116. Synthesis and Characterisation of the Sodium and Lithium Cryptates of Macrobicyclic Ligands Incorporating Pyridine, Bipyridine, and Biisoquinoline Units

by **Béatrice Alpha**[1]), **Elke Anklam**[2]), **Robert Deschenaux**[3]), **Jean-Marie Lehn***, and **Marek Pietraskiewicz**[4])

Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, F–67000 Strasbourg[5])

Dedicated to the memory of Professor *David Ginsburg*

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Synthetic procedures have been developed for the preparation of sodium and lithium cryptates of the macrobicyclic ligands **1**–**11** containing pyridine, bipyridine, and biisoquinoline groups. They involve stepwise construction of the bicyclic system as well as direct macrobicyclisation procedures *(Scheme 1)* and give access to both symmetrical and dissymmetrical structures. Marked cation template effects have been found that facilitate the cyclisation processes. The ligands **1**–**11** were isolated as their cryptates with Na^+ or Li^+ cations.

Incorporation of biheteroaryls into macropolycyclic structures leads to ligands that combine the complexation features of cryptands, forming metal-ion inclusion complexes [1], with the rich photophysical and photochemical properties conferred by heterocyclic binding sites, such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), 2,2′-biquinoline (bqi), or 2,2′-biisoquinoline (biqi) [2] [3].

We have reported earlier the synthesis [4] and crystal structure [5] of macrobicyclic cryptates containing bpy and phen groups, as well as the luminescent properties of some of the corresponding lanthanide cryptates [6–9]. We have extended our work and describe here a detailed study of synthetic routes towards a variety of macrobicyclic cryptands **1**–**11**, containing py, bpy, and biqi units. Macrotricyclic cryptands of cylindrical type [10] **24** and **25** were also obtained in the process.

Synthesis of Cryptands 1–11. – *Synthetic Strategies.* Several synthetic paths may be followed for the construction of macrobicyclic ligands *(Scheme 1)*. Depending on the sequence of steps, the final structure may contain identical or different groups in the bridges.

Paths A and *B (Scheme 1)* represent *stepwise* approaches *via* an intermediate macrocyclic unit. *Path A* involves the synthesis of a symmetrical macrocyclic diamine **AA**, which is further condensed with the same bridging unit **A** or with a different one **B** to give **AAA**- or **AAB**-type macrobicycles. *Path B* comprises the initial preparation of a bis(*p*-toluenesulfonamide) unit **B** (Z = Ts) from the corresponding bis(bromomethyl) com-

[1]) Present address: Addenbrooke's Hospital, Hills Road, GB–Cambridge CB2 2QR.

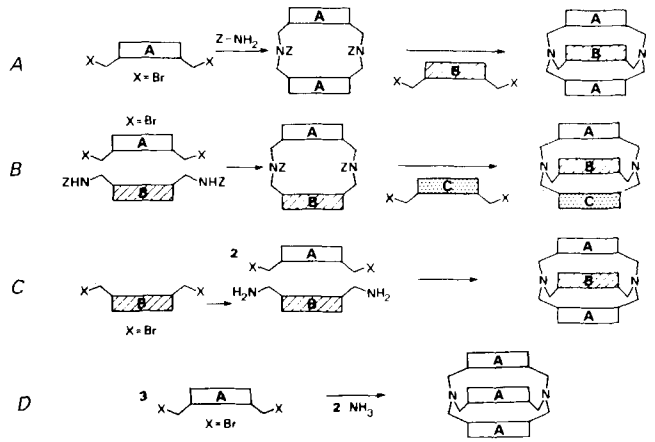
[2]) Present address: *Hahn-Meitner-Institut Berlin GmbH*, Glienicker Strasse, D–1000 Berlin 39.

[3]) Present address: *Ciba-Geigy SA*, Werk Fribourg/Marly, Centre de Recherche MPA, CH–1701 Fribourg.

[4]) Present address: Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL–01231 Warsaw.

[5]) UA 422 of the *CNRS*.

Scheme 1. *Synthetic Strategies towards Macrobicyclic Ligands*



pound, followed by its condensation with 1 equiv. of a bis(bromomethyl) unit **A**, yielding an unsymmetrical macrocycle **AB**; the latter may, thereafter, be reacted with a different bis(bromomethyl) moiety **C**, thus giving access to macrobicycles possessing three different bridges **ABC**.

Paths C and *D (Scheme 1)* are *macrobicyclisation* procedures that generate the macrobicyclic structure directly from the acyclic basic units without going through a macrocyclic intermediate. The double-bridging *Path C* involves the transformation of a bis(bromomethyl) compound **B** into the corresponding bis(aminomethyl) unit **B**, which by condensation with 2 equiv. of a bis(bromomethyl) unit **A** gives a macrobicycle of **AAB** type. *Path D* is a none-step macrobicyclisation in which NH_3 is directly reacted with a bis(bromomethyl) moiety **A** to yield the symmetrical macrobicycle **AAA**.

Selection of the strategy gives access to either symmetrical or unsymmetrical macrobicycles **AAA**, **AAB**, or **ABC**. *Paths A* and *D* have been employed earlier for the synthesis of cryptands such as [bpy · bpy · bpy], [phen · bpy · bpy], and [phen · phen · phen] [4].

Now, the macrobicyclic ligands **1**–**11** have been synthesized as their alkali-metal cryptate complexes. Bis-macrocyclic and macrotricyclic structures were obtained as secondary materials in some condensation reactions.

Synthesis of Cryptates **1**–**11**. Reaction of 2,6-bis(aminomethyl)pyridine (**12c**) with TsCl gave **12d** (85% yield) which was converted to its disodium salt by treatment with Na in EtOH. The salt was condensed with 2,6-bis(bromomethyl)pyridine (**12b**; obtained from **12a**, see [16]) to produce the macrocyclic bis(*p*-toluenesulfonamide) **13a** (55% yield) which, on detosylation with conc. H_2SO_4, afforded the macrocyclic bis(pyridinediyl)diamine **13b** (82% yield)[6]).

Dropwise addition of bis(bromomethyl)bipyridine **14b** (obtained from **14a**, see [4]) to a solution of macrocycle **13b** in MeCN at reflux in the presence of Li_2CO_3 yielded the LiBr complex of the macrobicyclic cryptand **1** ([bpy · py · py]; 63% yield). No compound **1** was isolated when Na_2CO_3 was used instead of Li_2CO_3 in the macrobicyclisation step. Independently, the intermediates **12b** (2 equiv.) and **14c** were reacted to give the same macrobicycle **1** in 45% yield.

