Bipyridine / NMR spectroscopy / Pyridinophanes / X-ray crystal structure determination / Macrocycles

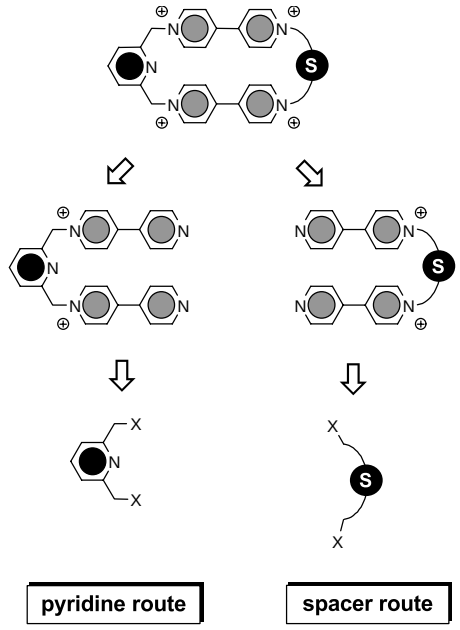
Syntheses of nine novel phanes derived from 4,4′-bipyridine incorporating new spacer elements are described together with their structural and spectroscopic properties. Starting from the previously unknown pyridine-bridged bis(4,4′-bipyridinium) dication **2** and various bis(bromomethyl)-arenes, macrocycles **3–7** were prepared in a simple heterogeneous liquid-liquid reaction in satisfactory yields. In complementary experiments starting from bis(4,4′-bipyridinium) compounds **12–14** with substituted xylenes as spacers, ring closure was performed with 2,6-bis(bromomethyl)pyridine (**1**) to furnish compounds **16–18** in low yield. Temperature-dependent NMR-spectroscopic studies of the macrocycles were performed to investigate their conformational behaviour. The X-ray crystal structures for phanes **3, 4** and **6** illustrate the preferred *anti* conformation of the macrocycles in the solid state. Consecutive reactions at the pyridine bridge were not successful; however, anisolophane **7** was converted into nitroanisolophane **11** by simple nitration of the anisolo spacer in excellent yield.

Introduction

Dications based on 4,4′-bipyridine are model compounds for electron-transfer processes since they are apt to accept two electrons in a reversible manner.[2] Macrocyclic derivatives of 4,4′-bipyridine dications were introduced by Hünig et al.[3] and further developed and varied by Stoddart's group and others. Now a wide range of carbocyclic[4] and heterocyclic[5] bridged phanes are available; also systems containing transition metals[6] and macrocycles with surface activity[7] are known. Stoddart's group first prepared a twofold *para*-xylene-bridged phane of 4,4′-bipyridine, which is an ideal building block for supramolecular chemistry due to its defined cavity and its rigid electron-deficient bipyridinium moieties.[4d] With electron-rich aromatic substrates deeply coloured 1:1 charge-transfer complexes are formed,[8] a propensity which can be exploited as a template effect in the syntheses of these macrocycles.[9] Higher aggregated systems such as pseudorotaxanes,[10] rotaxanes,[11] and [*n*]catenanes[12] could elegantly be constructed by taking advantage of this quality. A particularly attractive approach for separation of enantiomers uses chiral 4,4′-bipyridine phanes.[13] If such compounds should gain practical importance as stationary phases for separation, it would be necessary to introduce additional functionalities to allow binding to a polymer. In our study we report on syntheses and properties of novel pyridine-bridged phanes based on 4,4′-bipyridine. We investigated structural pecularities and compared them with properties of the corresponding carbocyclic-bridged phanes. In addition, the influences of intraannular substituents on the dynamic behaviour and the spectroscopic properties of these novel macrocycles were studied. Furthermore, we report the first extraannular reaction of a phane derived from 4,4′-bipyridine.

Results and Discussion

As illustrated in the retrosynthetic analysis (Scheme 1), preparation of novel pyridinophanes containing 4,4′-bipyridine moieties may be envisaged by two routes. Starting from



Scheme 1. Retrosynthetic analysis

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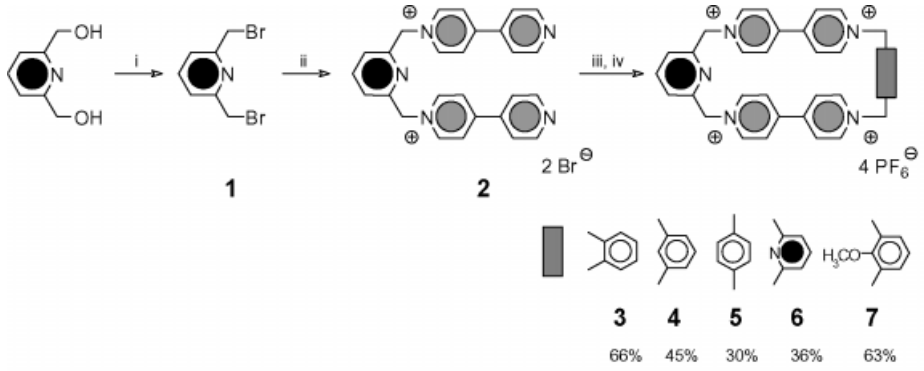
  1434–193X/99/0909–2373 $ 17.50+.50/0



Scheme 2. Reagents and conditions: i) PBr_3, CCl_4, 88%; ii) excess of 4,4′-bipyridine, CH_3CN, 92%; iii) bis(bromomethyl)arene, CH_3NO_2/H_2O, room temp., 30d; iv) NH_4PF_6, H_2O

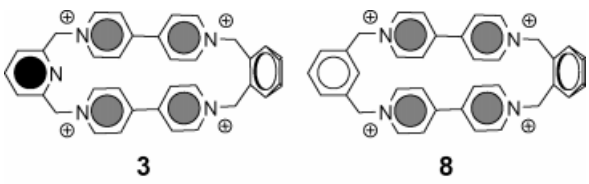
the side-chain dihalogenated pyridine, a bis(4,4′-bipyridinium) dication with a heterocyclic bridge has to be synthesized in the first step, and the ring closure proceeds with a bis(halomethyl)arene (pyridine route). The two steps may also be interchanged, first using the bis(halomethyl)arene spacer for preparation of the bridged bis(4,4′-bipyridinium) dication, which will furnish the macrocycle by reaction with a 2,6-bis(halomethyl)pyridine (spacer route).

According to published procedures 2,6-bis(bromomethyl)-pyridine (**1**) was prepared from the corresponding diol and phosphorous tribromide in tetrachloromethane.[14] Conversion into the previously unknown pyridine-bridged dication **2** was achieved in 92% yield by reaction of **1** with an excess of 4,4′-bipyridine in acetonitrile. The crucial macrocyclization was carried out in a liquid-liquid system: Dication **2**−2Br was dissolved in water, the appropriate bis(bromomethyl)arene in nitromethane and, after mixing the two solutions, they were vigorously shaken at room temperature for 30 d. Simple chromatographic workup of the aqueous phase and counterion exchange provided the desired pyridinophanes **3**−**7** as crystalline tetrakis(hexafluorophosphates) in 30−66% yield (Scheme 2).

