Syntheses of Acyclic and Macrocyclic Compounds Derived from 9,9-Diethylfluorene (Part I)

Pierre Seidel and Monika Mazik*[a]

A series of new 9,9-diethylfluorenes consisting of three side-arms each bearing a heterocyclic, bis(carboxymethyl)amino, bis(carbamoylmethyl)amino, bis(ethoxycarbonylmethyl)amino or an amino group were prepared on the basis of 2,4,7-tris(bromomethyl)-9,9-diethylfluorene. Imidazolyl, benzimidazolyl, pyrazolyl, pyrrolyl, 1,3-dioxoisoindolyl and pyridinium groups were taken into account as heterocyclic units, attached to the aromatic skeleton via –CH_2–, –CH_2NHCH_2– or –CH_2N=CH– linkers. In addition to the seventeen 2,4,7-trisubstituted 9,9-diethylfluorenes, two macrocyclic compounds were prepared on the basis of 2,7-bis(aminomethyl)-9,9-diethylfluorene. The excellent yield of the macrocyclization reaction is worth a special mention. Both the acyclic and the macrocyclic fluorene-based compounds have, among other things, the potential to act as artificial receptors for different substrates in analogy to the known receptors consisting of a benzene or biphenyl core.

Introduction

Fluorene-based acyclic and macrocyclic molecules[1] as well as polymers[2] have been reported to have the potential for numerous applications ranging from organic transistors, solar cells and organic light-emitting diodes to lasers. Compounds featuring a fluorene moiety have been further recognized as chemosensors for some cationic,[3a–c] anionic[3d] and neutral substrates[4] as well as agents for cell imaging.[5] In addition, fluorene derivatives have shown interesting biological activities, including antibacterial,[6a] antiviral,[6b] anticancer[7] and some others.[8] Due to the above mentioned manifold application possibilities of fluorene-based compounds, the syntheses of new representatives of this class of compounds and the investigation of their chemical, physical and biological properties remain the subject of intensive research.

Recently we have described the syntheses and crystal structures of halogenomethyl-substituted 9,9-diethylfluorenes **1**–**3** (Figure 1), which are not only valuable starting materials for the preparation of various fluorene-based compounds, but also interesting building blocks for the formation of different supramolecular motifs in the crystalline state.[9] For example, the crystal structure of the iodomethyl substituted derivative **3** is characterized by the presence of an unusual triangular I_3 synthon consisting of two I···I contacts with type I geometry and one I···I contact that corresponds to the polarization-induced type II category. Regarding the synthetic applications described in our previous work,[9] the efficient one-step synthesis of 9,9-diethylfluorene-2,4,7-tricarbaldehyde (**4**) on the basis of 2,4,7-tris(bromomethyl)-9,9-diethylfluorene (**2**), providing three-fold higher yield of **4** than the known three-step reaction sequence, is worthy of particular mention.

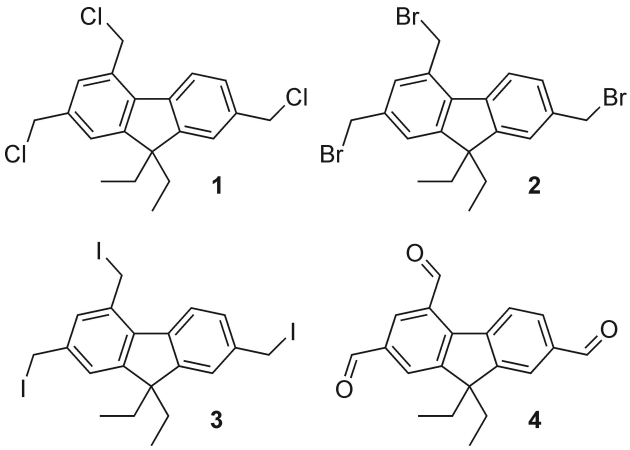


Figure 1. Structures of fluorene derivatives **1**–**4**, the syntheses and crystal structures of which we have previously reported.[9]

