266. Photoactive Cryptands

Synthesis of the Sodium Cryptates of Macrobicyclic Ligands Containing Bipyridine and Phenanthroline Groups

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Summary

The NaBr cryptates of five macrobicyclic ligands containing bipyridine (bpy) and phenanthroline (phen) groups, *i.e.* of [bpy.bpy.bpy] **1** [bpy.bpy.phen] **2** [phen.phen.-phen] **3** [2.1.phen] **4** and [2.2.phen] **5**, have been prepared. **1**, **2**, **4** and **5** have been obtained in high yield by condensation of bis(bromomethyl)bipyridine **6** or -phenanthroline **9** with the corresponding macrocyclic diamines in presence of Na_2CO_3. Direct access to the NaBr complexes of the symmetrical cryptands **1** and **3** was achieved by a one-step macrobicyclisation procedure. The metal-ion complexes of ligands **1–5** have the attractive feature of combining the *cation inclusion* nature of cryptates with the *photoactivity* of bipyridine and phenanthroline groups; they may thus be expected to possess a variety of interesting physical and chemical properties.

Introduction of polypyridine binding subunits into macropolycyclic frameworks may be expected to combine within the same molecule two features of interest in ligand chemistry: *i*) the remarkable metal ion binding properties provided by inclusion into a molecular cavity to give *cryptate*-type complexes [1]; *ii*) the versatile *photoactivity* of metal complexes of polypyridine ligands such as 2,2′-bipyridine (bpy), or 1,10-phenanthroline (phen) in electron- and energy-transfer processes [2] [3]. $[M(bpy)_3]^{n+}$ and analogous complexes, especially $[Ru(bpy)_3]^{2+}$, have been subject to intense research in recent years, in particular because of their use in the development of systems performing photo-induced processes related to solar energy conversion [2–4].

Macropolycyclic polypyridine ligands should present novel properties on both counts, allowing control of metal-ion binding as well as of photophysical and photochemical behaviour *via* ligand design, while at the same time increasing the thermal and photostability of the complexes by means of the highly connected molecular framework.

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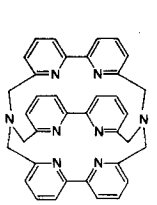
Along these lines, we have earlier studied polynucleating macrotricyclic cryptands containing two bpy units [5]. On the other hand, the active recent work on the photo-induced activation of H_2O and CO_2 has employed extensively polypyridine-metal complexes as photosensitizers and as catalysts [6] (see also [2–4]). We now report efficient syntheses of the NaBr complexes of five polypyridine macrobicyclic cryptands: [bpy.bpy.bpy] **1**, [bpy.bpy.phen] **2**, [phen-phen-phen] **3**, [2.1.phen] **4** and [2.2.phen] **5**.

Macrocycles containing pyridine [7], 2,2′-bipyridine [8–12] or phenanthroline [12–15] groups have been described earlier, as well as macrobicyclic cryptands with a single bpy [9].



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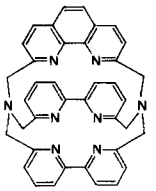

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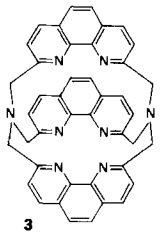

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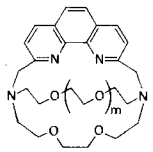

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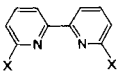

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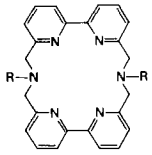

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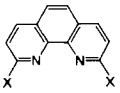
8 R = H



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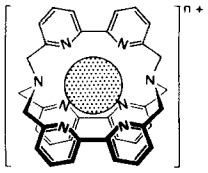

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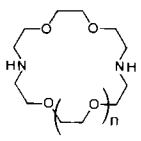

11 n = 0 [2.1], [15]-N_2O_3
12 n = 1 [2.2], [18]-N_2O_4

Synthesis of the NaBr Complexes of the Macrobicyclic Polypyridine Cryptands 1–5. – Macrobicyclic molecules are accessible by a *stepwise procedure* involving the synthesis of an intermediate macrocycle and its subsequent bridging. Such a sequence was followed for **1**, **2**, **4**, and **5**.