Table 1. Data of dynamic processes for pyridinophane **3**−$4PF_6$[a,b]

Proton	T_c [K]	$k(T_c)$ [s^{-1}]	$\Delta G^{\neq}$ [kJ mol^{-1}]
bipy-α	210 ± 3	240.6	41.3 ± 0.6
bipy-α′	243 ± 2	619.3	46.1 ± 0.4
bipy-β	213 ± 5	229.0	42.0 ± 1.0
bipy-β′	233 ± 5	267.5	45.8 ± 1.0

[a] Values were determined and calculated by the coalescence method according to ref.[15]. − [b] α,β: pyridine-related protons; α′,β′: *ortho*-xylene related protons of 4,4′-bipyridinium.



Scheme 3. Pyridinophane **3** and carbophane **8**

According to ^{1}H-NMR spectroscopy *ortho*-xylene-bridged pyridinophane **3** shows an interesting difference in its dynamic behaviour from that of the related carbophane **8** investigated by Geuder and Hünig.[3] In CD_3CN the signals of the bipyridinium protons of **8** were broadened at 233 K, but no coalescence points could be determined because the solvent froze. Surprisingly, broadened signals of the bipyridinium protons were observed for pyridinophane **3** at room temperature indicating that the exchange processes slow down. Temperature-dependent NMR spectra in [D_6]acetone demonstrate that the rotation of both pyridinium rings can be frozen; coalescence temperatures and free activation enthalpies are given in Table 1.

We cannot present a clear explanation for the different behaviour of **8** and **3**. Undoubtedly, both phanes are highly strained compounds. Whereas the larger bridge is entirely flexible in solution the *ortho*-xylene spacer is rigid in **8** and **3** as reflected by an AB spin system for the methylene protons. Although the lone pair at the pyridine nitrogen atom of **3** should be less space-filling than the intraannular proton of the spacer in **8**, pyridinophane **3** seems to adopt a conformation which transfers the strain to a higher degree into the bipyridinium groups than in carbophane **8**. The structure of **3**−$4PF_6$ was unambiguously confirmed by an X-ray analysis as illustrated in Figure 1. This is the first example of a crystal structure of an *ortho*-xylene-bridged phane of 4,4′-bipyridine.

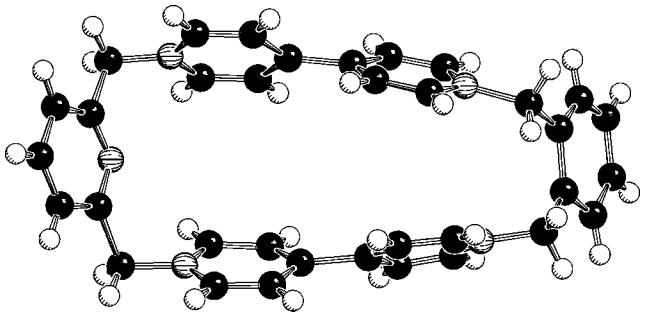
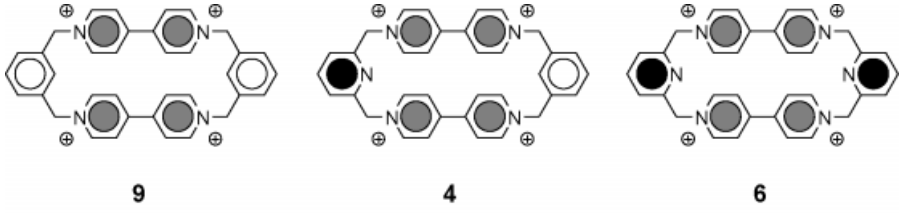


Figure 1. Structure of pyridinophane **3**−$4PF_6$ in the solid state;[16] counterions are omitted for clarity

In the solid state, tetracation **3** prefers an *anti* conformation of the bridging arenes with respect to the plane of

the methylene groups. The pyridine ring is inclined by 55°, whereas the *ortho*-xylene bridge has an inclination angle of 64°. The torsion angles between the connected pyridinium rings amount to 34.4° and 39.3°, and the distances between the bridging methylene groups were calculated for the xylene part to be 3.0 Å and for the pyridine part to be 4.8 Å. The bipyridinium groups are characteristically bent out of plane with bending angles of 6° and 12.5°, thus clearly indicating the proposed distribution of strain within the molecule.

This assumption of strain transfer is impressively demonstrated by comparison of *meta*-bridged phanes **9**,[3] **4** and **6** (Scheme 4). The intraannular protons of **9** and **4** serve as a spectroscopic anchor in the ^{1}H-NMR spectra. While for **9** this proton has a chemical shift of $\delta = 7.19$ (in [D$_6$]DMSO) the corresponding value for **4** is $\delta = 6.40$! Thus, the intraannular proton of pyridinophane **4** approaches the cationic pyridine rings considerably closer than that of carbophane **9**. **9** these pyridinophanes crystallize in the preferred *anti* conformation (Figure 2). All geometric parameters of **9**, **4** and **6** are almost identical. The N−C−C angles at the methylene groups are 110 ± 1°, the distances between the methylene carbon atoms are 4.8 ± 0.2 Å and those between the intraannular C or N atoms are 10.0 ± 0.2 Å. The inclination angles range between 51.5° and 57.5°. The most striking difference consists in the torsion angle between the pyridinium rings which amounts to 31° for **9**, increases to 49.6° in pyridinophane **4** and finally attains 54° in bispyridinophane **6**. A related phane with two thiophene bridges was analysed by Stoddart et al. and shows a similar high torsion angle of 47°.[5] These results can be compared with those obtained for pyridinophane **3**. The formal substitution of an intraannular proton by a lone pair provides a larger cavity inside the phanes. As a consequence, similar strain energies to those for the compounds are transferred to the bipyridinium groups in these compounds.