In this paper we describe the application of compound **2** for the syntheses of seventeen 9,9-diethylfluorenes consisting of three side-arms each bearing a heterocyclic, bis(carboxymethyl)amino, bis(carbamoylmethyl)amino, bis(ethoxycarbonylmethyl)amino or an amino group (compounds **5**–**21**; see Figure 2). The above mentioned heterocyclic units, including 1*H*-imidazol-1-yl, 1*H*-imidazol-2-yl, 1*H*-benzimidazol-1-yl, 2-bromo-1*H*-benzimidazol-1-yl, 3,5-dimethyl-1*H*-pyrazol-1-yl, 4-bromo-1*H*-pyrazol-1-yl, 4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl, 4-iodo-3,5-dimethyl-1*H*-pyrazol-1-yl, 1*H*-pyrrol-2-yl, 1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl and pyridinium groups, are linked to the fluorene skeleton by –CH_2– (compounds **5**–**12**), –CH_2NHCH_2– (**19** and **21**) or –CH_2N=CH– units (**18** and **20**).

[a] *P. Seidel, Prof. Dr. M. Mazik*
Institut für Organische Chemie
Technische Universität Bergakademie Freiberg
Leipziger Strasse 29
09599 Freiberg (Germany)
E-mail: monika.mazik@chemie.tu-freiberg.de

Supporting information for this article is available on the WWW under https://doi.org/10.1002/open.202000268

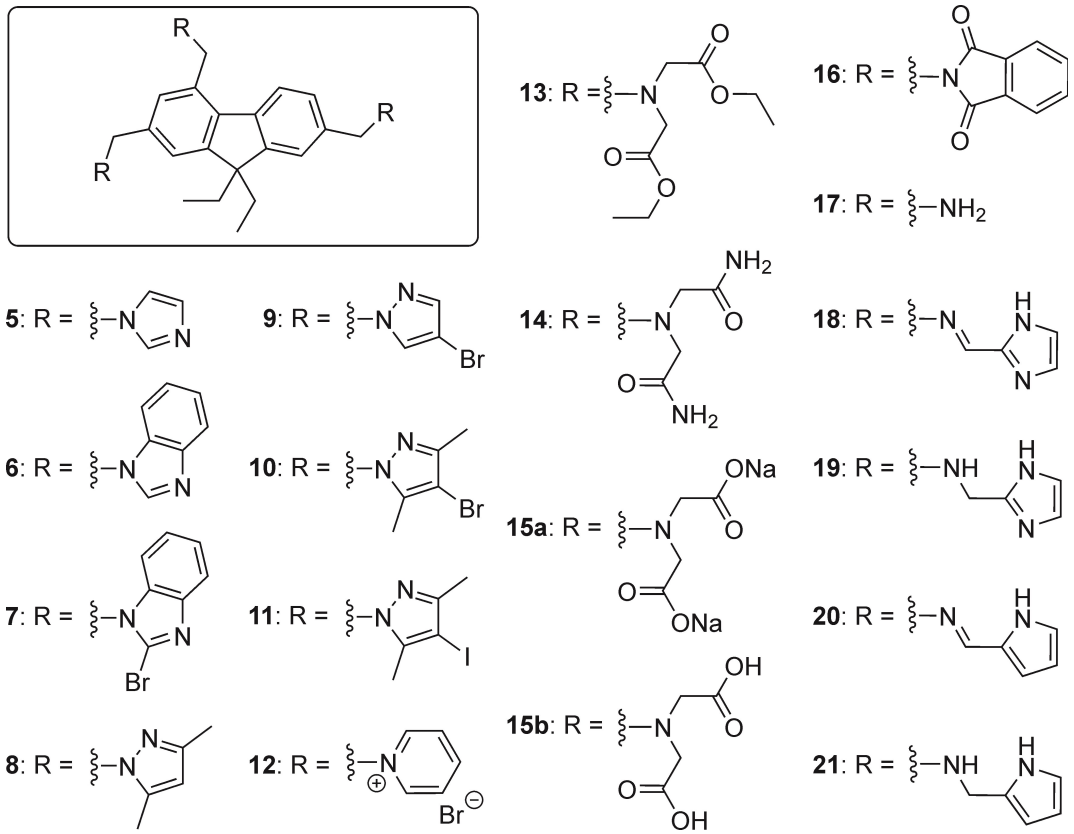


Figure 2. Structures of the 2,4,7-trisubstituted 9,9-diethylfluorenes **5**–**21**.

