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Synthesis of some novel tetraimidazolium salts derived from diphenyl- and dimethylglycolurils

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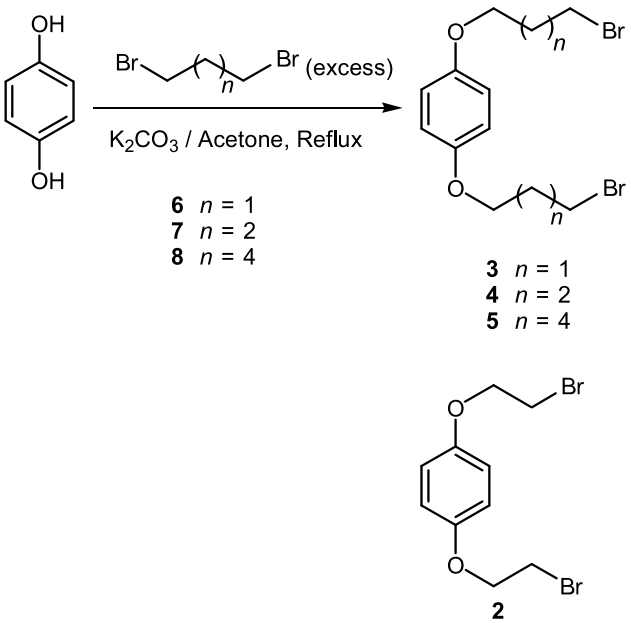
Abstract Several new tetrabromo compounds based on diphenyl- and dimethylglycolurils were synthesized. Sequential treatment of these compounds with imidazole, methyl iodide, and sodium tetrafluoroborate gave their corresponding tetra imidazolium salts. Some of these compounds because of their low melting points can be registered as a potential and new class of ionic liquids.

Keywords Receptors; Heterocycles; Electrophilic substitution; Molecular clips; Ionic liquids.

Introduction

The design and synthesis of host molecules for the binding of neutral guest molecules continues to be an area of interest in supramolecular chemistry [1]. In the past decade, *Nolte* and his co-workers introduced a series of host molecules derived from the concave molecule diphenylglycoluril which were able to bind neutral aromatic guest molecules, such as resorcinol [2].

These ''U-shaped'' clips bind dihydroxybenzenes by means of hydrogen bonding between the hydroxyl groups of the guest and the urea carbonyl groups of the host and by $\pi-\pi$ stacking interactions between the guest and the host side walls [3]. Also, molecular clips with a large variety of side walls have been synthesized, and the supramolecular chemistry of these clips has been extensively studied [4]. Some effort has been directed toward modifying the glycoluril framework of the hosts. The urea functionalities in the glycoluril framework have been replaced by thiourea and guanidine groups [5] and clips have been synthesized starting from dimethylglycoluril [6], dipyridylglycoluril [7], ditoluylglycoluril [8], and bipyridylglycoluril [9].