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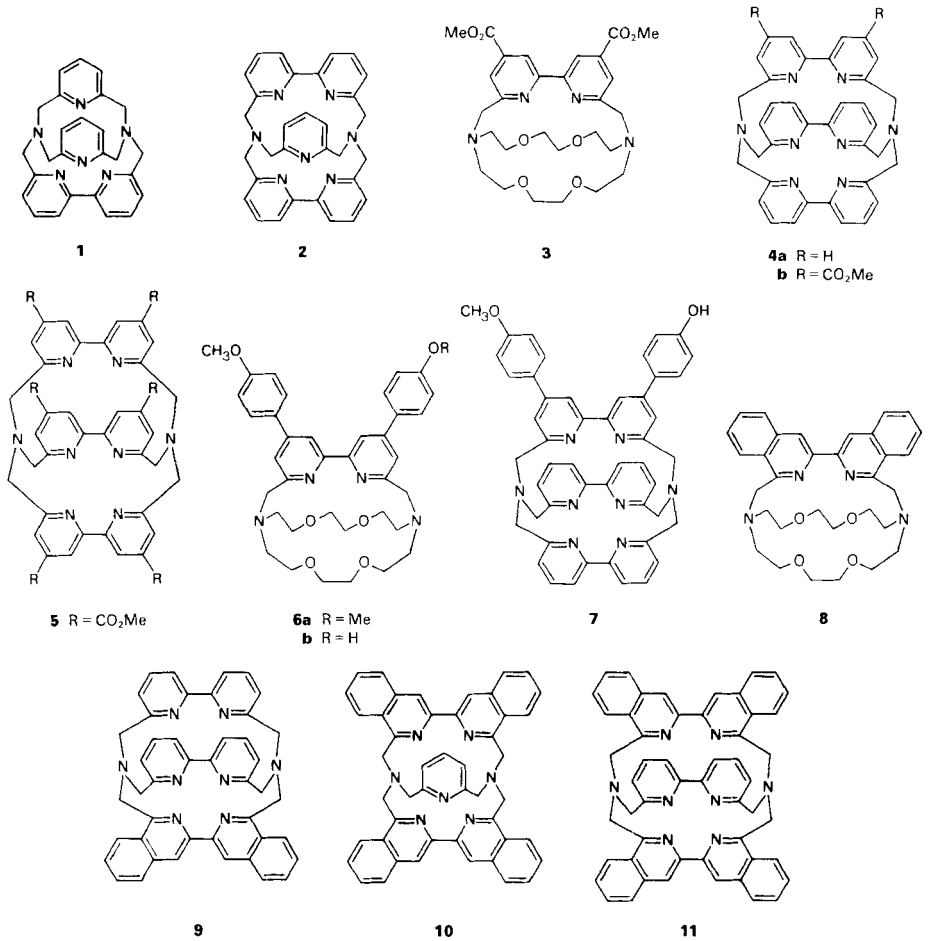
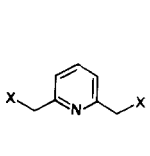
[6]) Compounds **12c**, **12d**, **13a**, and **13b** were first prepared by *N. Maak* [11].

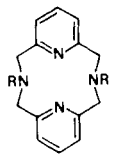


Under similar reaction conditions as above, the NaBr and LiBr complexes of the macrobicycle **2** ([bpy·bpy·py]) were prepared first from the macrocycle bis(bipyridinediyl)diamine **15** ([18]-N_2(bpy)$_2$) [4] [12] and **12b** in presence of an alkali carbonate. Using Li_2CO_3, the NaBr complex of **2** was isolated in 60% yield, after chromatography of the reaction mixture on a silica/alumina column where Li exchanged for Na (see *Exper. Part*); the Na complex was formed in 25% yield by carrying out the synthesis with Na_2CO_3; however, no complex of **2** was isolated when K_2CO_3 was employed. Similar isolated yields were observed when **2** was synthesized *via* the macrobicyclisation process *(Path C, Scheme 1)*. Indeed, condensation of 1 equiv. of **12c** with 2 equiv. of **14b** in the presence of either Li_2CO_3 or Na_2CO_3 afforded the Na complex in *ca.* 60 and 25% yield, respectively, after chromatography.

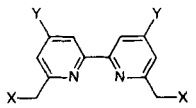
The strong dependence of the yields on the nature of the salt employed may be attributed to a *cation template effect*. High yields are observed when the size of ion complements the dimensions of the molecular cavity or is somewhat smaller. Cations that are too large strongly decrease the yields.



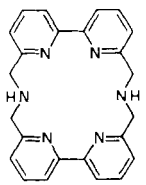
12a X = OH
b X = Br
c X = NH_2
d X = NHTs



13a R = Tosyl
b R = H



14a X = H, Y = H
b X = Br, Y = H
c X = NH_2, Y = H
d X = H, Y = CO_2Me
e X = Br, Y = CO_2Me
f X = N_3, Y = CO_2Me
g X = NH_2, Y = CO_2Me



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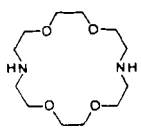

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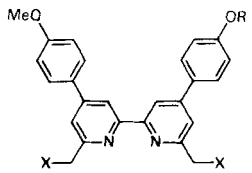


17a X = H, R = Me
b X = H, R = Me; *N,N'*-dioxide
c X = AcO, R = Me
d X = Br, R = Me
e X = Br, R = H

Bromination of dimethyl 6,6′-dimethyl-2,2′-bipyridine-4,4′-dicarboxylate (**14d**) with *N*-bromosuccinimide (NBS) afforded the bis(bromomethyl) compound **14e** (30% yield)[7]). Condensation of **14e** with the macrocycles **16** [14] and **15** [4] [12] with Na_2CO_3 in MeCN yielded the NaBr complexes of the functionalised cryptands **3** ([2.2.bpy$(CO_2Me)_2$]; 60% yield) and **4b** ([bpy$(CO_2Me)_2$·bpy·bpy]; 40% yield), respectively.

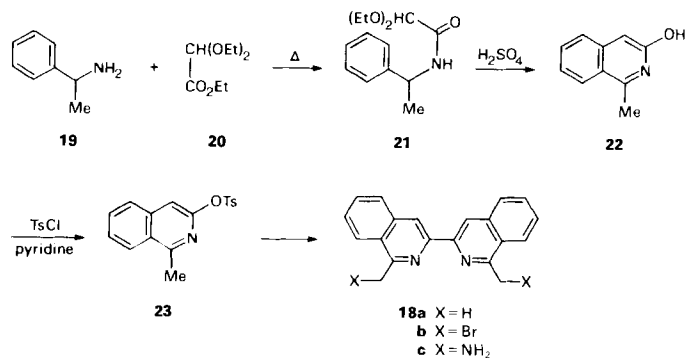
Treatment of **14e** with NaN_3 in THF afforded the bis(azidomethyl)-2,2′-bipyridine **14f** (95% yield) which was catalytically reduced (10% Pd/C) to the bis(aminomethyl) compound **14g** (93% yield). Condensation of **14g** with 2 equiv. of **14e** in refluxing MeCN in presence of Na_2CO_3 yielded (45%) the NaBr complex of the macrobicyclic cryptand **5** ([bpy$(CO_2Me)_2$·bpy$(CO_2Me)_2$·bpy$(CO_2Me)_2$]) bearing six ester functions.

Oxidation of 4,4′-bis(*p*-methoxyphenyl)-6,6′-dimethyl-2,2′-bipyridine (**17a**) with *m*-chloroperbenzoic acid in $CHCl_3$ afforded the *N,N'*-dioxide **17b** (80% yield), which was then heated at reflux in Ac_2O to give the bis(acetoxymethyl) compound **17c** (90% yield; for methyl functionalisation *via* *N*-oxide rearrangement, see [15–17]). Treatment of **17c** with 33% HBr/AcOH afforded, after column chromatography, the dibromo derivatives **17d** and **17e** in 16 and 35% yield, respectively. The NaBr complexes of cryptands **6a** ([2.2.bpy(*p*-$MeOC_6H_4)_2$]; 67% yield), **6b** ([2.2.bpy(*p*-HOC_6H_4)(*p*-$MeOC_6H_4$)]; 60% yield), and **7** ([bpy(*p*-HOC_6H_4)(*p*-$MeOC_6H_4$)·bpy·bpy]; 45% yield) were synthesized by reacting **17d** or **17e** with either **16** or **15**.

Scheme 2 shows the preparation of 1,1′-substituted 3,3′-biisoquinolines **18**. Racemic (1-phenylethyl)amine (**19**) was reacted at elevated temperature with ethyl diethoxyacetate (**20**) to give the amide **21** [18]. Cyclisation of **21** in conc. H_2SO_4 afforded 1-methyliso-

[7]) Compounds **14d** and **14e** were first obtained by *J. Malthête* [13].