Furthermore, we report the synthesis of macrocyclic compounds **24** and **25** (Figure 3) on the basis of 2,7-bis(aminomethyl)-9,9-diethylfluorene (**23**). The synthesis of the last mentioned compound from the analogue bearing two 1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl groups (compound **22**) is also considered in this work.

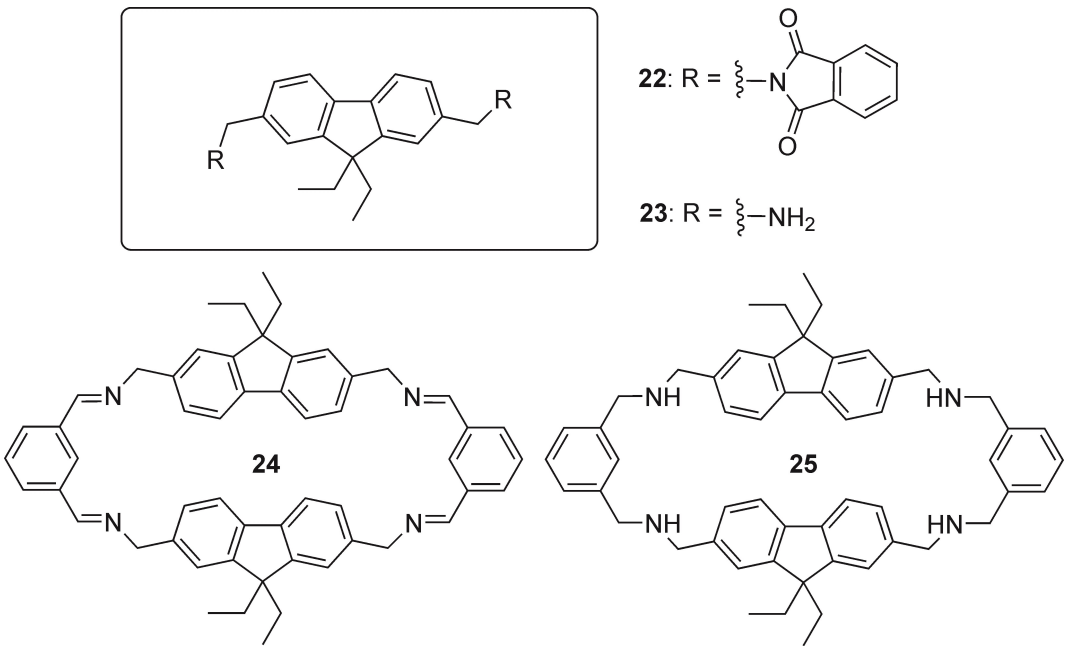


Figure 3. Structures of the 2,7-disubstituted 9,9-diethylfluorenes **22** and **23** as well as of the fluorene-based macrocycles **24** and **25**.

Both the acyclic and the macrocyclic fluorene-based compounds have among other things the potential to act as artificial receptors for different ionic and neutral substrates in the analogy to the known receptors possessing a benzene[10–14] or biphenyl[15] core. For example, some representatives of the acyclic and macrocyclic compounds consisting of the central benzene or biphenyl unit were found to be effective receptors for such substrates as ammonium ions,[11] ion pairs[12] or carbohydrates.[10,14]