Scheme 1

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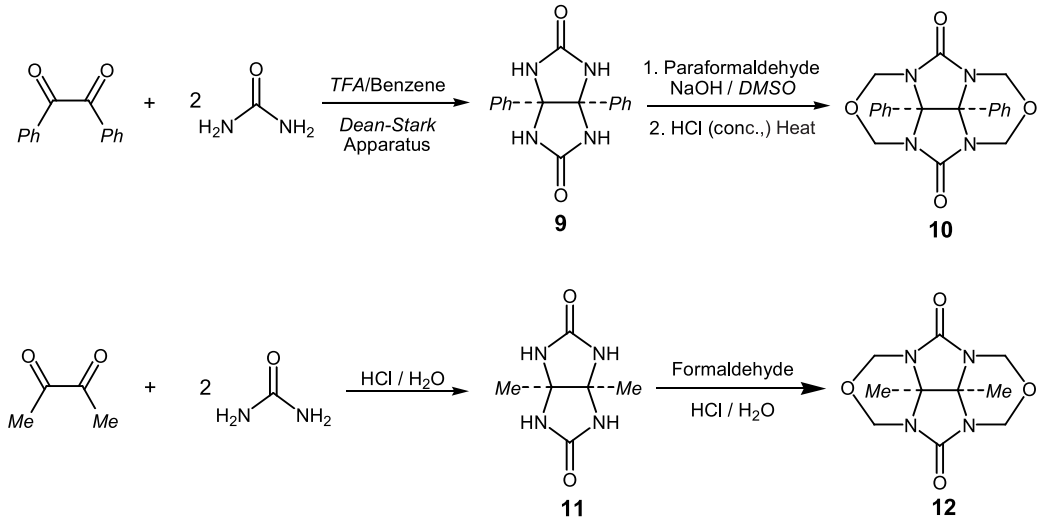
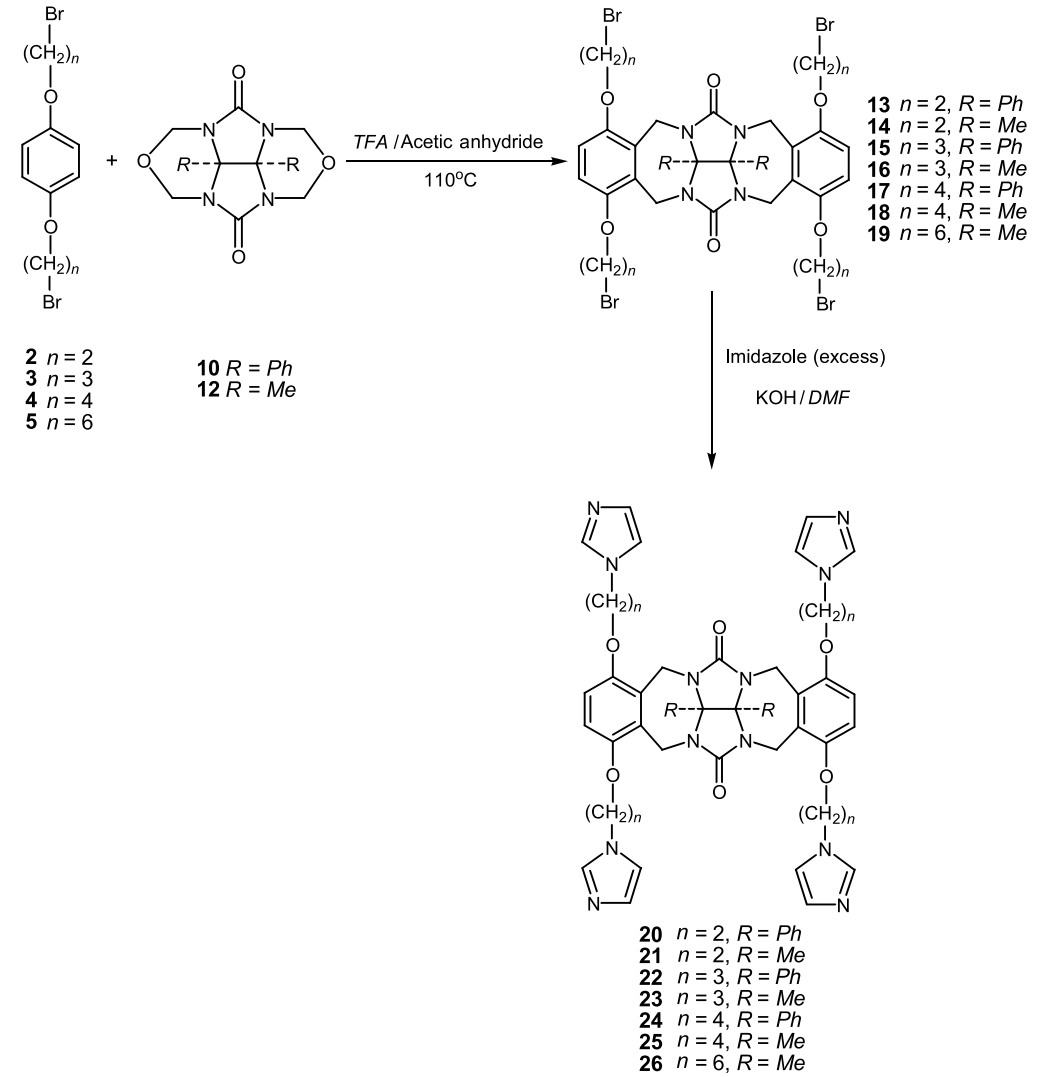