Bromination of 6,6′-dimethyl-2,2′-bipyridine with *N*-bromosuccinimide in refluxing CCl_4 gave the dibromide **6** (55–60% yield). Condensation of **6** with sodium *p*-toluenesulfonamide in EtOH at reflux, afforded the macrocyclic bis(*p*-toluenesulfonamide) **7** [8] (57% yield) which was converted to the macrocyclic bis(bipyridinediyl)diamine **8** ([18]-$N_2(bpy)_2$) [8] by treatment with conc. H_2SO_4 (94% yield).

Dropwise addition of the dibromide **6** to a solution of macrocycle **8** in refluxing MeCN in presence of Na_2CO_3 gave the NaBr complex of the macrobicyclic tris(bipyridine) cryptand **1** ([bpy.bpy.bpy]) in 62% yield. In a similar fashion, reaction of the dibromide **9** [16] with the macrocycle **8** afforded the NaBr complex of the bis(bipyridine)-phenanthroline macrobicycle **2** ([bpy.bpy.phen]) in 71% yield.

Condensation of the dibromide **9** with the macrocycles **11** [2.1] ([15]–N_2O_3) [17] and **12** [2.2] ([18]–N_2O_4) [17] by the same procedure gave the NaBr complexes of the corresponding macrobicyclic mono-phenanthroline cryptands **4** ([2.1.phen]) and **5** ([2.2.phen]) in 38% and 50% yield, respectively. The sodium complex of **5** has been prepared earlier by a different route [9].

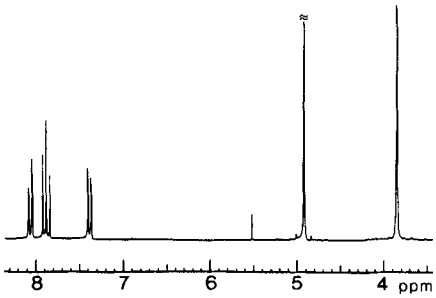

Figure. *200-MHz ^{1}H-NMR spectrum of the NaBr cryptate of the macrobicyclic ligand [bpy.bpy.bpy]* **1** (in CD_3OD at about +20°; the signals around 4.9 and 5.5 ppm are due to the solvent (–OH) and to CH_2Cl_2 reference, respectively)

The high yields of macrobicycle formation obtained without adhering to high dilution conditions are noteworthy. They may result from both a templating effect of the sodium cation and from a rigid-group effect of the bridging units introduced. No [bpy.bpy.bpy] **1** was isolated when Cs_2CO_3 was used instead of Na_2CO_3 in the macrobicyclisation reaction.

These observations led us to attempt the direct, *one-step macrobicycle formation* from the dibromides **6** and **9**. Indeed, when these compounds were heated in MeCN in presence of NH_3 and Na_2CO_3, the NaBr complexes of the macrobicyclic cryptands [bpy.bpy.bpy] **1** and [phen.phen.phen] **3** were formed in about 25–30% isolated yield. Optimisation of the reaction conditions has not yet been performed and may allow to increase the yields.

Although the NaBr complexes of **1–5** obtained from the cyclisation reactions may be used directly as starting materials for preparing complexes of other, more strongly bound cations, it is desirable to devise a method for generating the free cryptands. Such work is presently underway[4]).

The spectral and analytical data of the substances obtained agree with the proposed structures. The *Figure* presents the ^{1}H-NMR spectrum of the Na^+ cryptate of [bpy.bpy.bpy] **1**. The NaBr complexes of **1–5** are soluble in polar organic solvents (CH_2Cl_2, $CHCl_3$, CH_3OH *etc.*) and slightly in neutral or basic H_2O. They dissolve in acidified H_2O, probably with decomplexation by protonation.

Properties of the cryptates of macrobicycles 1–5. – The macrobicyclic molecules **1–5** are polypyridine analogues of the initial [2.2.2] cryptand [17] [18] and of its polyaza derivatives [19]. As such their metal cation complexes are expected to be of the *cryptate* type in which the ion is contained in the intramolecular cavity of the ligand as schematically represented by **10** for $[M^{n+} \subset \mathbf{1}]$.

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[4]) Preliminary results on the preparation of the free [bpy.bpy.bpy] cryptand **1** have been obtained. Reaction of the Na^+ cryptate of **1** with excess $AgNO_3$ gave the Ag^+ cryptate which was isolated and treated with H_2S, leading to precipitation of Ag_2S and formation of the free cryptand **1**. Reaction of the latter with NaBr regenerated the starting Na^+ cryptate. Other decomplexation methods, in particular through protonation, are being investigated.