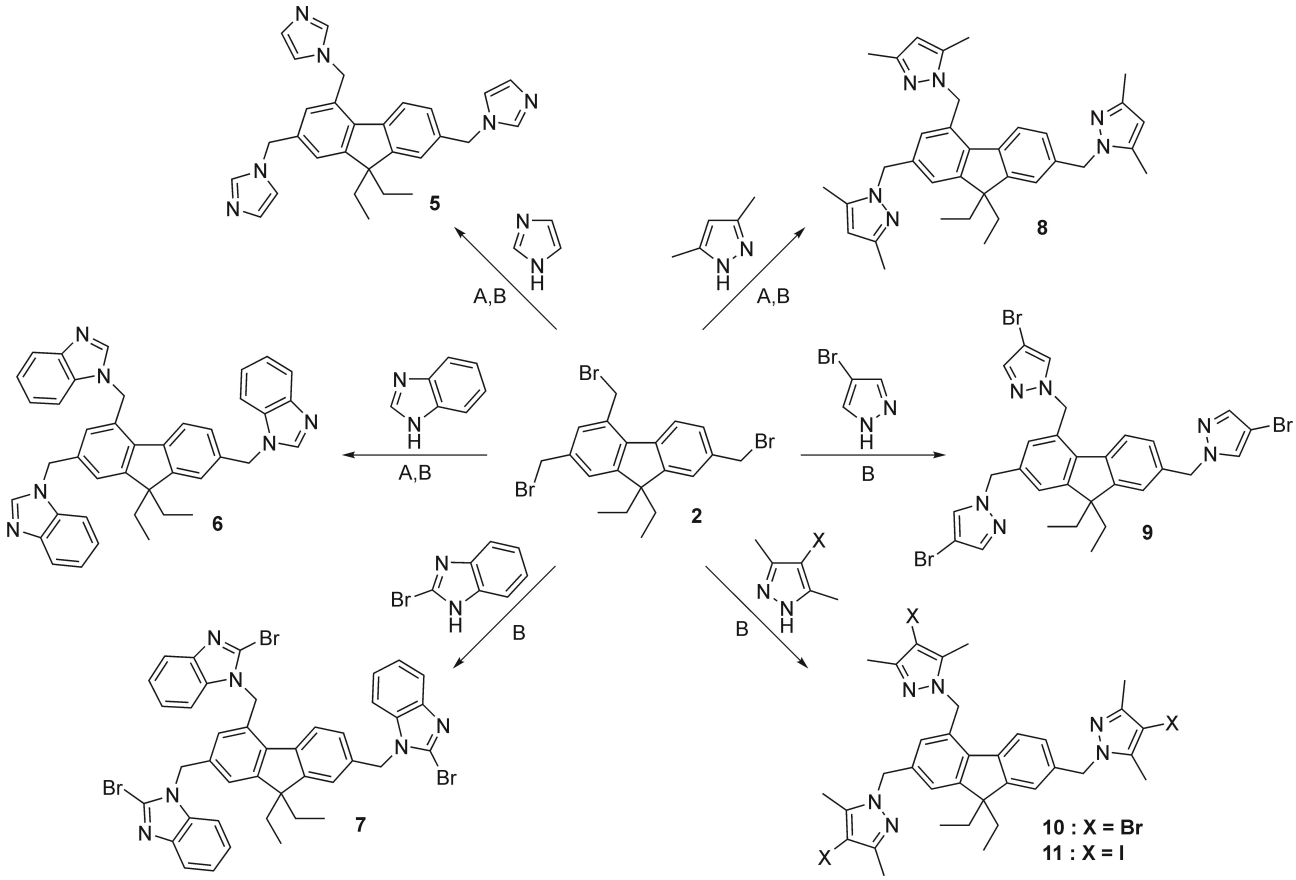
Results and discussion

Syntheses of compounds 5–11

Imidazolyl, benzimidazolyl, pyrazolyl and pyrrolyl groups were shown to be valuable building blocks of benzene- and biphenyl-based compounds, which have been developed as artificial receptors for carbohydrates[10c,f–j,14,15c] or ammonium ions.[11a–e] In this context, these groups have been also considered as subunits of fluorene-based derivatives **5**–**11** and **18**–**21**.