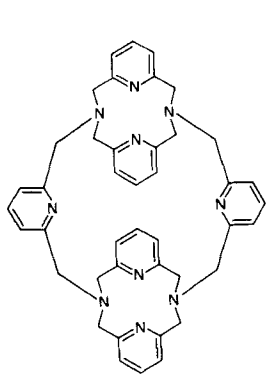
Scheme 2. *Synthesis of Functionalised 1,1'-Dimethyl-3,3'-biisoquinolines* **18**



quinolin-3-ol (**22**; 90% yield). Substitution of the OH group by a Cl- or a Br-atom using standard reagents ($SOCl_2$, $POCl_2$, PBr_3, Ph_3PBr_2) was unsatisfactory. However, treatment of **22** with TsCl afforded, in 86% yield, the tosyloxy derivative **23**, which was reductively coupled with $NiCl_2/PPh_3/Zn$ [19] to give 1,1'-dimethyl-3,3'-biisoquinoline (**18a**; 80% yield). Bromination of **18a** with NBS in CCl_4 led to the bis(bromomethyl) derivative **18b** (68% yield). The bis(aminomethyl) compound **18c** was obtained by reacting **18b** with hexamethylenetetramine in $CHCl_3$, followed by hydrolysis.

The NaBr complex of macrobicycle **8** ([2.2.biqi]) was formed in 14% yield from **16** and **18b**. The one-pot procedure *(Path C, Scheme 1)* was applied to synthesise the NaBr or LiBr complexes of cryptands **9** ([biqi·bpy·bpy]), **10** ([biqi·biqi·py]), and **11** ([biqi·biqi·bpy]); reaction of **18c** with **14b** gave **9** (20% yield), and condensation of **18b** with either **12c** or **14c** afforded **10** (39% yield) and **11** (19% yield), respectively.

Attempts to synthesize the [py·py·py] macrobicycle by treatment of the diamine **12c** with 2 equiv. of the dibromide **12b** in MeCN at reflux in presence of Li_2CO_3 were unsuccessful. The reaction mixture obtained in this case, as well as that resulting from a similar condensation of 2 equiv. of **14b** with 1 equiv. of **14c** (which gave **4a** as main product) contained compounds whose spectral and analytical properties corresponded to



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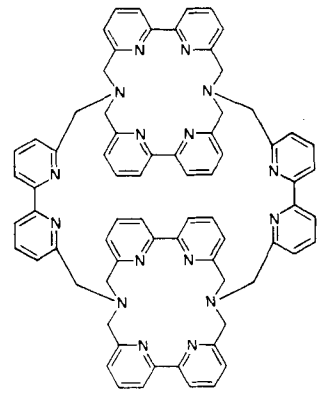

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those expected for the macrotricycles **24** and **25**, respectively; bismacrocycles, in which two rings are linked by a single bridge, also appeared to be formed. Compounds **24** and **25** are cylindrical macrotricyclic cryptands that should be able to form di- or polynuclear cryptates [10] [20]. Further studies on the synthesis and the characterization of these by-products as well as on their complexation properties are under way and will be described elsewhere.

Properties of the Cryptates of the Macrobicyclic Ligands 1–11. – The alkali-metal complexes of the macrobicyclic molecules **1**–**11** are solids soluble in polar organic solvents ($CHCl_3$, CH_2Cl_2, MeCN, MeOH). Crystals suitable for X-ray analysis were grown in a few cases (Li^+ complexes of **1** and **10**; La^{3+} complex of **4a**; Eu^{3+} complex of **4b**) and crystal-structure determination confirmed both the structure of the ligand and of the cryptate, *i.e.* the cation-inclusion nature of the complexes. A detailed discussion of these results will be the subject of a future publication.

All the macrobicyclic compounds described herein are stable in solution as well as in the solid state. They were purified by crystallisation and/or by chromatography (see *Exper. Part*). In most cases, the ^{1}H-NMR spectra were sufficient to ascertain the structure of the cryptates; two examples are presented in *Figs. 1* and *2*. In a few cases, the

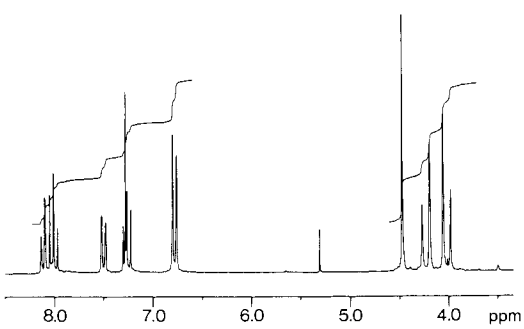

Fig. 1. *200-MHz ^{1}H-NMR spectrum of the LiBr cryptate of the macrobicyclic ligand* **1** ([bpy·py·py]) *in $CDCl_3$*. Solvent at 7.25 ppm; CH_2Cl_2 peak at 5.3 ppm.

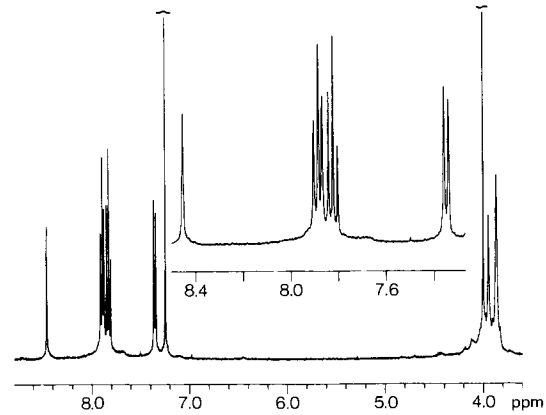

Fig. 2. *400-MHz ^{1}H-NMR spectrum of the NaBr cryptate of the macrobicyclic ligand* **4b** ([bpy(CO_2Me)$_2$·bpy·bpy]) *in $CDCl_3$*. Insert: expansion of the heterocyclic-moiety domain. Solvent at 7.25 ppm.

presence of complexed Li^+ and Na^+ ions was detected by ^{7}Li- and ^{23}Na-NMR spectroscopy, which gave signals markedly shifted from those of the uncomplexed cations.

The cryptates of ligands **1**–**11** possess strong absorption bands in the UV region (see *Exper. Part*), a feature of much interest for the preparation and use of photosensitive cryptates. In particular, exchange of the alkali-metal ion was readily effected by treatment of a NaBr or LiBr complex with a lanthanide salt. Luminescent cryptates were thus prepared in high yield; they present very interesting photophysical properties (see, *e.g.* [6–9]). Other metal ions may also be complexed by these ligands. This work will be described elsewhere.

Experimental Part

General. ^{1}H- and ^{13}C-NMR spectra: spectrometers *Bruker SY-200* at 50.3 (^{13}C) or 200.1 MHz (^{1}H) and *Bruker SY-400* at 100.654 MHz (^{13}C) or 400.135 MHz (^{1}H) with either TMS ($CDCl_3$) or the solvent as reference; the chemical shifts are given in ppm and the coupling constants in Hz. IR spectra: *Perkin-Elmer-597* spectrometer. M.p.: *Thomas-Hoover* apparatus, uncorrected. MS and microanalyses were performed by the 'Service de spectrométrie de masse' and by the 'Service de microanalyse', resp., Institut de chimie, Strasbourg. Solvents: MeCN (CaH_2), C_6H_6 (CaH_2), and THF (Na, benzophenone) freshly distilled under N_2 before use. NBS = *N*-bromosuccinimide, AIBN = 2,2'-azobis(2-methylpropiononitrile).

Materials. The following compounds were employed as starting materials: **12a** (commercial, *Aldrich*), **12b** [16], **14a** [17], **14b** [4], **15** [4] [12], **16** (commercial, *Merck*) [14].

6,6'-Bis(aminomethyl)-2,2'-bipyridine (**14c**). To a soln. of hexamethylenetetramine (1.46 g, 10.4 mmol) in $CHCl_3$ (50 ml) heated at reflux, a soln. of **14b** [4] (1.70 g, 4.97 mmol) in $CHCl_3$ (50 ml) was added dropwise, and the mixture was refluxed for further 3 h. The mixture was allowed to cool to r.t. and to stand. The solid deposited was filtered off, dried, and suspended in H_2O (12 ml)/EtOH (60 ml)/conc. HCl (15 ml). The mixture was stirred at 70° until the solid had completely dissolved. The salt **14c**·4 HCl which crystallised from the soln. on standing overnight at r.t. was filtered off and dried: 1.25 g (70%). ^{1}H-NMR (D_2O): 4.61 (*s*, 2 CH_2N); 7.75 (*d*, 2 H); 8.24 (*t*, 2 H); 8.51 (*d*, 2 H). Anal. calc. for $C_{12}H_{14}N_4 \cdot 4$ HCl (360.10): C 40.03, H 5.08, N 15.56; found: C 40.01, H 5.05, N 15.62.