Scheme 2



Scheme 3

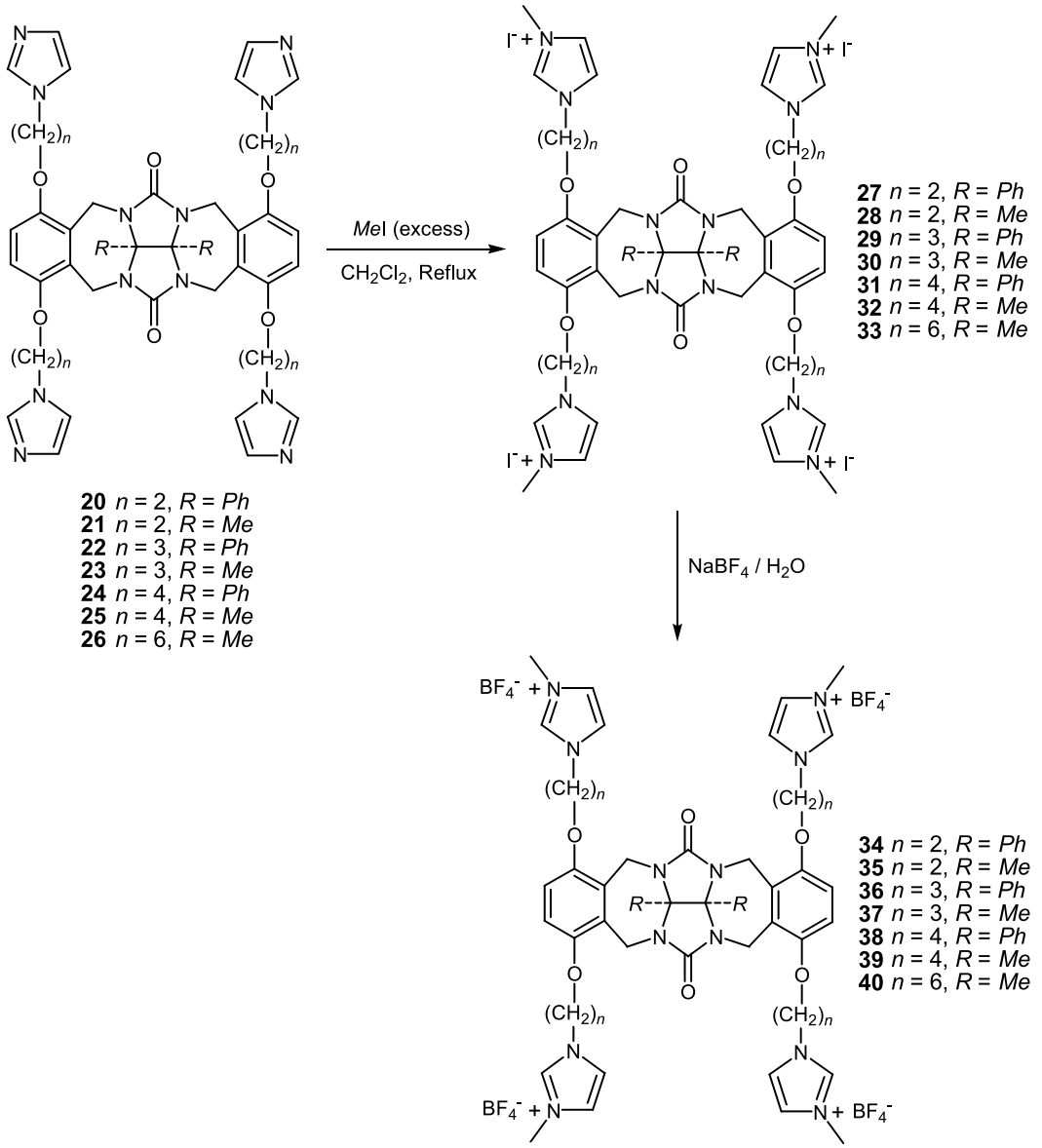
In this paper we describe the synthesis of new molecular clips which contain four alkyl arms substituted with bromine atoms, imidazole, and imidazolium rings.

Results and discussion

The starting **2** was prepared by bromination of 1,4-bis(2-hydroxyethoxy)benzene (**1**) using carbon tetrabromide and triphenylphosphine [10]. Compounds **3**–**5** were obtained from hydroquinone by means of a base-catalyzed oxygen alkylation reaction with **6**–**8** (Scheme 1).

The building block **9** was prepared from urea and 1,2-diphenylethanedione under azeotropic distillation [11]. Subsequent reaction of **9** with paraformaldehyde in the presence of NaOH in *DMSO* yielded the cyclic ether **10** [12] (Scheme 2). The glycoluril derivative **11** that was used as second building block was synthesized from urea and 2,3-butanedione [13]. Reaction of **11** with formaldehyde solution yielded the cyclic ether **12** [13].

To obtain the clip molecules **13**–**19**, the cyclic ethers **10** and **12** were reacted with the aromatic side walls **2**–**5** in a mixture of acetic anhydride and *TFA*



Scheme 4

at 110°C. The reaction took place *via* a *Friedel-Crafts* alkylation mechanism (Scheme 3).

Spectral evidence and elemental analyses clearly confirmed the formation of the molecular clips **13–19**. For example, the ^{1}H NMR spectrum of **14** showed the methyl protons as a singlet at $\delta = 1.75$ ppm, the methylene protons of the four bromoalkyl arms as two multiplets at $\delta = 3.56$–3.66 and 4.06–4.26 ppm, the nonequivalent CH_2N protons as two doublets at $\delta = 3.89$ and 5.47 ppm ($J = 16$ Hz), and finally the aromatic protons as a singlet at $\delta = 6.63$ ppm.