9,9-Diethylfluorenes consisting of three side-arms each bearing an imidazolyl (compound **5**), a benzimidazolyl (compounds **6** and **7**) or a pyrazolyl group (compounds **8**–**11**) were prepared by the reaction of 2,4,7-tris(bromomethyl)-9,9-diethylfluorene (**2**) with 1*H*-imidazole, 1*H*-benzimidazole, 2-bromo-1*H*-benzimidazole, 3,5-dimethyl-1*H*-pyrazole, 4-bromo-1*H*-pyrazole, 4-bromo-3,5-dimethyl-1*H*-pyrazole or 4-iodo-3,5-dimethyl-1*H*-pyrazole (see Scheme 1). Reaction conditions like temperature, time and the used base were varied to obtain the highest yields of the desired products.

Starting with the synthesis of the derivative **5** consisting of side-arms bearing 1*H*-imidazol-1-yl groups, precursor **2** was treated with 1*H*-imidazole in tetrahydrofuran at room temperature in the presence of *N*,*N*-diisopropylethylamine as a base. The progress of the reaction was monitored by thin layer chromatography (TLC), indicating a complete conversion of the starting material after 24 hours. The purification of the raw product via column chromatography provided compound **5** with 43% yield. One factor responsible for this low yield is the formation of cationic species by a substitution of the second ring-nitrogen of the imidazole-moiety under the used reaction conditions. The same reaction procedure was tested for the synthesis of the analogue bearing 1*H*-benzimidazol-1-yl groups (compound **6**); however, remarkably large quantities of the 2,7-disubstituted intermediate were detected even after three days of reaction time. The low reaction rate is caused by the more bulky nucleophilic reagent (1*H*-benzimidazole) in combination with the steric interactions between the substituents in C-4 and



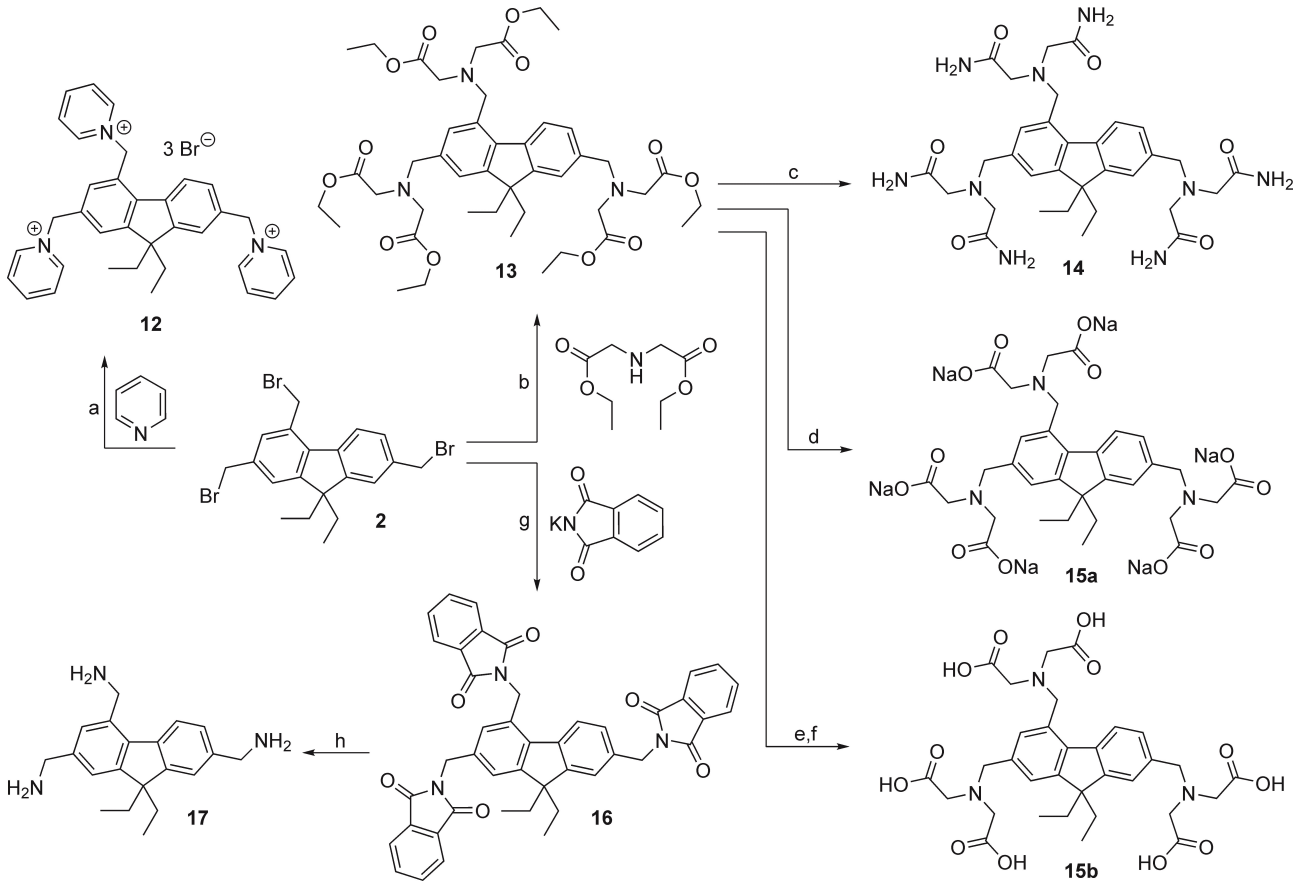
Scheme 1. Syntheses of the imidazolyl-, benzimidazolyl- and pyrazolyl-functionalized derivatives **5**–**11**. Procedure A: THF, DIPEA, room temperature (24 h) or reflux (8 h); Procedure B: THF, NaH, reflux (8 h); compound **11** was synthesized and purified under exclusion of light. Yields: 43% (**A**) and 80% (**B**) of **5**; 36% (**A**) and 87% (**B**) of **6**; 94% (**B**) of **7**; 67% (**A**) and 82% (**B**) of **8**; 77% (**B**) of **9**; 83% (**B**) of **10**; 97% (**B**) of **11**.