The soln. of **14c**·4 HCl (1.20 g, 0.034 mol) in H_2O (10 ml) was basified with 6N NaOH and extracted with CH_2Cl_2 (3 × 10 ml). The org. phase was dried ($MgSO_4$) and evaporated: **14c** (0.66 g, 93%). M.p. 86–88°. ^{1}H-NMR ($CDCl_3$): 1.80 (br. *s*, 2 NH_2); 4.04 (*s*, 2 CH_2); 7.27 (*d*, J = 7.6, 2 H); 7.77 (*t*, J = 7.6, 2 H); 8.34 (*d*, J = 7.6, 2 H).

Methyl 2-Methyl-6-[(p-toluenesulfonyl)oxy]pyridine-4-carboxylate. A suspension of methyl 6-methyl-2-hydroxypyridine-4-carboxylate (80 g, 0.48 mol) [21] in pyridine (150 ml) was cooled to 0°, and TsCl (137 g, 0.72 mol) was added portionwise. The mixture was kept overnight in the refrigerator, poured onto ice (400 g), and allowed to stand at r.t. until the product precipitated as a white solid. Filtration and drying afforded 143 g (95%) which were used without further purification. M.p. 62–64°. ^{1}H-NMR ($CDCl_3$): 2.46 (*s*, CH_3); 2.48 (*s*, CH_3); 3.94 (*s*, $COOCH_3$); 7.35 (*s*, 2 H, $CH_3C_6H_4$); 7.44 (*s*, 1 H, py); 7.62 (*s*, 1 H, py); 7.91 (*d*, 2 H, $CH_3C_6H_4$). Anal. calc. for $C_{15}H_{15}NO_5S$ (321.35): C 56.06, H 4.70, N 4.70; found: C 55.10, H 4.64, N 4.24.

Dimethyl 6,6'-Dimethyl-2,2'-bipyridine-4,4'-dicarboxylate (**14d**)[8])[9]) was prepared by a procedure adapted from the method described for the phosphinenickel complex mediated coupling of halopyridines [19]: To a soln. of Ph_3P (122 g, 0.47 mol) in DMF (600 ml) at 50°, $NiCl_2 \cdot 6\ H_2O$ (27.6 g, 0.12 mol) was added under N_2. After 1 h, methyl 2-methyl-6-[(*p*-toluenesulfonyl)oxy]pyridine-4-carboxylate (72 g, 0.22 mol) was added and the mixture stirred for further 4 h. After cooling to r.t., a soln. of 33% NH_3 soln. (225 ml) in H_2O (750 ml) was added and the mixture stirred overnight under a stream of air. The mixture was then continuously extracted with CH_2Cl_2. Evaporation of the solvent gave a solid which, on recrystallisation from CH_2Cl_2 afforded pure **14d** (18.2 g, 55%). M.p. 222–224°. ^{1}H-NMR ($CDCl_3$): 2.73 (*s*, 2 CH_3); 3.99 (*s*, 2 $COOCH_3$); 7.75 (*d*, J = 1.1, 2 H); 8.74 (*d*, J = 1.1, 2 H). ^{13}C-NMR ($CDCl_3$): 24.6 (CH_3Ar); 52.6 (CH_3O); 117.7, 122.6 (arom. CH); 138.6, 156.3, 159.2 (arom. C); 166.1 (COO). Anal. calc. for $C_{16}H_{16}N_2O_4$ (300.31): C 63.99, H 5.37, N 9.33; found: C 63.91, H 5.22, N 9.31.

Dimethyl 6,6'-Bis(bromomethyl)-2,2'-bipyridine-4,4'-dicarboxylate (**14e**)[7]). A mixture of **14d** (2.0 g, 6.7 mmol), NBS (3.0 g, 1.7 mmol), and AIBN (25 mg) was heated under N_2 at 60° in C_6H_6 (45 ml) for 36 h under light irradiation (tungsten lamp, 50 W). The mixture was cooled to r.t. and poured onto a sat. $NaHCO_3$ soln. (400 ml). The org. layer was retained and the aq. phase extracted with $CHCl_3$. The combined org. extracts were washed with H_2O, dried (Na_2SO_4), and evaporated. The residue was chromatographed on a silica-gel column ($CHCl_3$). The desired **14e** and a dibromomethyl isomer were collected (TLC (SiO_2, $CHCl_3$): R_f 0.32). This mixture was rechromatographed on silica gel (cyclohexane/AcOEt 85:15), yielding first (R_f 0.38) the dibromomethyl isomer followed by **14e** (R_f 0.30). Complete recovery of **14e** was achieved by elution with $CHCl_3$. Evaporation gave **14e** (0.92 g, 30%). M.p. 198–200°. ^{1}H-NMR ($CDCl_3$): 4.03 (*s*, 2 $COOCH_3$); 4.71 (*s*, 2 CH_2Br); 8.06 (*d*, J = 1.3, 2 H); 8.91 (*d*, J = 1.3, 2 H). Anal. calc. for $C_{16}H_{14}Br_2N_2O_4$ (458.10): C 41.95, H 3.08, N 6.12; found: C 42.02, H 3.15, N 5.93.

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[8]) Compound **14d** was first obtained by *J. Malthête via* coupling of methyl 2-chloro-6-methylpyridine-4-carboxylate [21] using the same general procedure [13].

[9]) All compounds containing 4,4'-bis(methoxycarbonyl)-2,2'-bipyridine groups must be handled with care so as to avoid hydrolysis and loss in purification procedures. This is especially true for the cryptates of **3**, **4b**, and **5** as well as for the dibromo derivative **14e**. Short chromatography columns and short elution times were employed.

The bromination gave yields varying between 15 and 30% depending on exact conditions.

Dimethyl 6,6'-Bis(azidomethyl)-2,2'-bipyridine-4,4'-dicarboxylate (**14f**). A mixture of **14e** (0.50 g, 1.09 mmol) and NaN_3 (1.0 g, 15.4 mmol) in THF (15 ml) was heated at reflux for 36 h. The mixture was cooled to r.t., and $CHCl_3$ (5 ml) was added. The suspension was centrifuged and the soln. evaporated. The residue in $CHCl_3$ was chromatographed on silica gel ($CHCl_3$): **14f** (0.40 g, 95%). M.p. 168–170°. ^{1}H-NMR ($CDCl_3$): 4.02 (*s*, 2 $COOCH_3$); 4.63 (*s*, 2 CH_2N_3); 7.94 (*d*, *J* = 1.3, 2 H); 8.96 (*d*, *J* = 1.3, 2 H). ^{13}C-NMR ($CDCl_3$): 52.7 (CH_3O); 55.1 (CH_2N_3); 120.0, 121.5 (arom. CH); 139.7, 156.0, 156.8 (arom. C); 165.3 (COO). IR (KBr): 1715 (ester), 2090 (azide). MS: 383 ($(M\,H)^+$). Anal. calc. for $C_{16}H_{14}N_8O_4$ (382.34): C 50.27, H 3.69, N 29.31; found: C 50.37, H 3.51, N 27.69.

Dimethyl 6,6'-Bis(aminomethyl)-2,2'-bipyridine-4,4'-dicarboxylate (**14g**). A mixture of **14f** (0.126 g, 0.33 mmol) and 10% Pd/C (12.6 mg) in CH_2Cl_2/EtOH 2:1 (38 ml) was stirred under H_2 (1 atm) at r.t. for 12 h. After filtering through *Celite*, evaporation afforded **14g** (0.10 g, 93%) which was used without further purification. ^{1}H-NMR (D_2O/DCl): 4.03 (*s*, 2 $COOCH_3$); 4.57 (*s*, 2 CH_2NH_2); 8.07 (*d*, *J* = 1.3, 2 H); 8.95 (*d*, *J* = 1.3, 2 H).