Scheme 4. *meta*-Bridged phanes **9**, **4**, and **6**

Whereas the crystal structure of **9**−4BF$_4$ monohydrate has been reported earlier[17] we now present the solid-state structures of **4**−4PF$_6$ and **6**−4PF$_6$. As observed for **3** and

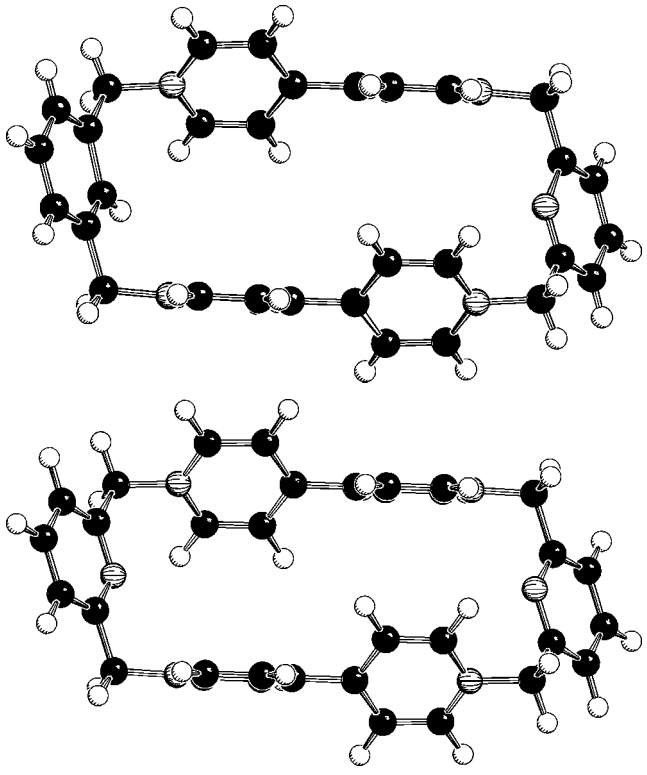
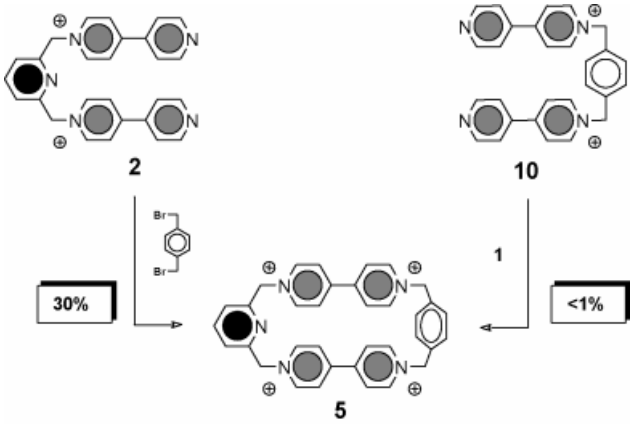


Figure 2. X-ray crystal structures of the pyridinophanes **4**−4PF$_6$ (top) and **6**−4PF$_6$ (bottom);[16] counterions are omitted for clarity

Synthesis of *para*-xylene-bridged pyridinophane **5** was attempted by both routes of Scheme 1. The pyridine route with dication **2** as intermediate furnished the desired macrocyclic target **5** in moderate yield, whereas the spacer pathway employing dication **10**[3] and dibromide **1** as building blocks produced only traces of **5** (Scheme 5). This result may be explained by geometrical factors. The X-ray analysis of **10**−2ClO$_4$ illustrates that this molecule prefers the *anti* conformation with respect to the two bipyridine units at the *para*-xylene ring (Figure 3). The distance between the free nitrogen atoms which should react with **1** is in the range of 20 Å. This upper limit for the distance favours formation of oligomers and polymers. Thus, *meta*-bridged dications such as **2** are more favourable for macrocyclization.



Scheme 5. Syntheses of pyridinophane **5**

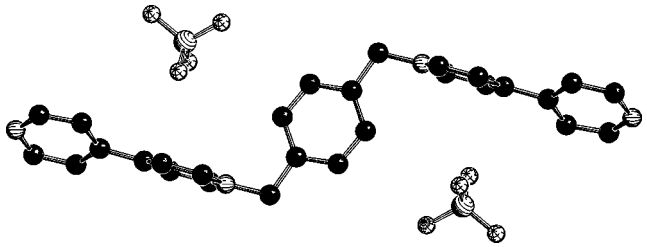


Figure 3. X-ray crystal structure of dication **10**−2ClO_4;[16] hydrogen atoms are omitted

Another interesting phenomenon was recognized during crystallization of **10**−2ClO_4 from water/acetonitrile: The starting material was colourless, but the single crystals obtained were slightly blue. We assume formation of small concentrations of the radical cation derived from **10**, presumably by sunlight irradiation (possibly catalysed by traces of heavy metal ions on the glassware used). However, we could not identify a radical by EPR because of low concentration of the species.

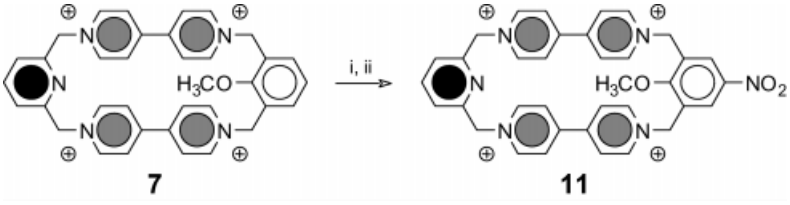
The yield of pyridinophanes regularly decreases from **3** to **5** (Scheme 2). Therefore, we were surprised that the anisolo-bridged phane **7** was formed in high yield from dication **2** and 2,6-bis(bromomethyl)anisole.[18] Although the macrocycle **7** is transparent above 270 nm in the UV/Vis spectrum, we suggest that a weak *intra*molecular template effect caused by the electron-rich spacer may facilitate the ring closure. In contrast to the flexible unsubstituted **4** the ^{1}H-NMR spectrum of phane **7** shows a strongly broadened AB spin system for the methylene group at the anisolo spacer. Temperature-dependent NMR spectra illuminate the dynamic behaviour of macrocycle **7**. The coalescence temperature was determined to be 293 ± 5 K and the free activation enthalpy $\Delta G^{\neq}$ to 58.8 ± 1.0 kJ mol^{-1}. No broadening of the signals of the methylene protons at the heterocyclic spacer was observed, indicating the higher flexibility of the heterocyclic bridge at 243 K.

So far no chemical transformations have been reported for 4,4′-bipyridinium-based phanes. The donor-substituted phane **7** is predestinated for extraannular functionalizations and we could indeed transform it into nitroanisolophane **11**. By a simple nitration of **7** with nitrating acid, **11** was obtained as a yellow solid in excellent yield (Scheme 6).

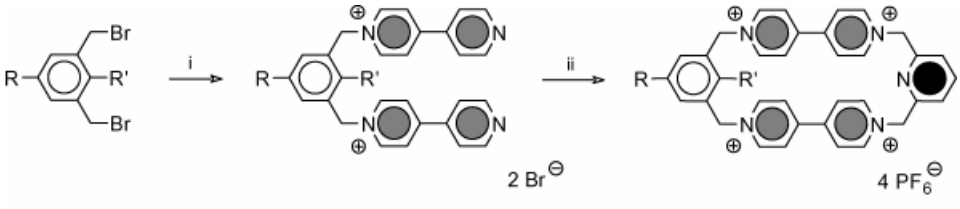
On the other hand, intraannular reactions at the free nitrogen atom of pyridinophane **4** failed. Attempted alkylations of **4** with methyl iodide or 1,4-bis(bromomethyl)benzene revealed the inertness of this pyridine nitrogen atom. The stronger electrophile ethyl triflate caused difficulties since primarily the solvent acetonitrile was attacked with formation of a nitrilium triflate. As a subsequent reaction, **4**−4PF_6 underwent only counterion exchange with the excess of triflate anions to provide insoluble **4**−4OTf. The failure of these reactions may be explained by steric hindrance which shields the central nitrogen atom, as well as deactivating electronic effects by the positively charged neighbouring bipyridinium groups.