The molecular clips **13–19** could now be used as starting materials for the preparation of several new clips (**20–26**). So, upon reaction of **13–19** with an excess of imidazole in *DMF* in the presence of KOH, the clip molecules **20–26** were synthesized (Scheme 3). In the ^{1}H NMR spectrum of **21**, three singlet peaks pertaining to the imidazole rings protons appeared clearly at $\delta = 6.88$, 7.04, and 7.59 ppm. In the next step, **20–26** were converted to imidazolium salts **27–33** using methyl iodide as methylating agent. These salts were water-soluble and the treatment of them with sodium tetrafluoroborate in hot water gave **34–40** *via* an anion exchange reaction (Scheme 4). The success of the methylation was confirmed well by the ^{1}H NMR spectra. Firstly, by emerging of a singlet peak belonging to the methyl groups bonded to the positively charged nitrogen atoms and secondly, by taking place of downfield shifts in the imidazole rings protons due to the positive charge created on the rings. So in the ^{1}H NMR spectrum of **35**, the methyl groups bonded to the positively charged nitrogens appeared as a singlet at $\delta =$ 3.94 ppm and the imidazole rings protons were observed as three singlets at $\delta = 7.52$, 7.73, and 9.09 ppm.

Experimental

Melting points were recorded on an Electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrometer and only noteworthy absorptions are listed. The ^{1}H NMR (100 MHz) spectra were recorded on a Bruker AC 100 spectrometer. Chemical shifts are reported in ppm downfield from *TMS* as internal standard; coupling constant *J* are given in Hertz. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. 1,4-Di(2-bromoethoxy)benzene (**2**) was synthesized according to Ref. [10]; mp 111–113°C.

*General procedure for synthesis of aromatic side walls **3–5***
A mixture of 0.36 mol dibromo **6–8**, 9.90 g hydroquinone (90 mmol), and 37.26 g potassium carbonate (0.27 mol) in 60 cm^3 acetone was refluxed under N_2 for 24 h. The reaction mixture was concentrated *in vacuo* and the resulting residue was partitioned between 150 cm^3 water and 150 cm^3 chloroform. The organic layer was evaporated to dryness and the precipitate was washed with sodium hydroxide solution (3×50 cm^3, 1 *N*), water (2×50 cm^3), and *n*-hexane (2×50 cm^3), and dried *in vacuo*.

1,4-Di(3-bromopropoxy)benzene (**3**, $C_{12}H_{16}Br_2O_2$)
The title compound was obtained according to the general procedure starting with **6** and hydroquinone. Yield 12.7 g (40%); mp 64–66°C; ^{1}H NMR (100 MHz, $CDCl_3$): $\delta = 2.29$ (qui, $J =$ 6 Hz, 4H), 3.80 (t, $J = 6$ Hz, 4H), 4.05 (t, $J = 6$ Hz, 4H), 6.84 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 822$, 1030, 1233, 1505, 2945 cm^{-1}.

1,4-Di(4-bromobutoxy)benzene (**4**, $C_{14}H_{20}Br_2O_2$)
The title compound was obtained according to the general procedure starting with **7** and hydroquinone. Yield 18.8 g (55%); mp 82–84°C; ^{1}H NMR (100 MHz, $CDCl_3$): $\delta = 1.70$–2.20 (m, 8H), 3.48 (t, $J = 6$ Hz, 4H), 3.94 (t, $J = 6$ Hz, 4H), 6.81 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 826$, 1017, 1233, 1510, 2946 cm^{-1}.

1,4-Di[(6-bromohexyl)oxy]benzene (**6**, $C_{18}H_{28}Br_2O_2$)
The title compound was obtained according to the general procedure starting with **8** and hydroquinone. Yield 15.7 g (40%); mp 81–83°C; ^{1}H NMR (100 MHz, $CDCl_3$): $\delta =$ 1.04–1.40 (m, 8H), 1.65–2.00 (m, 8H), 3.41 (t, $J = 6$ Hz, 4H), 3.90 (t, $J = 6$ Hz, 4H), 6.80 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 835$, 1035, 1225, 1510, 2950 cm^{-1}.

3*a*,6*a*-Diphenylperhydroimidazo[4,5-d]imidazole-2,5-dione (**9**) was synthesized according to Ref. [11]; IR and ^{1}H NMR spectra of the compound were identical with the one described in Ref. [11].