*4,4'-Bis(*p*-methoxyphenyl)-6,6'-dimethyl-2,2'-bipyridine 1,1'-Dioxide* (**17b**). A soln. of **17a** [22] [23] (3.45 g, 8.7 mmol) in $CHCl_3$ (800 ml) was cooled to 0°, and *m*-chloroperbenzoic acid (6.0 g, 34.8 mmol) in $CHCl_3$ (360 ml) was added dropwise. The soln. was stirred overnight at r.t. The mixture was washed with a sat. $NaHCO_3$ soln. The org. phase was concentrated and hexane added. The resultant precipitate was filtered off and dissolved in CH_2Cl_2/MeOH 9:1. The org. phase was washed with 2N NaOH, dried (Na_2SO_4), and evaporated: pure **17b**. The above filtrate was washed with 2N NaOH, evaporated, and chromatographed on alumina (CH_2Cl_2): further pure **17b**. Total yield: 3.05 g (80%). M.p. > 250°. ^{1}H-NMR ($CDCl_3$): 2.65 (*s*, 2 CH_3); 3.86 (*s*, 2 CH_3O); 6.97 (*m*, 4 H, 2 $CH_3OC_6H_4$); 7.56 (*s*, 2 H, H–C(5,5')); 7.56 (*m*, 4 H, 2 $CH_3OC_6H_4$); 7.59 (*s*, 2 H, H–C(3,3')). ^{13}C-NMR ($CDCl_3$): 18.0 (CH_3–C(6,6')); 55.3 (CH_3O); 122.8, 123.6 (CH of bpy); 114.6, 127.7 (CH of Ar); 129.1, 136.7, 143.4, 149.3, 160.3 (arom. C). Anal. calc. for $C_{26}H_{24}N_2O_4 \cdot \frac{1}{2}\,H_2O$ (437.50): C 71.38, H 5.76, N 6.40; found: C 71.47, H 5.37, N 6.23.

*4,4'-Bis(*p*-methoxyphenyl)-2,2'-bipyridine-6,6'-dimethyl Diacetate* (**17c**). A mixture of **17b** (1.21 g, 2.82 mmol) and Ac_2O (18 ml) was heated at reflux for 1.5 h. The soln. was cooled to r.t. and evaporated. H_2O (5 ml) and CH_2Cl_2 (20 ml) were added to the residue, and the mixture was basified with a sat. $NaHCO_3$ soln. The layers were separated, the aq. phase was extracted with CH_2Cl_2 (3 × 30 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue chromatographed on alumina (CH_2Cl_2): **17c** (1.30 g, 90%). M.p. 140–141°. ^{1}H-NMR ($CDCl_3$): 2.20 (*s*, 2 CH_3COO); 3.89 (*s*, 2 CH_3O); 5.38 (*s*, 2 CH_2O); 7.03 (*m*, 4 H, 2 $CH_3OC_6H_4$); 7.57 (*d*, *J* = 1.4, 2 H, H–C(5,5')); 7.74 (*m*, 4 H, 2 $CH_3OC_6H_4$); 8.61 (*d*, *J* = 1.4, 2 H, H–C(3,3')). ^{13}C-NMR ($CDCl_3$): 20.9 (CH_3COO); 55.4 (CH_3O); 67.2 (CH_2O); 118.0, 119.0 (CH of bpy); 114.6, 128.4 (CH of Ar); 130.8, 149.6, 155.7, 156.2, 160.7 (arom. C); 170.5 (COO). Anal. calc. for $C_{30}H_{28}N_2O_6$ (512.56): C 70.30, H 5.51, N 5.47; found: C 70.20, H 5.62, N 5.24.

*6,6'-Bis(bromomethyl)-4,4'-bis(*p*-methoxyphenyl)-2,2'-bipyridine* (**17d**) *and 6,6'-Bis(bromomethyl)-4-(*p*-hydroxyphenyl)-4'-(*p*-methoxyphenyl)-2,2'-bipyridine* (**17e**). A mixture of **17c** (0.31 g, 0.60 mmol) and of a 33% soln. of HBr in AcOH (5 ml) was heated at reflux for 12 h. The soln. was cooled to r.t. and CH_2Cl_2 (60 ml) added. The org. phase was washed with a sat. $NaHCO_3$ soln. and the aq. phase extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extract was dried (Na_2SO_4) and evaporated and the residue chromatographed on alumina with CH_2Cl_2: **17d** (54 mg, 16%). Then, elution with CH_2Cl_2/MeOH 95:5 afforded **17e** (110 mg, 35%).

Data of **17d**: M.p. 210–215° (dec.). ^{1}H-NMR ($CDCl_3$): 3.89 (*s*, 2 CH_3O); 4.70 (*s*, 2 CH_2Br); 7.05 (*m*, 4 H, 2 $CH_3OC_6H_4$); 7.67 (*d*, *J* = 1.5, 2 H, H–C(5,5')); 7.75 (*m*, 4 H, 2 $CH_3OC_6H_4$); 8.61 (*d*, *J* = 1.5, 2 H, H–C(3,3')). ^{13}C-NMR ($CDCl_3$): 34.2 (CH_2Br); 55.4 (CH_3O); 118.1, 120.8 (CH of bpy); 114.6, 128.4 (CH of Ar); 130.5, 150.0, 156.1, 156.7, 160.8 (arom. C). Anal. calc. for $C_{26}H_{22}Br_2N_2O_2 \cdot \frac{1}{2}\,H_2O$ (563.28): C 55.44, H 4.12, N 4.97; found: C 55.73, H 4.10, N 5.08.

Data of **17e**: M.p. 165–170° (dec.). ^{1}H-NMR ($CDCl_3$): 3.87 (*s*, CH_3O); 4.68 (*s*, CH_2Br); 4.70 (*s*, CH_2Br); 6.94 (*m*, 2 H, Ar); 7.03 (*m*, 2 H, Ar); 7.59 (*m*, 2 H, Ar); 7.62 (*d*, *J* = 1.7, H–C(5')); 7.66 (*d*, *J* = 1.6, H–C(5)); 7.72 (*m*, 2 H, Ar); 8.49 (*d*, *J* = 1.6, H–C(3')); 8.59 (*d*, *J* = 1.7, H–C(3)). ^{13}C-NMR ($CDCl_3$): 33.88, 33.92 (CH_2Br); 55.2 (CH_3O); 118.0, 118.2, 120.7, 120.8 (CH of bpy); 114.4, 115.9, 128.2, 128.25, 128.29 (CH of Ar); 120.1, 130.2, 149.9, 150.2, 155.9, 156.0, 156.6, 156.7, 158.1, 160.6 (arom. C). Anal. calc. for $C_{25}H_{20}N_2O_2$ (540.25): C 55.58, H 3.73, N 5.19; found: C 55.24, H 3.83, N 5.13.

3,11-Ditosyl-3,11,17,18-tetraazatricyclo[11.3.1^{5,9}]octadeca-1(17),5(18),6,8,13,15-hexaene (**13a**) [11][6]. Compound **12d** (4.45 g, 10 mmol) in EtOH (50 ml) was added to a soln. of Na (0.50 g, 21.7 mmol) in EtOH (100 ml). The mixture was heated at reflux for 0.5 h. After cooling to r.t., the disodium salt of **12d**, which crystallised quantitatively, was filtered off, dried, and used without further purification in the following step. A mixture of the disodium salt of **12d** (4.90 g, 10 mmol) and DMF (100 ml) was heated to 100°, and **12b** (2.65 g, 10 mmol) in DMF

(50 ml) was added dropwise over 0.5 h. The mixture was heated at 100° for a further 2 h and poured onto H_2O (400 ml). The solid was filtered off, washed with H_2O, MeOH, and EtOH, and dried. Recrystallisation from $CHCl_3$/MeOH afforded **13a** (3.0 g, 54.6%). M.p. 256–258°. ^{1}H-NMR ($CDCl_3$): 2.45 (*s*, 2 CH_3); 4.48 (*s*, 4 CH_2); 7.15 (*d*, 4 H); 7.35 (*d*, 4 H); 7.78 (*d*, 4 H).