The macrocyclization to *meta*-xylene-bridged pyridinophanes can also be executed on the spacer route. Thus, the readily available dications **12**−**15**, which could be prepared from the corresponding substituted bis(bromomethyl)arenes, were treated with dibromide **1** under standard conditions (Scheme 7).

In general, these reactions proceed with lower efficiency. Whereas the yield for conversion of **12** to **16** is acceptable, for dications **13** and **14** steric repulsions have to be assumed for the ring closure to **17** and **18**, since intraannular groups have to be tolerated. The electron-withdrawing groups in pyridinophanes **17** and **18** exercise a large influence on the bipyridinium protons. Surprisingly, compound **17** is rather



Scheme 6. Reagents and conditions: i) HNO_3 (100%), conc. H_2SO_4, 10 min, 0°C; ii) NH_4PF_6, H_2O, 90%



R = Br, R' = H
R = H, R' = NO_2
R = H, R' = CO_2CH_3
R = H, R' = OCH_3

12: R = Br, R' = H 86%
13: R = H, R' = NO_2 84%
14: R = H, R' = CO_2CH_3 77%
15: R = H, R' = OCH_3 96%

16: R = Br, R' = H 29%
17: R = H, R' = NO_2 14%
18: R = H, R' = CO_2CH_3 7%

Scheme 7. Reagents and conditions: i) excess of 4,4′-bipyridine, CH_3CN; ii) CH_3NO_2/H_2O, **1**, room temp., 30d; iii) NH_4PF_6, H_2O

flexible at room temperature, since the nitro group seems to oscillate through the cavity of the phane, thus causing strong anisotropy effects on bipyridinium protons. Relative to unsubsituted **4** (α-proton, δ = 9.22) an expected high-field shift was observed for the corresponding protons (δ = 8.95). Even more pronounced effects can be seen for **18**. Here, an almost identical chemical shift was determined for the bipyridinium protons (δ = 8.88), but now both bridging arene moieties are hindered in their flip movement. The protons of the methylene groups are split into AB spin systems with coupling constants of J = 16.2 Hz and 16.5 Hz, which are slightly larger than those of more narrow pyridinophane **3** (J = 15.2 Hz). The difference between **17** and **18** may be explained by comparing the bulkiness of the nitro group with that of the methoxycarbonyl substituent. The latter is sterically more demanding and therefore it will more strongly influence the mobility of **18**. The interaction of the methoxy group with the interior of the phane is also shown by its chemical shift of δ = 3.36 whereas in precursor **14** this signal appears at δ = 3.93.

Conclusion

In our study we present a simple and versatile procedure for the synthesis of several pyridine-bridged phanes of 4,4′-bipyridine. The structural properties of the new pyridinophanes differ considerably from their carbocyclic counterparts, which is attributed to diminished steric interactions inside the cavity of the phanes. The pyridine ring designed as a reaction centre was proven to be inert against common alkylation reagents. This may be explained either by the decrease of electron density of the pyridine ring caused by the two bipyridinium groups, or by steric restrictions in the course of the alkylation sequence. On the other hand, the electron-rich anisole bridge was successfully functionalized by simple nitration in high yield, thus establishing the first example for an extraannular reaction of a macrocycle derived from 4,4′-bipyridine. Intraannular π-acceptor substituents cause strong anisotropy effects in the NMR spectra. This corresponds to the low yields in the synthesis of these phanes due to repulsions of the acceptor groups during ring closure reaction. In contrast, macrocyclization using the anisole bridge afforded the desired pyridinophane in high yield, which can probably be attributed to a weak *intra*molecular template effect. In similar fashion we have prepared carbocyclic analogues[19] of these pyridinophanes as well as other heterocyclic-bridged compounds (furan, thiophene, and benzo[*b*]thiophene used as spacer).[20] These results and the studies on the electrochemical properties of the new compounds will be the subject of future reports.[21]

Experimental Section

General Techniques: Melting points were determined with a Kofler-Boëtius apparatus and are corrected. − NMR spectra were recorded with Bruker DRX-500, ASP-300, AC-300 or AC-200P instruments using CHD_2SOCD_3 (in [D_6]DMSO; δ = 2.50 (^{1}H), δ = 39.56 (^{13}C)], $CHCl_3$ [in $CDCl_3$; δ = 7.25 (^{1}H)] and CHD_2COCD_3 (in [D_6]acetone; δ = 2.08 (^{1}H)] as internal standards. − IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. − UV/Vis spectra were recorded with a Cary-3 double-beam spectrometer. − Elemental analyses were carried out with a Carlo Erba CHN-S-Analyser. − All reactions were monitored by thin-layer chromatography (TLC) carried out on Macherey−Nagel silica gel precoated plates Polygram Sil G/UV_{254} with UV light and iodine (iodine chamber) as developing reagent. − Merck silica gel (G60, particle size 0.063−0.200 mm) was used for column chromatography; as eluent a mixture of methanol and 2 M aqueous NH_4Cl solution (3:2, v/v) was used. − The nonaqueous alkylation reactions were performed with exclusion of moisture. − Yields refer to chromatographically homogeneous materials. − All reagents were obtained from Aldrich, Fluka or Acros and used as received. 2-Nitro-1,3-bis(bromomethyl)benzene and methyl 2,6-bis(bromomethyl)benzoate were kindly provided by Prof. F. Vögtle, Universität Bonn. 5-Bromo-1,3-bis(bromomethyl)benzene,[22] 2,6-bis(bromomethyl)anisole,[18] macrocycles **8**,[3] **9**[3] and dication **10**[3] were prepared as described in the literature.

Crystal Structure Determinations for 3, 4, 6 and 10:[23] Colourless single crystals of macrocycles **3**−4PF_6, **4**−4PF_6, and **6**−4PF_6 were obtained by slow vapour diffusion of diisopropyl ether in acetonitrile solutions of the compounds. Suitable single crystals of **10**−2ClO_4 were obtained by slow evaporation of aqueous acetonitrile solution. Diffraction data were collected with a Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator) in the ω-scan mode. Crystal data and details of the measurements are summarized in Table 2. The structures were solved by direct methods (SHELXS86, SHELXS97)[24] and refined by full-matrix least squares (SHELXL93, SHELXL97)[24] based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically placed and refined in a riding model. The PF_6 and ClO_4 counterions are disordered and were refined in 50:50 split positions.