8*b*,8*c*-Diphenylperhydro-2,6-dioxa-3*a*,4*a*,7*a*,8*a*-tetraazacyclopenta[*def*]fluorene-4,8-dione (**10**) was synthesized according to Ref. [12]; IR and ^{1}H NMR spectra of the compound were identical with the one described in Ref. [12].

3*a*,6*a*-Dimethylperhydroimidazo[4,5-*d*]imidazole-2,5-dione (**11**) was synthesized according to Ref. [13]; mp 343–345°C.

8*b*,8*c*-Dimethylperhydro-2,6-dioxa-3*a*,4*a*,7*a*,8*a*-tetraazacyclopenta[def]fluorene-4,8-dione (**12**) was synthesized according to Ref. [13]; mp 350.

*General Procedure for Synthesis of Molecular Clips **13–19***
A 2.64 mmol cyclic ether **10** and **12** were dissolved in a mixture of 2.64 cm^3 *TFA* and 2.64 cm^3 acetic anhydride and the solution was heated at 95°C for 30 min. Then, 5.28 mmol dibromo **2–5** were added to the solution and the mixture heated for 1 h. After cooling, *Me*OH was added carefully and the resulting precipitate was filtered off, washed with *Me*OH, and dried *in vacuo.*

1,4,8,11-Tetra(2-bromoethoxy)-13b,13c-diphenyl-5,7,12, 13b,13c,14-hexa-hydro-5a,6a,12a,13a-tetraazabenzo-[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**13**, $C_{40}H_{38}Br_4N_4O_6$)
The title compound was obtained according to the general procedure starting with **2** and **10**. Yield 1.96 g (75%);

mp 244–246°C; ^{1}H NMR ($CDCl_3$): $\delta = 3.45$–4.40 (m, 20H), 5.55 (d, $J = 16$ Hz, 4H), 6.59 (s, 4H), 7.09 (s, 10H) ppm; IR (KBr): $\bar{\nu} = 1090$, 1260, 1505, 1690, 3065 cm^{-1}.

1,4,8,11-Tetra(2-bromoethoxy)-13b,13c-dimethyl-5,7,12, 13b,13c,14-hexa-hydro-5a,6a,12a,13a-tetraazabenzo-[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**14**, $C_{30}H_{34}Br_4N_4O_6$)
The title compound was obtained according to the general procedure starting with **2** and **12**. Yield 1.83 g (80%); mp 259–262°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.75$ (s, 6H) 3.54–4.40 (m, 20H), 5.47 (d, $J = 16$ Hz, 4H), 6.62 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1090$, 1265, 1360, 1500, 1690, 2920 cm^{-1}.

1,4,8,11-Tetra(3-bromopropoxy)-13b,13c-diphenyl-5,7,12, 13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo-[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**15**, $C_{44}H_{46}Br_4N_4O_6$)
The title compound was obtained according to the general procedure starting with **3** and **10**. Yield 2.00 g (73%); mp 250–253°C; ^{1}H NMR ($CDCl_3$): $\delta = 2.36$ (qui, $J = 6$ Hz, 8H), 3.55–3.90 (m, 12H), 4.07 (t, $J = 6$ Hz, 8H), 5.55 (d, $J = 16$ Hz, 4H), 6.72 (s, 4H), 7.08 (s, 10H) ppm; IR (KBr): $\bar{\nu} = 1070$, 1255, 1460, 1705, 2940 cm^{-1}.

1,4,8,11-Tetra(3-bromopropoxy)-13b,13c-dimethyl-5,7,12, 13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo-[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**16**, $C_{34}H_{42}Br_4N_4O_6$)
The title compound was obtained according to the general procedure starting with **3** and **12**. Yield 1.90 g (78%); mp 132–134°C. ^{1}H NMR ($CDCl_3$): $\delta = 1.89$ (s, 6H), 2.32 (qui, $J = 6$ Hz, 8H), 3.50–4.20 (m, 20H), 5.45 (d, $J = 16$ Hz, 4H), 6.72 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1100$, 1260, 1355, 1470, 1695, 2940 cm^{-1}.

1,4,8,11-Tetra(4-bromobutoxy)-13b,13c-diphenyl-5,7,12,-13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo-[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**17**, $C_{48}H_{54}Br_4N_4O_6$)
The title compound was obtained according to the general procedure starting with **4** and **10**. Yield 2.53 g (87%); mp 199–202°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.70$–2.35 (m, 16H), 3.30–4.13 (m, 20H), 5.50 (d, $J = 16$ Hz, 4H), 6.62 (s, 4H), 7.03 (s, 10H) ppm; IR (KBr): $\bar{\nu} = 1070$, 1254, 1353, 1461, 1711, 2925 cm^{-1}.