3,11,17,18-Tetraazatricyclo[11.3.1.1^{5,9}]octadeca-1(17),5(18),6,8,13,15-hexaene (**13b**) [11][6]. A soln. of **13a** (7.5 g, 0.014 mol) in conc. H_2SO_4 soln. (25 ml) was heated at 100° for 2 h. After cooling to r.t., the mixture was carefully added to aq. NaOH soln. (20%, 50 ml). The resultant precipitate was extracted into $CHCl_3$ and dried (Na_2SO_4) and the solvent removed. Recrystallisation from $CHCl_3$/MeCN 1:4 afforded **13b** (2.7 g, 82%). ^{1}H-NMR ($CDCl_3$): 3.24 (*s*, 2 NH); 3.98 (*s*, 4 CH_2); 6.51 (*d*, J = 7.6, 4 H); 7.08 (*t*, J = 7.6, 2 H). Anal. calc. for $C_{14}H_{16}N_4$ (240.31): C 69.97, H 6.71, N 23.31; found: C 69.98, H 6.79, N 23.24.

1-Methylisoquinolin-3-ol (**22**). Conc. H_2SO_4 soln. (400 ml) was cooled to 10°, and **21** [18] (72.0 g) was added dropwise over 1 h. The temp. was kept below 10° during the addition. The mixture was stirred at r.t. for 10 h and poured onto ice (600 g). After filtration, the soln. was carefully neutralized with a 20% NH_3 soln. The yellow precipitate was filtered off, washed with H_2O, and dried *in vacuo*. Recrystallisation from EtOH yielded **22** (41.5 g, 90%). M.p. 204° (dec.). ^{1}H-NMR ($CDCl_3$): 2.94 (*s*, CH_3); 6.74 (*s*, 1 H); 7.10–7.20 (*m*, 1 H); 7.40–7.50 (*m*, 2 H); 7.79 (*dd*, J = 0.9, 8.8, 1 H). Anal. calc. for $C_{10}H_9NO$ (159.19): C 75.45, H 6.00, N 8.80; found: C 75.42, H 5.53, N 8.64.

1-Methylisoquinolin-3-yl p-Toluenesulfonate (**23**). To a suspension of **22** (41.5 g, 0.26 mol) in pyridine (250 ml), TsCl (70 g, 0.37 mol) was added portionwise within 30 min. After the dissolution of **22**, H_2O (50 ml) was added and stirring maintained for 1 h. The mixture was diluted with H_2O (700 ml) and neutralized with solid Na_2CO_3. The precipitate was filtered off, washed with H_2O, and dried. Recrystallisation from $CHCl_3$/hexane yielded **23** (70.5 g, 86%). M.p. 102°. ^{1}H-NMR ($CDCl_3$): 2.46 (*s*, $CH_3C_6H_4$); 2.82 (*s*, CH_3–C(1)); 7.34 (*m*, 3 H); 7.56–7.82 (*m*, 2 H); 7.80 (*d*, 1 H); 7.82 (*d*, 2 H); 8.08 (*d*, 1 H). Anal. calc. for $C_{17}H_{15}NO_3S$ (313.38): C 65.16, H 4.82, N 4.47; found: C 65.18, H 4.88, N 4.50.

1,1'-Dimethyl-3,3'-biisoquinoline (**18a**). A soln. of Ph_3P (236.3 g, 0.90 mol) and $NiCl_2 \cdot 6\,H_2O$ (53.5 g, 0.22 mol) in DMF (1 l) under N_2 was heated to 50°, and Zn powder (14.64 g) was added. After 1 h, a soln. of **23** (70.5 g, 0.22 mol) in DMF (200 ml) was added and the mixture stirred at 50° for further 6 h. The mixture was cooled to r.t., and a 5% NH_3 soln. (4 l) was added. The mixture was flushed with air until it turned light-blue and filtered. The solid was washed with H_2O and suspended in a 20% HCl soln. (400 ml). The suspension was stirred with Et_2O (400 ml) and filtered. The solid was washed with H_2O and acetone, stirred overnight in a 20% NH_3 soln. (200 ml), filtered off, and dried overnight *in vacuo*. Recrystallisation from $CHCl_3$ afforded **18a** (26.0 g, 81%). M.p. 270–272°. ^{1}H-NMR ($CDCl_3$): 3.11 (*s*, 2 CH_3); 7.55–7.74 (*m*, 4 H); 7.99 (*d*, J = 7.7, 2 H); 8.17 (*d*, J = 7.7, 2 H); 8.79 (*s*, 2 H). Anal. calc. for $C_{20}H_{16}N_2$ (284.36): C 84.48, H 5.67, N 9.85; found: C 84.46, H 5.67, N 9.98.

1,1'-Bis(bromomethyl)-3,3'-biisoquinoline (**18b**). A mixture of **18a** (1.20 g, 4.22 mmol), NBS (2.26 g, 12.7 mmol); and AIBN (30 mg) in CCl_4 (500 ml) was heated at reflux for 3 h. The mixture was cooled to r.t. and evaporated. The solid was stirred in MeOH (150 ml), filtered off, washed with MeOH (100 ml), and dried. Recrystallisation from toluene afforded **18b** (1.28 g, 68%). M.p. 262° (dec.). ^{1}H-NMR ($CDCl_3$): 4.92 (*s*, 2 CH_2Br); 7.73 (*m*, 4 H); 8.08 (*m*, 2 H); 8.32 (*d*, 2 H); 8.97 (*d*, 2 H). Anal. calc. for $C_{20}H_{14}Br_2N_2$ (442.15): C 54.33, H 3.13, N 6.34; found: C 53.42, H 3.10, N 6.15.

1,1'-Bis(aminomethyl)-3,3'-biisoquinoline (**18c**) was synthesised according to the procedure used for **14c**. Yield 30%. ^{1}H-NMR ($CDCl_3$): 1.84 (*s*, 2 NH_2); 4.60 (*s*, 2 CH_2); 7.62 (*dd*, 2 H); 7.71 (*m*, 2 H); 8.03 (*d*, 2 H); 8.13 (*d*, 2 H); 8.89 (*s*, 2 H).

LiBr Complex of 6,6'-{N,N':N,N'-[Bis(pyridine-2,6-dimethyl)]bis(aminomethyl)}-2,2'-bipyridine ([bpy·py·py]; **1**). To a mixture of **13b** (60 mg, 0.25 mmol) and Li_2CO_3 (185 mg, 2.5 mol) in MeCN (300 ml) heated at reflux under N_2, a soln. of **14b** (85 mg, 0.25 mmol) in MeCN (200 ml) was added dropwise over 2 h. The mixture was refluxed for further 15 h. After cooling to r.t., the insoluble solid was filtered off, the filtrate evaporated, and the residue chromatographed on an alumina column with a short plug of silica gel on top (CH_2Cl_2/MeOH 98:2), giving **1** as main product (76 mg, 63%). M.p. > 260°. UV (MeOH): 244 (8500), 291 (6500). ^{1}H-NMR ($CDCl_3$): 3.96–4.25 (*AB*, 4 CH_2-py); 4.46 (*s*, 2 CH_2-bpy); 6.77 (*d*, J = 7.8, 4 H); 7.19 (*t*, J = 7.6, 2 H); 7.50 (*d*, J = 7.6, 2 H); 8.00 (*t*, J = 7.6, 2 H); 8.11 (*d*, J = 7.8, 2 H). ^{13}C-NMR ($CDCl_3$): 63.3 (CH_2-py); 63.8 (CH_2-bpy); 119.5, 121.1, 123.4, 137.5, 139.3 (arom. CH); 154.0, 157.5, 158.8 (arom. C). MS: 427 ([MLi]$^+$). Anal. calc. for $C_{26}H_{24}N_6 \cdot LiBr \cdot H_2O$ (525.11): C 59.44, H 4.98, N 15.98; found: C 59.50, H 5.00, N 15.70.