Only a few properties of the NaBr cryptates of macrobicycles **1–5** have been studied at present. Complexes of other metal cations may be prepared by displacement of the bound Na^+; Ag^+ cryptates have thus been obtained.

The ^{1}H-NMR spectra of the Na^+ cryptates of macrobicycles **1**, **2**, and **3** present a temperature dependence for the signals of the CH_2 protons which form *AB* systems ($J \approx 14$ Hz) at low temperature and coalesce into single bands as the temperature is raised. These changes may be attributed to a kinetic process involving torsional motion of the ligand around the N,N bridgehead axis, as was observed earlier for the [2.2.2] cryptand [17]. The coalescence temperatures increase from about 235 K, to 247 K and 320 K along the series **1**, **2**, and **3** indicating, as one may expect, an increasing hindrance to the torsional motions when the bpy units are replaced by the more rigid phen groups. These data also show that these macrobicyclic cryptates adopt preferentially a *twisted shape* in which the CH_2 protons are non-equivalent. More detailed description and discussion of these phenomena will be given at a later date.

The results described here provide an efficient access to a novel class of macrobicyclic cryptands and cryptates which may present interesting photophysical and photochemical properties. Work is pursued in order to further explore and improve the synthetic procedures for obtaining the cryptates as well as the free ligands, to extend the methods to other macropolycyclic ligands, to prepare and study cryptates of various metal ions, to investigate their physical and chemical properties, in particular their photoactivity and use in processes of artificial photosynthesis.

Experimental Part

General. ^{1}H- and ^{13}C-NMR spectra were recorded on a *Bruker SY-200* spectrometer at 200 MHz and 50.3 MHz, respectively; the chemical shifts are given in ppm from TMS (= 0 ppm) as internal standard. The mass spectra and the microanalyses were performed at the Laboratoire de Spectrométrie de Masse and at the Service Central de Microanalyse du CNRS, Institut de Chimie, Strasbourg, respectively. All commercially available chemicals employed were reagent grade and used without further purification, unless stated otherwise.

6,6'-Bis(bromomethyl)-2,2'-bipyridine (**6**). A mixture of 6,6'-dimethyl-2,2'-bipyridine (2.76 g, 15 mmol) and *N*-bromosuccinimide (5.10 g, 28.6 mmol) in CCl_4 (150 ml) was refluxed for 30 min, and then benzoyl peroxide (30 mg) was added. The mixture was refluxed for another 2 h and then the succinimide was filtered off. The solution was cooled to 0° and the solid which deposited was filtered and washed with MeOH to give **6** (1.65 g, 32% yield) as a white crystalline solid which may be recrystallized from CCl_4. The CCl_4 filtrate obtained above was concentrated and chromatographed on a silica column with CH_2Cl_2/MeOH 98:2 to give another crop of **6** (1.38 g; 27% yield), 6-methyl-6'-bromomethyl-2,2'-bipyridine (0.55 g, 14% yield), and 6,6'-bis(dibromomethyl)-2,2'-bipyridine (0.9 g, 12% yield). Total yield of **6**: *ca.* 59% (3.03 g); m.p. 180°–181°. ^{1}H-NMR ($CDCl_3$): 4.63 (*s*, 2 CH_2); 7.47 (*dd*, J = 7.8, 1.1, H–C(5), H–C(5')); 7.83 (*t*, J = 7.8, H–C(4), H–C(4')); 8.39 (*dd*, J = 7.8, 1.1, H–C(3), H–C(3')). Anal. calc. for $C_{12}H_{10}Br_2N_2$ (342.0): C 42.11, H 2.92, N 8.19; found: C 41.85, H 2.74, N 8.13.

6-Bromomethyl-6'-methyl-2,2'-bipyridine. M.p. 88°. ^{1}H-NMR ($CDCl_3$): 2.63 (*s*, CH_3); 4.63 (*s*, CH_2); 7.17 (*d*, J = 7.9, H–C(5')); 7.44 (*dd*, J = 7.9, 0.9, H–C(5)); 7.70 (*t*, J = 7.9, H–C(4')); 7.80 (*t*, J = 7.9, H–C(4)); 8.23 (*d*, J = 7.9, H–C(3')); 8.33 (*dd*, J = 7.9, 0.9, H–C(3)). Anal. calc. for $C_{12}H_{11}BrN_2$ (263.1): C 54.75, H 4.18, N 10.65; found: C 54.67, H 4.19, N 10.69.