1,4,8,11-Tetra(4-bromobutoxy)-13b,13c-dimethyl-5,7,12,-13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo-[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**18**, $C_{38}H_{50}Br_4N_4O_6$)
The title compound was obtained according to the general procedure starting with **4** and **12**. Yield 2.37 g (92%); mp 176–179°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.63$ (s, 6H) 1.75–2.24 (m, 16H), 3.43 (t, $J = 6$ Hz, 8H), 3.65–4.10 (m, 12H), 5.37 (d, $J = 16$ Hz, 4H) 6.64 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1088$, 1254, 1356, 1465, 1703, 2942 cm^{-1}.

1,4,8,11-Tetra[(6-bromohexyl)oxy]-13b,13c-dimethyl-5,7,12, 13b,13c,14-hexa-hydro-5a,6a,12a,13a-tetraazabenzo-[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**19**, $C_{46}H_{66}Br_4N_4O_6$)
The title compound was obtained according to the general procedure starting with **5** and **12**. Yield 2.59 g (90%); mp 176–180°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.33$–2.17 (m, 32H), 1.66 (s, 6H), 3.41 (t, $J = 6$ Hz, 8H), 3.65–4.10 (m, 12H), 5.42 (d, $J = 16$ Hz, 4H), 6.68 (s, 4H) ppm.

*General procedure for synthesis of molecular clips **20–26***
To a mixture of 0.90 g KOH (16 mmol) in 10 cm^3 *DMF* was added 0.27 g imidazole (4 mmol) and the mixture was stirred at room temperature for 30 min. Then, a solution of 1 mmol tetrabromo clips **13–19** in 10 cm^3 *DMF* was gradually added and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was poured into 200 cm^3 water, filtered, and the product was dried *in vacuo*.

1,4,8,11-Tetra[2-(1H-1-imidazolyl)ethoxy]-13b,13c-diphenyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**20**, $C_{52}H_{50}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **13** and imidazole. Yield 0.81 g (86%); mp 285–289°C; ^{1}H NMR ($CDCl_3$): $\delta = 3.74$ (d, $J = 16$ Hz, 4H), 4.05–4.55 (m, 16H), 5.51 (d, $J = 16$ Hz, 4H), 6.52 (s, 4H), 7.02 (s, 4H), 7.13 (s, 14H), 7.68 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1240$, 1462, 1705, 2960, 3070 cm^{-1}.

1,4,8,11-Tetra[2-(1H-1-imidazolyl)ethoxy]-13b,13c-dimethyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**21**, $C_{42}H_{46}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **14** and imidazole. Yield 0.56 g (69%); mp 248–252°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.71$ (s, 6H) 3.65–4.35 (m, 20H), 5.36 (d, $J = 16$ Hz, 4H), 6.40 (s, 4H), 6.88 (s, 4H), 7.04 (s, 4H), 7.59 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1260$, 1355, 1470, 1700, 3075 cm^{-1}.

1,4,8,11-Tetra[3-(1H-1-imidazolyl)propoxy]-13b,13c-diphenyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**22**, $C_{56}H_{58}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **15** and imidazole. Yield 0.85 g (86%); mp 230–233°C; ^{1}H NMR ($CDCl_3$): $\delta = 2.03$ (qui, $J = 6$ Hz, 8H), 3.50–4.08 (m, 12H), 4.22 (t, $J = 6$ Hz, 8H), 5.67 (d, $J = 16$ Hz, 4H), 6.59 (s, 4H), 6.90 (s, 4H), 7.01 (s, 4H), 7.16 (s, 10H), 7.52 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1255$, 1358, 1465, 1705, 2970 cm^{-1}.

1,4,8,11-Tetra[3-(1H-1-imidazolyl)propoxy]-13b,13c-dimethyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione
(**23**, $C_{46}H_{54}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **16** and imidazole. Yield 0.60 g

(69%); mp 86–88°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.78$ (s, 6H), 2.04 (qui, $J = 6$ Hz, 8H), 3.50–4.30 (m, 20H), 5.54 (d, $J = 16$ Hz, 4H), 6.55 (s, 4H), 6.83 (s, 4H), 6.95 (s, 4H), 7.43 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1085$, 1260, 1473, 1702, 3055 cm^{-1}.

1,4,8,11-Tetra[4-(1H-1-imidazolyl)butoxy]-13b,13c-diphenyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione (**24**, $C_{60}H_{66}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **17** and imidazole. Yield 0.90 g (86%); mp 163–166°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.60$–2.25 (m, 16H), 3.60–4.23 (m, 20H), 5.58 (d, $J = 16$ Hz, 4H), 6.60 (s, 4H), 6.95 (s, 4H), 7.10 (s, 14H), 7.55 (s, 4H), 7.08 (s, 10H) ppm; IR (KBr): $\bar{\nu} = 1073$, 1256, 1353, 1461, 1706, 2934 cm^{-1}.