Compounds **2**, **3**, **6a**, **6b**, **7**, and **8** were synthesized according to the same procedure as **1** using Na_2CO_3 instead of Li_2CO_3.

NaBr Complex of 6,6'':6',6'''-{N,N'-(Pyridine-2,6-dimethyl)bis[iminobis(methylene)]}bis(2,2'-bipyridine) ([bpy·bpy·py]; **2**). From **15** [4] [12] and **12b**. Yield 25%. M.p. > 260°. UV (MeOH): 240 (20000), 286 (17000). ^{1}H-NMR ($CDCl_3$): 3.99 (*s*, 2 CH_2-py); 4.01 (*s*, 4 CH_2-bpy); 7.20 (*d*, J = 7.8, 2 H); 7.36 (*dd*, J = 3.4, 4.4, 4 H); 7.63

(t, J = 7.8, 1 H); 7.88 (d, J = 4.4, 4 H); 7.89 (d, J = 3.4, 4 H). ^{13}C-NMR ($CDCl_3$): 59.4 (CH_2-py); 59.5 (CH_2-bpy); 119.6, 122.6, 123.1, 137.7, 138.5 (arom. CH); 154.7, 158.1, 158.7 (arom. C). MS: 498 ([MH]$^+$), 520 ([MNa]$^+$). Anal. calc. for $C_{31}H_{27}N_7 \cdot NaBr \cdot CHCl_3$ (719.87): C 53.39, H 3.92, N 13.62; found: C 54.16, H 3.80, N 13.98.

*NaBr Complex of Dimethyl 6,6′-[*N,N′:N,N′*-Bis(3,6-dioxaoctamethylene)bis(aminomethyl)]-2,2′-bipyridine-4,4′-dicarboxylate* ([2.2.bpy(CO_2Me)$_2$]; **3**)[9]. From **16** [14] and **14e**. Elution with $CHCl_3$/MeOH 98:2. Yield 61%. M.p. > 260°. UV ($CHCl_3$/MeOH 9:1): 315 (11900). IR (KBr): 1730 (ester). ^{1}H-NMR ($CDCl_3$): 2.50–3.00 (m, 4 CH_2N); 3.50–3.80 (m, 8 CH_2O); 3.96 (s, 2 CH_2-bpy); 4.05 (s, 2 CO_2Me); 7.91 (d, J = 1.2, 2 H); 8.49 (d, J = 1.2, 2 H). ^{13}C-NMR ($CDCl_3$): 52.9 (CH_3O); 53.4 (CH_2N); 59.8 (CH_2-bpy); 66.4, 68.6 (CH_2O); 120.2, 123.4 (arom. CH); 139.9, 155.8, 160.6, (arom. C); 164.6 (COO). MS: 559 ([MH]$^+$), 581 ([MNa]$^+$). Anal. calc. for $C_{28}H_{38}N_4O_8 \cdot NaBr \cdot 2\,H_2O$ (697.55): C 48.21, H 6.07, N 8.03; found: C 48.24, H 6.03, N 8.03.

NaBr Complex of Dimethyl 6,6″,6‴,6⁗:6′,6‴,6⁗-Bis[nitrilotri(methylene)]tris(2,2′-bipyridine)-4,4′-dicarboxylate ([bpy(CO_2Me)$_2$·bpy·bpy]; **4b**)[9]. From **15** [4] [12] and **14e**. Elution with $CHCl_3$/MeOH 98:2. Yield 40%. M.p. > 240°. UV ($CHCl_3$): 290 (35000). ^{1}H-NMR ($CDCl_3$): 3.86 (s, 4 CH_2-bpy); 3.94 (s, 2 CH_2-bpy(CO_2Me)$_2$); 4.00 (s, 2 CO_2Me); 7.36 (dd, J = 7.5, 1.0, 4 H, bpy); 7.82 (t, J = 7.6, 4 H, bpy); 7.86 (d, J = 1.0, 2 H, *bpy*(CO_2Me)$_2$); 7.89 (d, J = 7.8, 4 H, bpy); 8.45 (d, J = 1.0, 2 H, *bpy*(CO_2Me)$_2$). ^{13}C-NMR ($CDCl_3$): 52.9 (CH_3O); 59.5 (CH_2); 119.7, 120.4, 123.4, 124.1, 138.2, 139.7, 155.2, 155.7, 158.3, 160.4 (arom. CH and C); 164.9 (COO). Anal. calc. for $C_{40}H_{34}N_8O_4 \cdot NaBr \cdot 4\,H_2O$ (865.71): C 55.49, H 4.89, N 12.94; found: C 55.44, H 4.33, N 13.10.

*NaBr Complex of 6,6′-[*N,N′:N,N′*-Bis(3,6-dioxaoctamethylene)bis(aminomethyl)]-4,4′-bis(*p*-methoxyphenyl)-2,2′-bipyridine* ([2.2.bpy(C_6H_4OMe)$_2$]; **6a**). From **16** [14] and **17d**. Yield 67%. M.p. > 250°. UV ($CHCl_3$/MeOH 9:1): 267 (29000), 288 (29000). ^{1}H-NMR ($CDCl_3$): 2.64–2.93 (m, 4 CH_2N); 3.49–3.74 (m, 8 CH_2O); 3.89 (s, 2 CH_3O, 2 CH_2-bpy); 7.07 (m, 4 H, 2 $CH_3OC_6H_4$); 7.52 (d, J = 1.1, 2 H, H–C(5,5′)); 7.71 (m, 4 H, 2 $CH_3OC_6H_4$); 8.04 (d, J = 1.1, 2 H, H–C(3,3′)). ^{13}C-NMR ($CDCl_3$): 53.7 (CH_2N); 55.4 (CH_3O); 60.4 (CH_2-bpy); 66.7, 68.8 (CH_2O); 118.1, 121.3 (CH of bpy); 114.8, 128.3 (CH of Ar); 129.5, 150.5, 156.5, 159.4, 161.1 (arom. C). MS: 677 (M^+). Anal. calc. for $C_{38}H_{46}N_4O_6 \cdot NaBr \cdot 2½\,H_2O$ (802.74): C 56.86, H 6.40, N 6.98; found: C 56.62, H 6.25, N 7.10.

*NaBr Complex of 6,6′-[*N,N′:N,N′*-Bis(3,6-dioxaoctamethylene)bis(aminomethyl)]-4′-(*p*-hydroxyphenyl)-4-(*p*-methoxyphenyl)-2,2′-bipyridine* ([2.2.bpy(*p*-HOC_6H_4)(*p*-$MeOC_6H_4$)]; **6b**). From **16** [14] and **17e**. Yield 60%. M.p. > 250°. UV ($CHCl_3$/MeOH): 270 (33000), 289 (33000). ^{1}H-NMR ($CDCl_3$): 2.55–2.97 (m, 4 CH_2N); 3.40–3.81 (m, 8 CH_2O); 3.87 (s, CH_3O); 3.90 (s, 2 CH_2-bpy); 7.01 (m, 2 H, Ar); 7.08 (m, 2 H, Ar); 7.50 (s, 2 H, H–C(5,5′)); 7.63 (m, 2 H, Ar); 7.71 (m, 2 H, Ar); 8.08 (s, 2 H, H–C(3,3′)). ^{13}C-NMR ($CDCl_3$): 53.7 (CH_2N); 55.3 (CH_3O); 60.4 (CH_2-bpy); 66.7, 68.7 (CH_2O); 117.8, 118.0, 120.8, 120.9 (CH of bpy); 114.7, 116.8, 128.0, 128.2 (CH of Ar); 127.0, 129.4, 150.3, 151.0, 156.2, 156.6, 158.9, 159.1, 160.2, 161.0 (arom. C). MS: 640 ([M – Na]$^+$), 663 (M^+). Anal. calc. for $C_{37}H_{44}N_4O_6 \cdot NaBr \cdot ½\,H_2O$ (752.68): C 59.04, H 6.03, N 7.44; found: C 58.86, H 6.10, N 7.34.