C-5 position of the fluorene ring, resulting from the close proximity between the two positions (bay region).[16] It should be noted that NOESY experiments of the synthesized 2,4,7-trisubstituted derivatives clearly indicate a strong coupling between the CH_2-group at C-4 and the proton at C-5. Performing the above mentioned reaction under reflux conditions for 8 hours enabled the synthesis of the desired product **6**, but only with 36% yield. Additionally to the higher reaction temperature, a stronger nucleophilicity of the substitution reagent is crucial to overcome the steric hindrance at the bay region, which can be easily achieved by using a strong base. Consequently, compound **6** was synthesized via a slightly varied route, including deprotonation of 1*H*-benzimidazole by sodium hydride (60% dispersion in mineral oil). Carrying out this reaction under reflux conditions for 8 hours was sufficient to prevent an incomplete substitution and compound **6** could be obtained with 87% yield. Applying the same procedure to the synthesis of compounds **5** and **7** allowed their preparation with 80% and 94% yield, respectively. In the case of **5**[17] stirring at room temperature for 24 hours yielded a better result than refluxing for 8 hours.

A similar observation as in the case of the synthesis of **6** was made synthesizing **8** by treatment of **2** with 3,5-dimethyl-1*H*-pyrazole in the presence of *N*,*N*-diisopropylethylamine. The 3,5-dimethyl-1*H*-pyrazole was also found to be less favourable for a substitution in the bay region of the fluorene, since refluxing the reaction mixture for 8 hours gave only a small amount of product **8**, as observed by TLC analysis. Increasing the reaction time to 16 hours accomplished 67% yield of **8**, but yet there were still disubstituted intermediates detectable. Consequently, both the compound **8** as well as the other derivatives containing pyrazolyl groups (compounds **9**–**11**) were prepared through refluxing the starting material **2** with the corresponding pyrazole derivative in the presence of sodium hydride. After 8 hours reaction time and the purification via column chromatography the desired compounds **8**–**11** could be obtained with yields ranged from good to excellent (82% of **8**, 77% of **9**, 83% of **10** and 97% of **11**).