2,6-Bis(bromomethyl)pyridine (1):[14] To a suspension of 1.39 g (10.0 mmol) of 2,6-bis(hydroxymethyl)pyridine in dry tetrachloromethane (20 mL) was slowly added 8.10 g (30.0 mmol) of phosphorous tribromide at −10°C. The solution was heated under reflux for 2 h, cooled to room temperature and treated with 20 mL of water. The organic layer was separated and the aqueous solution extracted three times with tetrachloromethane (20 mL each). The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. The residual solid was recrystallized from *n*-hexane to afford 2.32 g (88%) of **1** as colourless needles. ***Caution: Compound 1 is a strong lachrymator!*** Characterization of **1**: M.p. 86−87°C (ref.[25] 84−89°C). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (t, J = 7.8 Hz, 1 H, py-H), 7.31 (d, J = 7.8 Hz, 2 H, py-H), 4.48 (s, 4 H, CH_2).

1,1′′-[2,6-Pyridinebis(methylene)]bis-4,4′-bipyridinium Dibromide (2): 265 mg (1.00 mmol) of **1**, dissolved in a mixture of acetonitrile and dichloromethane (15 mL, 14:1), was slowly added to a boiling solution of 780 mg (5.00 mmol) of 4,4′-bipyridine in dry acetonitrile (10 mL) followed by heating for 2 h at 80°C. The solution was cooled and stored overnight at 7°C. The yellow precipitate was collected by filtration, washed with acetonitrile and ether, and air-dried to afford 557 mg (92%) of **2** as a yellow solid. − M.p. > 240°C (dec.). − R_f = 0.31 (silica gel). − IR: $\tilde{\nu}$ = 3420, 1640, 1610, 1600 cm^{-1}. − UV/Vis (H_2O): λ_{max} (ε) = 258 (25700), 213 nm (14000). − ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 9.09 (d, J = 7.0 Hz, 4 H, bipy-2-H), 8.69 (d, J = 6.2 Hz, 4 H, bipy-2′-H), 8.51 (d, J = 7.0 Hz, 4 H, bipy-3-H), 8.10 (t, J = 7.9 Hz, 1 H, py-H),

Table 2. Crystal and data-collection parameters for **3**, **4**, **6** and **10**

	3−$4PF_6$	**4**−$4PF_6$	**6**−$4PF_6$	**10**−$2ClO_4$
Empirical formula	$C_{35}H_{31}F_{24}N_5P_4$	$C_{35}H_{31}F_{24}N_5P_4$	$C_{34}H_{30}F_{24}N_6P_4$	$C_{28}H_{24}Cl_2N_4O_8$
M_r	1101.5	1101.5	1102.5	615.4
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Cc* (no. 6)	$P2_1/a$ (no. 14)	$P2_1/a$ (no. 14)	$P2_1/a$ (no. 14)
a [Å]	16.499(1)	11.270(1)	11.298(2)	7.558(1)
b [Å]	19.140(3)	16.937(3)	16.760(6)	18.974(3)
c [Å]	16.155(1)	11.677(1)	11.678(3)	9.765(1)
β [°]	118.71(1)	101.88(1)	100.90(2)	105.30(1)
V [Å^3]	4474.3(7)	2181.4(4)	2171.3(11)	1350.7(3)
Z	4	2	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.635	1.677	1.686	1.513
μ(Mo-K_α) [mm^{-1}]	0.304	0.311	0.313	0.301
Crystal form	plate-shaped prism	hexagonal prism	plate-like rhomb	plate-shaped prism
Crystal colour	colourless	colourless	colourless	blue
Crystal size [mm]	0.4 × 0.3 × 0.2	0.2 × 0.2 × 0.2	0.4 × 0.3 × 0.1	0.4 × 0.3 × 0.2
Wavelength [A]	0.71073	0.71073	0.71073	0.71073
T [K]	293(2)	293(2)	293(2)	293(2)
2 θ_{max} [°]	39.96	44.00	45.96	49.98
h,*k*,*l* range	−15/15, −18/18, −15/15	0/13, −20/0, −13/13	−12/12, −18/18, −12/0	−6/10, −26/0, 0/13
Reflns. collected	8134	2854	6332	2321
Reflns unique	4146	2672	3004	2202
observed ($I > 2\sigma\|I\|$)	2702	1312	2360	1381
Parameters refined	829	424	415	227
*R*1 (observed)	0.084	0.036	0.048	0.038
wR_2	0.196	0.079	0.129	0.103
GooF	1.281	1.173	1.006	1.176
ρ_{res} [e Å^{-3}]	1.18/−0.36	0.16/−0.18	0.43/−0.35	0.19/−0.18

7.83 (d, *J* = 6.2 Hz, 4 H, bipy-3′-H), 7.71 (d, *J* = 7.9 Hz, 2 H, py-H), 6.05 (s, 4 H, CH_2). − ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 152.80 (s), 152.75 (s), 151.12 (d), 146.66 (d), 140.50 (s), 139.32 (d), 125.03 (d), 122.94 (d), 121.87 (d), 63.03 (t). − $C_{27}H_{23}Br_2N_5$·1.5 H_2O (604.3): calcd. C 53.66, H 4.34, N 11.59; found C 53.61, H 4.28, N 11.73.

General Procedure for the Preparation of Pyridinophanes 3−7 Starting from 2 (Pyridine Route): Dication **2** was dissolved in water (5 mL) and the bis(bromomethyl)benzene was dissolved in nitromethane (5 mL). The two solutions were combined and shaken vigorously for 30 d. The aqueous layer was separated and the organic layer washed twice with water (0.5 mL each). The combined aqueous solutions were purified by column chromatography (50 g of silica gel). The fraction containing the phane was concentrated in vacuo to dryness and the residual solid (ammonium chloride and the tetrabromide of the phane) dissolved in a minimum of water. A saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The precipitate was collected, washed with water and dried at 70°C for 2 h.

34-Aza-5,14,21,28-tetraazoniaheptacyclo[27.2.2.2^{2,5}.2^{14,17}.2^{18,21}.1^{23,27}.0^{7,12}]tetraconta-2,4,7,9,11,14,16,18,20,23,25,27(34),29,31,32,35,37,39-octadecaene Tetrakis(hexafluorophosphate)(3): From 144 mg (0.25 mmol) of **2** and 84 mg (0.32 mmol) of 1,2-bis(bromomethyl)benzene was obtained 181 mg (66%) of **3** as colourless crystals. − M.p. > 260°C (dec.). − R_f = 0.33 (silica gel). − UV/Vis (H_2O): λ_{max} (ε) = 256 (41700), 210 nm (30900). − ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.13 (d, *J* = 6.9 Hz, 4 H, bipy-2-H), 8.81 (br. s, 4 H, bipy-2′-H), 8.51 (d, *J* = 6.9 Hz, 4 H, bipy-3-H), 8.32 (br. d, *J* = 4.9 Hz, 4 H, bipy-3′-H), 8.15 (t, *J* = 7.8 Hz, 1 H, py-H), 8.02 (m, 2 H, Ar-H), 7.92 (m, 2 H, Ar-H), 7.71 (d, *J* = 7.9 Hz, 2 H, py-H), 6.41, 6.02 (2 d, *J* = 15.2 Hz, 2 H each, Ar-CH_2, AB), 6.12, 6.08 (2 d, *J* = 15.8 Hz, 2 H each, py-CH_2, AB). − ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 152.04 (s), 148.26 (s), 147.38 (s), 147.14 (d), 145.04 (br. d), 139.02 (d), 135.97 (d), 132.38 (d), 131.52 (s), 126.63 (d), 126.11 (d), 122.68 (d), 63.11 (t), 61.49 (t). − $C_{35}H_{31}F_{24}N_5P_4$ (1101.5): calcd. C 38.16, H 2.84, N 6.36; found C 38.11, H, 2.87, N 6.26.