6,6'-Bis(dibromomethyl)-2,2'-bipyridine. M.p. 48–50°. ^{1}H-NMR ($CDCl_3$): 6.73 (*s*, 2 CH); 7.84 (*dd*, J = 7.6, 1.3, H–C(5), H–C(5')); 7.93 (*t*, J = 7.6, H–C(4), H–C(4')); 8.43 (*dd*, J = 7.6, 1.3, H–C(3), H–C(3')). Anal. calc. for $C_{12}H_8Br_4N_2$ (499.8): C 28.83, H 1.61, N 5.60; found: C 29.03, H 1.83, N 5.30.

8,21-Ditosyl-8,21,27,28,29,30-hexaazapentacyclo[21.3.1.1^{2,6}.1^{10,14}.1^{15,19}]triaconto-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene (**7**). A mixture of **6** (3.17 g, 9.27 mmol) and *p*-toluenesulfonamide monosodium salt (3.58 g, 18.5 mmol) in dry EtOH (350 ml) was refluxed for 24 h. After cooling to −5° to −10° in an ice-salt mixture, the mixture was filtered and the white, highly insoluble solid formed was washed on the filter with H_2O and EtOH to give **7** (1.35 g, 57% yield), m.p. > 260° ([8]: m.p. > 260°). The compound is used without further purification for the following step.

8,21,27,28,29,30-Hexaazapentacyclo[21.3.1.1^{2,6}.1^{10,14}.1^{15,19}]triaconta-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene (**8**). The diamide **7** (0.5 g, 0.7 mmol) was dissolved in conc. H_2SO_4 and heated to 110° for 2 h [8]. After cooling to r.t., H_2O (4 ml) was added, and the resulting mixture was added with caution to a solution of NaOH (4 g) in H_2O (30 ml). The product precipitated and was extracted with $CHCl_3$ (3 × 10 ml). After drying with $MgSO_4$, the $CHCl_3$ solution was evaporated giving **8** as colourless crystals (0.26 g, 94%), m.p. > 350 °C ([8]: m.p. > 260°).

NaBr Complex of 6,6′,6″,6‴,6⁗,6⁗′-Bis[nitrilotri(methylene)]tris(2,2′-bipyridine) ([bpy.bpy.bpy]; **1**). A mixture of **8** (0.15 g, 0.38 mmol) and Na_2CO_3 (0.4 g, 3.7 mmol) in freshly distilled MeCN (200 ml) was heated to reflux, and a solution of **6** (0.12 g, 0.38 mmol) was added dropwise within 3 h under efficient magnetic stirring. The resulting mixture was refluxed for further 20 h. After cooling to r.t., the insoluble solid was filtered off and the filtrate evaporated to dryness. The solid residue was redissolved in CH_2Cl_2/MeOH 98:2 (3 ml) and filtered over a short column of alumina (neutral, act. I) by eluting with the same solvent mixture. Evaporation of the solution gave the NaBr complex of **1** as a white crystalline solid (0.16 g, 62% yield), m.p. > 350°. ^{1}H-NMR ($CDCl_3$): 3.85 (*s*, 6 CH_2); 7.33 (*dd*, *J* = 7.2, 1.2, 6H, H–C(5), H–C(5′)); 7.82 (*t*, *J* = 7.2, 6H, H–C(4), H–C(4′)); 7.90 (*dd*, *J* = 7.2, 1.2, 6H, H–C(3), H–C(3′)). ^{13}C-NMR ($CDCl_3$): 59.5 (CH_2), 120.2, 123.9, 138.0 (CH-bpy); 155.2, 158.0 (C-bpy). MS: 575 ((*M*H)$^+$), 597 ((*M*Na)$^+$). Anal. calc. for $C_{36}H_{30}N_8$·NaBr (677.6): C 63.81, H 4.46, N 16.53; found: C 63.79, H 4.48, N 16.49.