Syntheses of compounds 12–17

The fluorene derivative containing pyridinium groups (compound **12**; see Figure 2 and Scheme 2) was readily accessible by refluxing the starting material **2** with pyridine in chloroform for 4 hours. As the transformation of all three bromomethyl units ran efficiently, this reaction was also applied as an intermediate step for purification purposes. This represents a particularly



Scheme 2. Syntheses of the compounds **12**–**17**. Reagents and conditions: (a) $CHCl_3$, 4 h, reflux, (92% of **12**); (b) THF/MeCN, K_2CO_3, 8 h, reflux (88% of **13**); (c) 7N NH_3 in MeOH, 7 d, room temperature (71% of **14**); (d) MeOH/THF, 1N aq. NaOH, 24 h, room temperature (51% of **15a**); (e) MeOH, KOH, 8 h, 40 °C; (f) 2N HCl, 1 h, room temperature (72% of **15b**); (g) DMSO, 4 h, 80 °C (91% of **16**); (h) EtOH/Toluene, N_2H_4 (64% aq. sol.), 8 h, reflux (84% of **17**).

valuable purification method, since in the case of some reactions of compound **2** with various nucleophiles, a relatively high purification effort was a remaining issue. Due to similar retention factors, even small amounts of incompletely substituted derivatives made a clean isolation of some target compounds somewhat troublesome. The successful application of this purification method can be demonstrated, for example, by the procedure used in the synthesis of compound **13**. Refluxing diethyl iminodiacetate and **2** in tetrahydrofuran/acetonitrile in the presence of potassium carbonate for 8 hours provided only 31% of the target compound **13** in pure form, because the major part was still contaminated with small amounts of the 2,7-disubstituted intermediate, even after an elaborate chromatographic purification. Treating the raw product with pyridine under reflux conditions transferred all remaining intermediates into pyridinium bromide salts, which can be easily separated from the product (see experimental part). In this way, the yield of compound **13** was increased to 88%.

Compound **13** also represents a precursor for the syntheses of further fluorene derivatives, such as **14** and **15a**/**b**, containing carboxamide and carboxyl groups, respectively. The ammonolysis of **13** in methanol at room temperature yielded 71% of **14** and the saponification of **13** with sodium hydroxide, diluted in a mixture consisting of tetrahydrofuran, methanol and water, provided the sodium salt **15a** (51%). For the synthesis of **15b** the saponification of **13** with potassium hydroxide in dry methanol[18] was used, followed by the acidification with 2N $HCl_{(aq.)}$. It should be noted, that the intermediate potassium salt has to be free of any traces of alcohol before adding acidic solutions, since reesterification already occurs at neutral pH. After several purification steps, the product **15b** was obtained as a white solid (72%).

In addition to fluorenes bearing halogenomethyl or formyl groups, the aminomethyl-functionalized derivatives are useful starting materials for a wide range of fluorene-based compounds. The *Gabriel synthesis* represents a common method to generate amino groups via a two-step procedure, starting with the reaction of potassium phthalimide with the corresponding bromomethyl derivative in dimethylsulfoxide. During the synthesis of **16**, significant amounts of the 4-formyl-substituted derivative were formed via *Kornblum oxidation*,[19] making the isolation of **16** complicated. Since this side reaction already occurred in significant amounts at room temperature, the contact time of compound **2** with the solvent was reduced to a necessary minimum. The reaction procedure included the heating of the suspension of potassium phthalimide in dimethylsulfoxide to the reaction temperature and afterwards the addition of compound **2** in portions without dissolving beforehand. After quenching and repeated washing with water, the dried raw product was found to be already of acceptable purity. Recrystallization from tetrahydrofuran/chloroform gave the pure product **16** with 91% yield. The subsequent *Ing-Manske* workup[20] yielded the 2,4,7-tris(aminomethyl)-9,9-diethylfluorene (**17**) in good yield (84%) and without further purification needs.