Pyridinophane 4: From 289 mg (0.48 mmol) of **2** and 264 mg (1.00 mmol) of 1,3-bis(bromomethyl)benzene was obtained 240 mg (45%) of **4** as colourless crystals. − M.p. > 305°C (dec.). − R_f = 0.29 (silica gel). − UV/Vis (H_2O): λ_{max} (ε) = 255 (16600), 211 nm (12900). − ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.26 (d, *J* = 6.8 Hz, 4 H, bipy-2-H), 9.22 (d, *J* = 6.8 Hz, 4 H, bipy-2′-H), 8.55 (d, *J* = 6.8 Hz, 4 H, bipy-3-H), 8.53 (d, *J* = 6.8 Hz, 4 H, bipy-3′-H), 8.15 (t, *J* = 7.8 Hz, 1 H, py-H), 7.76 (d, *J* = 7.8 Hz, 2 H, py-H), 7.72 (d, *J* = 7.7 Hz, 2 H, Ar-H), 7.67 (t, *J* = 7.7 Hz, 1 H, Ar-H), 6.40 (s, 1 H, Ar-H), 6.09 (s, 4 H, py-CH_2), 5.99 (s, 4 H, Ar-CH_2). − ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 152.12 (s), 148.74 (s), 148.48 (s), 146.93 (d), 146.33 (d), 139.29 (d), 136.01 (s), 130.00 (d), 129.32 (d), 126.63 (d), 126.01 (d), 123.96 (d), 123.43 (d), 63.25 (t), 63.11 (t). − $C_{35}H_{31}F_{24}N_5P_4$ (1101.5): calcd. C 38.16, H 2.84, N 6.36; found C 37.96, H 2.91, N 6.22.

Pyridinophane 5: From 289 mg (0.48 mmol) of **2** and 264 mg (1.00 mmol) of 1,4-bis(bromomethyl)benzene was obtained 161 mg (30%) of **5** as colourless crystals. − M.p. > 290°C (dec.). − R_f = 0.29 (silica gel). − UV/Vis (H_2O): λ_{max} (ε) = 261 (20900), 210 nm (10000). − ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.47 (d, *J* = 7.0 Hz, 4 H, bipy-2-H), 9.35 (d, *J* = 7.0 Hz, 4 H, bipy-2′-H), 8.43 (d, *J* = 7.0 Hz, 4 H, bipy-3-H), 8.35 (d, *J* = 7.0 Hz, 4 H, bipy-3′-H), 8.12 (t, *J* = 7.8 Hz, 1 H, py-H), 7.80 (d, *J* = 7.8 Hz, 2 H, py-H), 7.75 (s, 4 H, Ar-H), 5.95 (s, 4 H, py-CH_2), 5.89 (s, 4 H, Ar-CH_2). − ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ = 152.50 (s), 149.25 (s), 149.05 (s), 146.14 (d), 144.88 (d), 140.08 (d), 137.60 (s), 130.03 (d), 127.20 (d), 126.52 (d), 125.31 (d), 64.09 (t), 64.07 (t). − $C_{35}H_{31}F_{24}N_5P_4$ (1101.5): calcd. C 38.16, H 2.84, N 6.36; found C 38.03, H 2.90, N 6.27.

Pyridinophane 6: From 289 mg (0.48 mmol) of **2** and 265 mg (1.00 mmol) of **1** was obtained 192 mg (36%) of **6** as colourless crystals. − M.p. > 320°C (dec.). − R_f = 0.30 (silica gel). − UV/

Vis (H_2O): λ_{max} (ε) = 255 (25000), 214 nm (14100). − ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 9.13 (d, *J* = 6.9 Hz, 8 H, bipy-2-H), 8.56 (d, *J* = 6.9 Hz, 8 H, bipy-3-H), 8.16 (t, *J* = 7.8 Hz, 2 H, py-H), 7.74 (d, *J* = 7.8 Hz, 4 H, py-H), 6.12 (s, 4 H, CH_2). − ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 151.97 (s), 148.28 (s), 147.04 (d), 138.79 (d), 125.85 (d), 122.24 (d), 62.91 (t). − $C_{34}H_{30}F_{24}N_6P_4$ (1102.5): calcd. C 37.04, H 2.74, N 7.62; found C 37.11, H 2.72, N 7.43.

Pyridinophane 7: From 116 mg (0.20 mmol) of **2** and 74 mg (0.25 mmol) of 2,6-bis(bromomethyl)anisole was obtained 143 mg (63%) of **7** as colourless crystals. − M.p. 289−292°C (dec.). − R_f = 0.26 (silica gel). − UV/Vis (H_2O): λ_{max} (ε) = 256 (46800), 206 nm (43700). − ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 9.27 (d, *J* = 6.8 Hz, 4 H, bipy-2-H), 9.01 (d, *J* = 6.8 Hz, 4 H, bipy-2′-H), 8.55 (d, *J* = 6.9 Hz, 4 H, bipy-3-H), 8.35 (d, *J* = 6.9 Hz, 4 H, bipy-3′-H), 8.13 (t, *J* = 7.8 Hz, 1 H, py-H), 7.91 (d, *J* = 7.9 Hz, 2 H, Ar-H), 7.75 (d, *J* = 7.8 Hz, 2 H, py-H), 7.53 (t, *J* = 7.7 Hz, 1 H, Ar-H), 6.04 (s, 4 H, py-CH_2), 6.02, 5.85 (2 br. s, 2 H each, Ar-CH_2, AB), 3.86 (s, 3 H, OCH_3). − ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 157.94 (s), 152.10 (s), 148.57 (s), 148.38 (s), 146.80 (d), 145.84 (d), 139.37 (d), 134.61 (d), 129.57 (s), 126.06 (d), 125.94 (d), 125.73 (d), 123.66 (d), 63.26 (t), 62.14 (q), 60.88 (t). − $C_{36}H_{33}F_{24}N_5OP_4$ (1131.6): calcd. C 38.21, H 2.94, N 6.19; found C 38.21, H 2.96, N 6.07.