2,9-{N,N′N,N′-[Bis(2,2′-bipyridine-6,6′-dimethyl)]bis(aminomethyl)}-1,10-phenanthroline (= imino,imino′-*(1,10-Phenanthroline-2,9-dimethyl)-6,6′,6″,6‴-bis[iminodi(methylene)]bis(2,2′,bipyridine), [bpy.bpy.phen];* **2**). A mixture of **8** (0.2 g, 0.51 mmol) and Na_2CO_3 (0.53 g, 5 mmol) in freshly distilled MeCN (300 ml) was heated to reflux, and a solution of *2,9-bis(bromomethyl)-1,10-phenanthroline* (**9**; 0.19 g, 0.51 mmol; prepared by the procedure in [16]) in MeCN (100 ml) was added dropwise within 2.1 h under efficient magnetic stirring. Refluxing was continued for 18 h. After cooling to r.t., the insoluble solid was filtered off and the filtrate was evaporated to dryness. The crude solid product was redissolved in CH_2Cl_2 and purified by passage through a silica gel column (70–230 mesh) with CH_2Cl_2/MeOH 96:4. Evaporation of the solution gave **2** (0.25 g, 71% yield), m.p. > 350°. ^{1}H-NMR ($CDCl_3$): 3.91 (*s*, 8H, CH_2-bpy); 4,07 (*s*, 4H, CH_2-phen); 7.36 (*dd*, *J* = 7.2, 1.3, 4H, H–C(5), H–C(5′) of bpy); 7.64 (*d*, *J* = 8.2, 2H, H–C(3), H–C(8) of phen); 7.78 (*s*, 2H, H–C(5), H–C(6) of phen); 7.83 (*t*, *J* = 7.2, 4H, H–C(4), H–C(4′) of bpy); 7.91 (*dd*, *J* = 7.2, 1.3, 4H, H–C(3), H–C(3′) of bpy); 8.27 (*d*, *J* = 8.2, 2H, H–C(4), H–C(7) of phen). ^{13}C-NMR ($CDCl_3$): 59.7 (CH_2-bpy); 60.1 (CH_2-phen); 120.3, 124.0, 138.0 (CH-bpy); 123.6, 126.0, 137.1 (CH-phen); 155.3, 158.5 (C-bpy); 127.8, 145.6, 158.5 (C-phen). MS: 599 ((*M*H)$^+$), 621 ((*M*,Na)$^+$), 637 ((*M*K)$^+$). Anal. calc. for $C_{38}H_{30}N_8$·NaBr·H_2O (719.6): C 63.42, H 4.45, N 15.57; found: C 62.77, H 4.46, N 15.31.

NaBr Complex of **1** *by One-Step Macrobicyclisation.* A mixture of **6** (0.69 g, 2 mmol) and Na_2CO_3 (2.22 g, 20.9 mmol) in 500 ml of NH_3 in MeCN (8.8 mM, 4.4 mmol NH_3) was heated to 100° for 18 h in a sealed medium-pressure glass reactor. After cooling to r.t. the solution was filtered, and the inorg. solids were washed with warm MeCN. The combined solutions were evaporated to dryness, and the crude product was purified by column chromatography on silica gel (70–230 mesh; eluant CH_2Cl_2 containing 4% MeOH) giving the NaBr complex of **1** (120 mg, 27% yield).

NaBr Complex of 2,2′,2″,9,9′,9″-Bis[nitrilotri(methylene)]tris(1,10-phenanthroline) ([phen.phen.phen]; **3**), *by One-Step Macrobicyclisation.* A mixture of **9** (0.2 g, 0.55 mmol) and Na_2CO_3 (0.64 g, 5.7 mmol) in 160 ml of NH_3 in MeCN (7.5 mM, 1.2 mmol NH_3) was treated and worked up as described above for **1**, giving the NaBr complex of **3** (40 mg, 29% yield), m.p. > 260°. ^{1}H-NMR ($CDCl_3$): 4.03, 4.45 (very br. *AB*, 12H, CH_2); 7.66 (*d*, *J* = 8.1, 6H, H–C(3), H–C(8)); 7.78 (*s*, 6H, H–C(5), H–C(6)); 8.27 (*d*, *J* = 8.1, 6H, H–C(4), H–C(7)). ^{13}C-NMR ($CDCl_3$): 60.5 (CH_2); 123.8, 126.2, 137.3 (CH-phen); 128.1, 145.9, 158.9 (C-phen). MS: 668 ((*M*,Na)$^+$ − 1); 460 ((*M*,Na$^+$) − phen(CH_2)$_2$). Anal. calc. for $C_{42}H_{30}N_8$·NaBr·H_2O (767.6): C 65.71, H 4.17, N 14.6; found: C 65.23, H 4.26, N 13.10.