1,4,8,11-Tetra[4-(1H-1-imidazolyl)butoxy]-13b,13c-dimethyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione (**25**, $C_{50}H_{62}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **18** and imidazole. Yield 0.62 g (67%); mp 110–113°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.72$ (s, 6H), 1.80–2.25 (m, 16H), 3.65–4.10 (m, 20H), 5.48 (d, $J = 16$ Hz, 4H), 6.59 (s, 4H), 6.88 (s, 4H), 6.98 (s, 4H), 7.49 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1084$, 1255, 1357, 1697, 2931 cm^{-1}.

1,4,8,11-Tetra[6-(1H-1-imidazolyl)hexyl]oxy-13b,13c-dimethyl-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraaza-benzo[5,6]azuleno[2,1,8-ija]benzo[f]azulene-6,13-dione (**26**, $C_{58}H_{78}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **19** and imidazole. Yield 0.72 g (69%); viscous oil; ^{1}H NMR ($CDCl_3$): $\delta = 1.15$–2.05 (m, 32H), 1.89 (s, 6H), 3.60–4.15 (m, 20H), 5. 49 (d, $J = 16$ Hz, 4H), 6.65 (s, 4H), 6.91 (s, 4H), 7.03 (s, 4H), 7.47 (s, 4H) ppm.

*General procedure for synthesis of molecular clips **34–40***
A solution of 0.2 mmol tetraimidazo clips **20–26**, 5 cm^3 methyl iodide**,** and 5 cm^3 dichloromethane was refluxed for 16 h. After concentration *in vacuo*, the oily residue was dissolved in 30 cm^3 hot water and then a solution of 0.21 g sodium tetrafluoroborate (2 mmol) in 15 cm^3 water was added and the reaction mixture was stirred at room temperature for 48 h. Finally, the product was filtered off, washed with water, and dried *in vacuo*.

1-[2-(13b,13c-Diphenyl-4,8,11-tri[2-(3-methyl-1H-imidazol-3-ium-1-yl)ethoxy]-6,13-dioxo-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-ija]benzo-[f]azulen-1-yloxy)ethyl]-3-methyl-1H-imidazol-3-ium tetrakis(tetrafluoroborate) (**34**, $C_{56}H_{62}B_4F_{16}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **20** and methyl iodide. Yield 0.22 g (81%); mp 275–278°C; ^{1}H NMR (Acetone-d_6): $\delta = 3.83$ (d, $J = 16$ Hz, 4H), 4.01 (s, 12H), 4.34–4.50 (m, 8H), 4.76 (t, $J = 6$ Hz, 8H), 5.52 (d, $J = 16$ Hz, 4H), 6.77 (s, 4H), 7.16 (s, 10H), 7.57 (s, 4H), 7.77 (s, 4H), 9.21 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1104$, 1231, 1370, 1464, 1710, 2935 cm^{-1}.

1-[2-(13b,13c-Dimethyl-4,8,11-tri[2-(3-methyl-1H-imidazol-3-ium-1-yl)ethoxy]-6,13-dioxo-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-ija]benzo-[f]azulen-1-yloxy)ethyl]-3-methyl-1H-imidazol-3-ium tetrakis(tetrafluoroborate) (**35**, $C_{46}H_{58}B_4F_{16}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **21** and methyl iodide. Yield 0.20 g (82%); mp 225–227°C; ^{1}H NMR (Acetone-d_6): $\delta = 1.84$ (s, 6H), 3.94 (s, 12H), 4.14 (d, $J = 16$ Hz, 8H), 4.25–4.40 (m, 8H), 4.73 (t, $J = 6$ Hz, 8H), 5.32 (d, $J = 16$ Hz, 4H), 6.74 (s, 4H), 7.52 (s, 4H), 7.73 (s, 4H), 9.09 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1090$, 1272, 1365, 1475, 1690, 3050 cm^{-1}.