Nitrophane 11: 40.0 mg (0.035 mmol) of **7** was dissolved in conc. sulfuric acid (1 mL). At 0°C a 1:1 mixture of nitric acid (100%) and conc. sulfuric acid (0.2 mL) was added. The yellow solution was stirred for 10 min, poured on crushed ice, and neutralized with sodium bicarbonate. After precipitation with an aqueous NH_4PF_6 solution, the product was collected and dried at 80°C affording 37.6 mg (90%) of **11** as yellow crystals. − M.p. > 245°C (dec.). − R_f = 0.37 (silica gel). − IR (KBr): $\tilde{\nu}$ = 1540, 1355 cm^{-1} (NO_2). − ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 9.27 (d, *J* = 6.4 Hz, 4 H, bipy-2-H), 9.07 (d, *J* = 6.4 Hz, 4 H, bipy-2′-H), 8.90 (s, 2 H, Ar-H), 8.55 (d, *J* = 6.4 Hz, 4 H, bipy-3-H), 8.35 (d, *J* = 6.4 Hz, 4 H, bipy-3′-H), 8.14 (t, *J* = 7.8 Hz, 1 H, py-H), 7.75 (d, *J* = 7.7 Hz, 2 H, py-H), 6.05 (br. s, 8 H, Ar-CH_2, py-CH_2), 3.93 (s, 3 H, OCH_3). − ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 163.10 (s), 151.98 (s), 148.47 (s), 148.38 (s), 146.70 (d), 145.90 (d), 143.71 (s), 139.25 (d), 130.67 (s), 130.14 (d), 125.97 (d), 125.73 (d), 123.52 (d), 63.19 (t), 62.69 (q), 59.96 (t). − $C_{36}H_{32}F_{24}N_6O_3P_4$ (1176.6): calcd. C 36.75, H 2.74, N 7.14; found C 37.06, H 2.67, N 7.08.

Reaction of Pyridinophane 4 with Ethyl Triflate: 20 mg (0.02 mmol) of **4**−4PF_6 was dissolved in dry acetonitrile (3 mL) and treated at 0°C with ethyl triflate (0.1 mL). A colourless solid precipitated, which was collected, washed with ether and air-dried to afford 13 mg (64%) of **4**−4OTf as colourless crystals. − M.p. > 340°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1260, 1155, 1030, 640, 575, 515 cm^{-1} (CF_3SO_3). − ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 120.46 (q, J_{C-F} = 322 Hz, CF_3SO_3), other signals (^{1}H, ^{13}C) were identical to those obtained for **4**−4PF_6. − $C_{39}H_{31}F_{12}N_5O_{12}S_4$ (1117.9): calcd. C 41.90, H 2.80, N 6.26, S 11.47; found C 41.72, H 2.76, N 6.26; S 10.48.

General Procedure for Preparation of Dications 12−15: To a boiling solution of 4,4′-bipyridine in dry acetonitrile (20 mL) was slowly added the substituted bis(bromomethyl)benzene, dissolved in a mixture of acetonitrile (18 mL) and CH_2Cl_2 (2 mL). The mixture was refluxed for 2 h. After cooling to 7°C, filtration, and washing with acetonitrile and ether, the resulting solids were air-dried.

1,1′′-[5-Bromo-1,3-phenylenebis(methylene)]bis-4,4′-bipyridinium Dibromide (12): From 468 mg (3.00 mmol) of 4,4′-bipyridine and 343 mg (1.00 mmol) of 5-bromo-1,3-bis(bromomethyl)benzene was obtained 581 mg (86%) of **12** as yellow crystals. − M.p. > 255°C (dec.). − R_f = 0.26 (silica gel). − ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 9.23 (d, *J* = 6.7 Hz, 4 H, bipy-2-H), 8.83 (d, *J* = 5.9 Hz, 4 H, bipy-2′-H), 8.57 (d, *J* = 6.7 Hz, 4 H, bipy-3-H), 7.98 (d, *J* = 6.1 Hz, 4 H, bipy-3′-H), 7.89 (s, 2 H, Ar-H), 7.75 (s, 1 H, Ar-H), 5.87 (s, 4 H, CH_2). − $C_{28}H_{23}Br_3N_4{\cdot}H_2O$ (673.2): calcd. C 49.95, H 3.74, N 8.32; found C 49.60, H 3.58, N 8.06.

1,1′′-[2-Nitro-1,3-phenylenebis(methylene)]bis-4,4′-bipyridinium Dibromide (13): From 468 mg (3.00 mmol) of 4,4′-bipyridine and 309 mg (1.00 mmol) of 1,3-bis(bromomethyl)-2-nitrobenzene was obtained 537 mg (84%) of **13** as yellow crystals. − M.p. > 270°C (dec.). − R_f = 0.23 (silica gel). − IR (KBr): $\tilde{\nu}$ = 1535, 1355 cm^{-1} (NO_2). − ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 9.31 (d, *J* = 6.8 Hz, 4 H, bipy-2-H), 8.91 (d, *J* = 6.0 Hz, 4 H, bipy-2′-H), 8.78 (d, *J* = 6.8 Hz, 4 H, bipy-3-H), 8.10 (d, *J* = 6.1 Hz, 4 H, bipy-3′-H), 7.79 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.46 (d, *J* = 7.8 Hz, 2 H, Ar-H), 6.21 (s, 4 H, CH_2). − $C_{28}H_{23}Br_2N_5O_2{\cdot}H_2O$ (639.4): calcd. C 52.60, H 3.94, N 10.95; found C 52.61, H 3.74, N 10.88.

1,1′′-[1-Methoxycarbonyl-2,6-phenylenebis(methylene)]bis-4,4′-bipyridinium Dibromide (14): From 468 mg (3.00 mmol) of 4,4′-bipyridine and 322 mg (1.00 mmol) of methyl 2,6-bis(bromomethyl)-benzoate was obtained 514 mg (77%) of **14** as yellow crystals. − M.p. > 260°C (dec.). − R_f = 0.22 (silica gel). − IR (KBr): $\tilde{\nu}$ = 1724 cm^{-1} (C=O). − ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 9.25 (d, *J* = 6.8 Hz, 4 H, bipy-2-H), 8.89 (d, *J* = 6.0 Hz, 4 H, bipy-2′-H), 8.75 (d, *J* = 6.8 Hz, 4 H, bipy-3-H), 8.09 (d, *J* = 6.1 Hz, 4 H, bipy-3′-H), 7.77 (t, *J* = 7.7 Hz, 1 H, Ar-H), 7.61 (d, *J* = 7.8 Hz, 2 H, Ar-H), 6.17 (s, 4 H, CH_2), 3.93 (s, 3 H, OCH_3). − ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 166.6 (s), 152.9 (s), 151.0 (d), 145.6 (d), 140.6 (s), 132.8 (s), 132.4 (d), 132.3 (s), 131.7 (d), 127.0 (d), 121.9 (d), 60.9 (t), 53.5 (q). − $C_{30}H_{26}Br_2N_4O_2{\cdot}2H_2O$ (670.4): calcd. C 53.75, H 4.51, N 8.36; found C 53.51, H 4.35, N 8.26.