*NaBr Complex of 4-(*p*-Hydroxyphenyl)-4′-(*p*-methoxyphenyl)-6,6″,6‴,6⁗:6′,6‴,6⁗-bis[nitrilotri(methylene)]-tris(2,2′-bipyridine)* ([bpy(*p*-HOC_6H_4)(*p*-$MeOC_6H_4$)·bpy·bpy]; **7**). From **15** [4] [12] and **17e**. Yield 45%. M.p. > 250°. ^{1}H-NMR ($CDCl_3$): 3.88 (s, CH_3O, 6 CH_2); 7.04 (m, 2 H, Ar); 7.05 (m, 2 H, Ar); 7.30 (d, J = 6.8, 4 H, H–C(5″,5‴), H–C(5⁗,5⁗′)); 7.45 (s, H–C(5)); 7.46 (s, H–C(5′)); 7.58 (m, 2 H, Ar); 7.66 (m, 2 H, Ar); 7.83 (dd, J = 7.3, 7.8, 4 H, H–C(4″,4‴), H–C(4⁗,4⁗′)); 7.90 (d, J = 7.5, 4 H, H–C(3″,3‴), H–C(3⁗,3⁗′)); 8.09 (d, J = 1.1, 2 H, H–C(3,3′)). ^{13}C-NMR ($CDCl_3$): 55.3 (CH_3O); 59.6 (CH_2-bpy); 59.8 (CH_2-bpy(Ar)$_2$); 120.2, 123.9, 137.9 (CH of bpy); 117.3, 117.5, 120.8, 120.9 (CH of *bpy*(Ar)$_2$); 114.7, 117.0, 127.9, 128.2 (CH of Ar); 126.9, 129.5, 149.3, 150.8, 155.7, 156.2, 158.6, 158.8, 160.4, 160.9 (arom. C). MS: 773 ([MH – Na]$^+$), 795 (M^+). Anal. calc. for $C_{49}H_{40}N_8O_2 \cdot NaBr \cdot CH_2Cl_2$ (960.73): C 62.51, H 4.41, N 11.66; found: C 62.65, H 4.61, N 11.45.

*NaBr Complex of 1,1′-[*N,N′:N,N′*-Bis(3,6-dioxaoctamethylene)bis(aminomethyl)]-3,3′-biisoquinoline* ([2.2.biqi]; **8**). From **16** [14] and **18b**. Yield 14%. M.p. > 250°. UV ($CHCl_3$): 252 (62000), 320 (24000). ^{1}H-NMR ($CDCl_3$): 2.85 (m, 4 CH_2N); 3.58–3.84 (m, 8 CH_2O); 4.49 (s, 4 H, 2 CH_2-biqi); 7.74–7.84 (m, 4 H); 8.02 (d, 2 H); 8.29 (d, 2 H); 8.33 (s, 2 H). MS: 543 ([MH]$^+$), 565 ([MNa]$^+$). Anal. calc. for $C_{32}H_{38}N_4O_4 \cdot NaBr \cdot 2\,H_2O$ (681.60): C 56.39, H 6.21, N 8.22; found: C 56.46, H 6.85, N 7.93.

NaBr Complex of Hexamethyl 6,6″,6‴,6⁗:6′,6‴,6⁗-Bis[nitrilotri(methylene)]tris(2,2′-bipyridine)-4,4′,4″,4‴,4⁗,4⁗′-hexacarboxylate ([bpy(CO_2Me)$_2$·bpy(CO_2Me)$_2$·bpy(CO_2Me)$_2$]; **5**)[9]. A mixture of **14e** (0.280 g, 0.61 mmol) and Na_2CO_3 (0.80 g, 7.44 mmol) in MeCN (500 ml) was heated at reflux under N_2 for 0.5 h. Then **14g** (0.100 g, 0.30 mmol) was added and the mixture refluxed for further 48 h. After cooling to r.t., the insoluble solid was filtered off, the filtrate evaporated, and the residue chromatographed on an alumina column with a short plug of silica gel on top ($CHCl_3$/MeOH 98:2): **5** (0.147 g, 45%). M.p. > 250°. UV ($CHCl_3$): 312 (30000). ^{1}H-NMR ($CDCl_3$): 4.02 (s, 6 $COOCH_3$); 4.08 (s, 6 CH_2); 7.96 (d, J = 1.2, 6 H); 8.49 (d, J = 1.2, 6 H). ^{13}C-NMR ($CDCl_3$): 53.2 (CH_3O); 59.2 (CH_2); 120.0, 123.8 (arom. CH); 139.9, 155.6, 159.9 (arom. C); 164.8 (COO). Anal. calc. for $C_{48}H_{42}N_8O_{12} \cdot NaBr \cdot 3\,H_2O$ (1079.84): C 53.59, H 4.48, N 10.38; found: C 53.40, H 4.40, N 9.75.

Compounds **9–11** were synthesized according to the same procedure as **5**.

*NaBr Complex of 1,1'-[*N,N':N,N'-*[Bis(2,2'-bipyridine-6,6'-dimethyl)]bis(aminomethyl)]-3,3'-biisoquinoline* ([biqi·bpy·bpy]; **9**). From **14b** and **18c** with Na_2CO_3. Elution with CH_2Cl_2/MeOH 98:2. Yield 20%. M.p. > 260°. ^{1}H-NMR ($CDCl_3$): 3.79 (*AB*, 4 CH_2-bpy); 4.40 (*s*, 2 CH_2-biqi); 7.32 (*d*, 4 H, bpy); 7.63 (*t*, 2 H, biqi); 7.72 (*t*, 2 H, biqi); 7.79 (*t*, 4 H, bpy); 7.82 (*d*, 4 H, bpy); 7.92 (*d*, 2 H, biqi); 8.12 (*d*, 2 H, biqi); 8.18 (*s*, 2 H, biqi).

LiBr Complex of 1,1'':1',1'''-{N,N'-*(Pyridine-2,6-dimethyl)bis[iminobis(methylene)]}bis(3,3'-biisoquinoline)* ([biqi·biqi·py]; **10**). From **18b** and **12c** with Li_2CO_3. Yield 39%. M.p. > 250°. ^{1}H-NMR ($CDCl_3$): 4.47 (*d*, J_{gem} = 16.3, 4 H, biqi); 4.45 (*s*, 2 CH_2-py); 4.75 (*d*, J_{gem} = 16.3, 4 H, biqi); 7.47 (*d*, 2 H); 7.55–7.80 (*m*, 9 H); 7.91 (*d*, 4 H); 8.28–8.34 (*m*, 8 H). MS: 698 ([*M*H]$^+$), 704 ([*M*Li]$^+$). Confirmed by crystal structure determination.

NaBr Complex of 1,1'':1',1'''-{N,N'-*(2,2'-bipyridine-6,6'-dimethyl)bis[iminobis(methylene)]}bis(3,3'-biisoquinoline)* ([biqi·biqi·bpy]; **11**). From **18b** and **14c** with Na_2CO_3. Elution with CH_2Cl_2/MeOH 98:2. Yield 19%. M.p. > 260°. ^{1}H-NMR ($CDCl_3$): 3.60–3.95 (*s*, 2 CH_2-bpy); 4.40–4.75 (*AB*, 4 CH_2-biqi); 7.33 (*dd*, 2 H); 7.48–7.72 (*m*, 8 H); 7.81 (*d*, 4 H); 7.92 (*d*, 4 H); 8.00–8.13 (*d*, 4 H); 8.18 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 56.9 (*C*H_2-biqi); 59.9 (*C*H_2-bpy); 118.1, 119.7, 123.7, 126.2, 127.9, 130.7, 136.8, 149.7, 154.8, 157.7, 158.7.

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