1-[2-(13b,13c-Diphenyl-4,8,11-tri[3-(3-methyl-1H-imidazol-3-ium-1-yl)propoxy]-6,13-dioxo-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-ija]benzo-[f]azulen-1-yloxy)ethyl]-3-methyl-1H-imidazol-3-ium tetrakis(tetrafluoroborate) (**36**, $C_{60}H_{70}B_4F_{16}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **22** and methyl iodide. Yield 0.21 g (76%); mp 194–196°C; ^{1}H NMR (Acetone-d_6): $\delta = 2.35$ (qui, $J = 6$ Hz, 8H), 3.70–4.20 (m, 24H), 4.69 (t, $J = 6$ Hz, 8H), 5.63 (d, $J = 16$ Hz, 4H), 6.78 (s, 4H), 7.23 (s, 4H), 7.61 (s, 4H), 7.72 (s, 4H), 9.01 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1095$, 1260, 1370, 1465, 1695, 3070 cm^{-1}.

1-[2-(13b,13c-Dimethyl-4,8,11-tri[3-(3-methyl-1H-imidazol-3-ium-1-yl)propoxy]-6,13-dioxo-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-ija]benzo-[f]azulen-1-yloxy)ethyl]-3-methyl-1H-imidazol-3-ium tetrakis(tetrafluoroborate) (**37**, $C_{50}H_{66}B_4F_{16}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **23** and methyl iodide. Yield 0.21 g (82%); mp 68–70°C; ^{1}H NMR (Acetone-d_6): $\delta = 1.93$ (s, 6H), 2.30 (qui, $J = 6$ Hz, 8H), 3.70–4.35 (m, 24H), 4.62 (t, $J = 6$ Hz, 8H), 5.44 (d, $J = 16$ Hz, 4H), 6.76 (s, 4H), 7.56 (s, 4H), 7.65 (s, 4H), 8.96 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1105$, 1265, 1370, 1470, 1705, 3050 cm^{-1}.

1-[2-(13b,13c-Diphenyl-4,8,11-tri[4-(3-methyl-1H-imidazol-3-ium-1-yl)butoxy]-6,13-dioxo-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-ija]benzo-[f]azulen-1-yloxy)ethyl]-3-methyl-1H-imidazol-3-ium tetrakis(tetrafluoroborate) (**38**, $C_{64}H_{78}B_4F_{16}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **24** and methyl iodide. Yield 0.21 g (72%); mp 85–87°C; ^{1}H NMR (Acetone-d_6): $\delta = 1.65$–2.53 (m, 16H), 3.50–4.25 (m, 24H), 4.43 (t, $J = 6$ Hz, 8H), 5.60 (d, $J = 16$ Hz, 4H), 6.65 (s, 4H), 7.20 (s, 10H), 7.58 (s, 4H), 7.70

(s, 4H), 8.90 (s, 4H) ppm; IR (KBr): $\bar{\nu} = 1168$, 1257, 1304, 1463, 1695, 3071 cm^{-1}.

1-[2-(13b,13c-Dimethyl-4,8,11-tri[4-(3-methyl-1H-imidazol-3-ium-1-yl)butoxy]-6,13-dioxo-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-ija]benzo-[f]azulen-1-yloxy)ethyl]-3-methyl-1H-imidazol-3-ium tetrakis(tetrafluoroborate) (**39**, $C_{54}H_{74}B_4F_{16}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **25** and methyl iodide. Yield 0.21 g (79%); viscous oil; ^{1}H NMR (Acetone-d_6): $\delta = 1.60$–2.45 (m, 22H), 3.60–4.25 (m, 24H), 4.33 (t, $J = 6$ Hz, 8H), 5.38 (d, $J = 16$ Hz, 4H), 6.58 (s, 4H), 7.49 (s, 4H), 7.59 (s, 4H), 8.87 (s, 4H) ppm; IR (KBr): 1163, 1255, 1353, 1466, 1686, 3073 cm^{-1}.

1-[2-(13b,13c-Dimethyl-4,8,11-tri[6-(3-methyl-1H-imidazol-3-ium-1-yl)hexyl]oxy-6,13-dioxo-5,7,12,13b,13c,14-hexahydro-5a,6a,12a,13a-tetraazabenzo[5,6]azuleno[2,1,8-ija]benzo-[f]azulen-1-yloxy)ethyl]-3-methyl-1H-imidazol-3-ium tetrakis(tetrafluoroborate) (**40**, $C_{62}H_{90}B_4F_{16}N_{12}O_6$)
The title compound was obtained according to the general procedure starting with **26** and methyl iodide. Yield 0.20 g (69%); viscous oil; ^{1}H NMR (Acetone-d_6): $\delta = 1.10$–1.95 (m, 32H), 1.78 (s, 6H), 3.50–4.40 (m, 32H), 5.37 (d, $J = 16$ Hz, 4H), 6.58 (s, 4H), 7.53 (s, 4H), 7.64 (s, 4H), 8.79 (s, 4H) ppm; IR (KBr): 1163, 1255, 1353, 1466, 1686, 3073 cm^{-1}.

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