1,1′′-[1-Methoxy-2,6-phenylenebis(methylene)]bis-4,4′-bipyridinium Dibromide (15): From 468 mg (3.00 mmol) of 4,4′-bipyridine and 294 mg (1.00 mmol) of 2,6-bis(bromomethyl)anisole was obtained 582 mg (96%) of **15** as yellow crystals. − M.p. > 245°C (dec.). − R_f = 0.27 (silica gel). − ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 9.10 (d, *J* = 6.5 Hz, 4 H, bipy-2-H), 8.79 (br. d, *J* = 4.9 Hz, 4 H, bipy-2′-H), 8.51 (d, *J* = 6.5 Hz, 4 H, bipy-3-H), 7.94 (d, *J* = 5.8 Hz, 4 H, bipy-3′-H), 7.53 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.33 (t, *J* = 7.6 Hz, 1 H, Ar-H), 5.94 (s, 4 H, CH_2), 3.87 (s, 3 H, OCH_3). − ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 158.0 (s), 154.0 (s), 151.5 (d), 146.1 (d), 142.1 (s), 133.9 (d), 128.7 (s), 127.1 (d), 126.5 (d), 123.0 (d), 63.4 (q), 59.9 (t). − $C_{29}H_{26}Br_2N_4O$ (606.4): calcd. C 57.44, H 4.32, N 9.24; found C 57.14, H 4.36, N 9.17.

General Procedure for the Preparation of Pyridinophanes 16−18 Starting from 12−14 (Spacer Route): The dication (**12−14**) was dissolved in water (5 mL) and **1** was dissolved in nitromethane (5 mL). The two solutions were combined and shaken vigorously for 30 d. The workup was performed as described for the pyridine route.

Pyridinophane 16: From 87 mg (0.13 mmol) of **12** and 53 mg (0.20 mmol) of **1** was obtained 44 mg (29%) of **16** as colourless crystals. − M.p. > 330°C (dec.). − R_f = 0.34 (silica gel). − UV/Vis (H_2O): λ_{max} (ε) = 262 nm (41700). − ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 9.25 (d, *J* = 6.9 Hz, 4 H, bipy-2-H), 9.20 (d, *J* = 7.0 Hz, 4 H, bipy-2′-H), 8.54 (m_c, 8 H, bipy-3,3′-H), 8.12 (t, *J* = 7.8 Hz, 1 H, py-H), 8.00 (s, 2 H, Ar-H), 7.75 (d, *J* = 7.8 Hz, 2 H, py-H), 6.47 (s, 2 H, Ar-H), 6.06 (s, 4 H, py-CH_2), 5.96 (s, 4 H, Ar-CH_2). − ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 151.89 (s), 148.59 (s), 148.24 (s), 146.74 (d), 146.21 (d), 139.13 (d), 137.87 (s), 132.01 (d), 126.40 (d), 125.78 (d), 123.48 (d), 123.28 (d), 122.41 (d), 63.07

(t), 62.19 (t). − $C_{35}H_{30}BrF_{24}N_5P_4$ (1180.4): calcd. C 35.61, H 2.56, N 5.93; found C 35.83, H 2.41, N 5.72.

Pyridinophane 17: From 151 mg (0.24 mmol) of **13** and 78 mg (0.29 mmol) of **1** was obtained 39 mg (14%) of **17** as pale yellow crystals. − M.p. 258−260°C (dec.). − R_f = 0.32 (silica gel). − UV/Vis (H_2O): λ_{max} (ε) = 258 (34700), 224 (31600), 222 nm (31600). − IR (KBr): $\tilde{\nu}$ = 1535, 1380 cm^{-1} (NO_2). − ^1H NMR (500 MHz, [D_6]DMSO): δ = 9.43 (d, *J* = 6.9 Hz, 4 H, bipy-2-H), 8.95 (d, *J* = 6.8 Hz, 4 H, bipy-2′-H), 8.74 (d, *J* = 6.9 Hz, 4 H, bipy-3-H), 8.57 (d, *J* = 7.1 Hz, 4 H, bipy-3′-H), 8.25 (d, *J* = 7.7 Hz, 2 H, Ar-H), 8.18 (dd, *J* = 8.4, 7.1 Hz, 1 H, Ar-H), 8.12 (t, *J* = 7.8 Hz, 1 H, py-H), 7.80 (d, *J* = 7.8 Hz, 2 H, py-H), 6.16 (s, 4 H, Ar-CH_2), 6.02 (s, 4 H, py-CH_2). − ^{13}C NMR (125.7 MHz, [D_6]DMSO): δ = 152.28 (s), 148.81 (s), 148.40 (s), 148.08 (s), 146.48 (d), 146.21 (d), 139.73 (d), 136.91 (d), 134.22 (d), 127.57 (s), 126.20 (d), 125.86 (d), 124.56 (d), 63.63 (t), 60.55 (t). − $C_{35}H_{30}F_{24}N_6O_2P_4$ (1146.5): calcd. C 36.67, H 2.64, N 7.33; found C 36.85, H 2.82, N 6.89.

Pyridinophane 18: From 229 mg (0.36 mmol) of **14** and 129 mg (0.49 mmol) of **1** was obtained 27 mg (7%) of **18** as pale yellow crystals. − M.p. 260−263°C (dec.). − R_f = 0.27 (silica gel). − IR (KBr): $\tilde{\nu}$ = 1725 cm^{-1} (C=O). − ^1H NMR (300 MHz, [D_6]DMSO): δ = 9.43 (d, *J* = 6.9 Hz, 4 H, bipy-2-H), 8.88 (d, *J* = 6.8 Hz, 4 H, bipy-2′-H), 8.80 (d, *J* = 6.9 Hz, 4 H, bipy-3-H), 8.61 (d, *J* = 7.2 Hz, 4 H, bipy-3′-H), 8.0−8.2 (m, 4 H, Ar-H, py-H), 7.79 (d, *J* = 7.8 Hz, 2 H, py-H), 6.09, 6.03 (2 d, *J* = 16.5 Hz, 2 H each, Ar-CH_2, AB), 6.02, 5.97 (2 d, *J* = 16.2 Hz, 2 H each, py-CH_2, AB), 3.36 (s, 3 H, OCH_3). − ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 166.06 (s), 152.19 (s), 148.20 (s), 147.92 (s), 146.50 (d), 146.14 (d), 139.64 (d), 135.38 (d), 133.39 (s), 132.87 (d), 132.00 (s), 126.04 (d), 125.56 (d), 124.47 (d), 63.53 (t), 62.61 (t), 53.36 (q). − $C_{37}H_{33}F_{24}N_5O_2P_4$ (1159.6): calcd. C 38.33, H 2.87, N 6.04; found C 37.72, H 2.91, N 6.06.

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