NaBr Complex of 2,9-[N,N′-(3,6-Dioxaoctamethylene)-N,N′-(3-oxapentamethylene)bis(aminomethyl)]-1,10-phenanthroline ([2.1.phen]; **4**). A mixture of the diamine **11** [2.1] [17] (0.060 g, 0.27 mmol) and Na_2CO_3 (0.29 g, 2.74 mmol) in freshly distilled MeCN (80 ml) was heated to reflux, and a solution of **9** (0.099 g, 0.27 mmol) was added dropwise under efficient magnetic stirring. The resulting mixture was refluxed for further 18

h. After cooling to r.t., the insoluble solid was filtered off and the filtrate was evaporated. The solid residue was redissolved in CH_2Cl_2 and purified by passage through a silica gel column (70–230 mesh) with CH_2Cl_2/MeOH (96:4). Evaporation gave the NaBr complex of **4** as a white crystalline solid which was recrystallised from CH_2Cl_2/toluene (0.057 g, 38% yield), m.p. > 260°. ^{1}H-NMR ($CDCl_3$): 2.60 (*dd*, 4H); 2.86 (*td*, J = 13,3, 2H); 3.24–3.40 (*m*, 4H); 3.53 (*dd*, J = 13, 2.4, 2H); 3.73–4.08 (*m*, 10H); 4.55 (*d*, J = 17, 2H); 7.58 (*d*, J = 8.3 Hz, H–C(3), H–C(8)); 7.83 (*s*, H–C(5), H–C(6)); 8.29 (*d*, J = 8.3, H–C(4), H–C(7)). ^{13}C-NMR ($CDCl_3$): 52.05, 55.2 (NCH_2); 59.6 (NCH_2-phen); 67.3, 67.4, 69.7 (OCH_2); 122.7, 125.95, 137.2 (CH-phen); 127.9, 144.95, 158.5 (C-phen). MS: 423 ((*M*H)$^+$), 445 ((*M*,Na)$^+$). Anal. calc. for $C_{24}H_{30}O_3N_4 \cdot NaBr \cdot 2H_2O$. (561.4): C 51.34, H 6.10, N 9.98; found: C 51.79, H 5.87, N 10.28.

*NaBr Complex of 2,9-[*N,N′,N,N′*-Bis(3,6-dioxaoctamethylene)bis(aminomethyl)]-1,10-phenanthroline ([2.2.phen]; 5).* A mixture of diamine **12** [2.2] [17] (0.10 g, 0.38 mmol) and Na_2CO_3 (0.40 g, 3.77 mmol) in freshly distilled MeCN (110 ml) was heated to reflux and a solution of **9** (0.14 g, 0.35 mmol) was added dropwise under efficient magnetic stirring. The mixture was refluxed for further 18 h. After cooling to r.t., the insoluble solid was filtered off and the filtrate was evaporated. The crude solid product was redissolved in CH_2Cl_2 and purified by passage through a silica gel column (70–230 mesh) with CH_2Cl_2/MeOH (96/4). Evaporation gave the NaBr complex of **5** as a white solid which was recrystallised from CH_2Cl_2/toluene (0.112 g, 50% yield), m.p. > 260°. ^{1}H-NMR ($CDCl_3$): 2.64–2.95 (*ABm*, 8H, CH_2N); 3.55–3.82 (*m*, 16H, OCH_2); 4.12 (*s*, 4H, CH_2-phen); 7.64 (*d*, J = 8.2, H–C(3), H–C(8)); 7.83 (*s*, H–C(5), H–C(6)); 8.31 (*d*, J = 8.2, H–C(4), H–C(7)). ^{13}C-NMR ($CDCl_3$): 53.5 (NCH_2); 60.5 (NCH_2-phen); 66.6, 68.8 (OCH_2); 123.6, 126.2, 137.6 (CH-phen); 128.3, 145.5. 158.9 (C-phen). MS: 467 ((*M*H)$^+$), 489 ((*M*,Na)$^+$). Anal. calc. for $C_{26}H_{34}O_4N_4 \cdot NaBr \cdot H_2O$ (587.5): C 53.16, H 6.18, N 9.54; found: C 53.00, H 6.21, N 9.44.

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