Syntheses of compounds 18–21

The condensation reactions of 2,4,7-tris(aminomethyl)-9,9-diethylfluorene (**17**) with 1*H*-imidazole-2-carbaldehyde and 1*H*-pyrrole-2-carbaldehyde to the corresponding imine derivatives **18** and **20** (see Scheme 3) were executed under nitrogen atmosphere in dry solvents. Compound **18** was synthesized by reacting **17** with 1*H*-imidazol-2-carbaldehyde in methanol and a catalytic amount of acetic acid. The raw product was purified by repeated precipitation from diethylether, yielding 74% of **18**. Due to the problematic isolation of **18**, the in situ reduction of the imine was followed to obtain the corresponding amino-functionalized derivative **19**. To remove the water formed during the condensation reaction, triethyl orthoformate instead of acetic acid was added to the reaction mixture. After refluxing for 4 hours and subsequent cooling, sodium borohydride was added and the mixture stirred overnight at room temperature. Remaining borate residues were hydrolysed and the obtained raw product was purified by column chromatography, yielding 44% of **19**. The main concern is the poor solubility of **19** in organic solvents other than methanol or dimethylsulfoxide, causing a significant loss during the aqueous work up, which can hardly be circumvented.

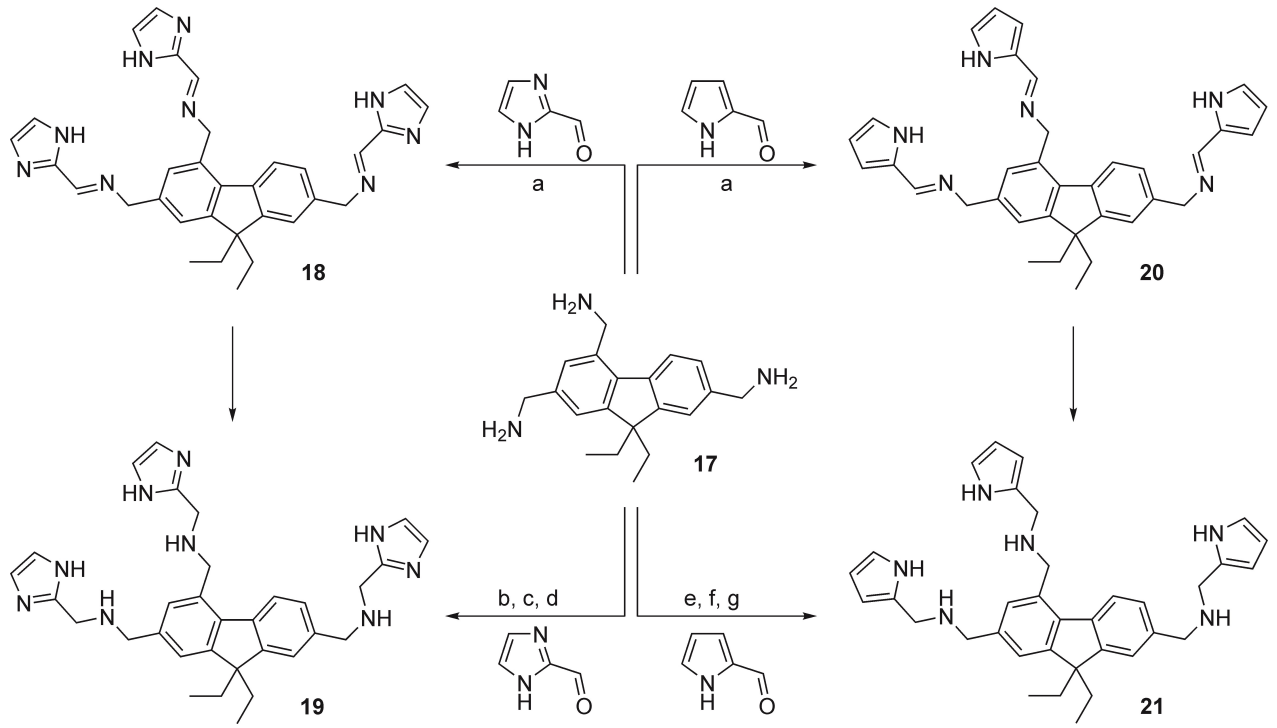
The same procedures were used for the synthesis of compounds **20** and **21** bearing 1*H*-pyrrol-2-yl groups and gave these two products with 24% and 20% yield, respectively.

Syntheses of compounds 22–25

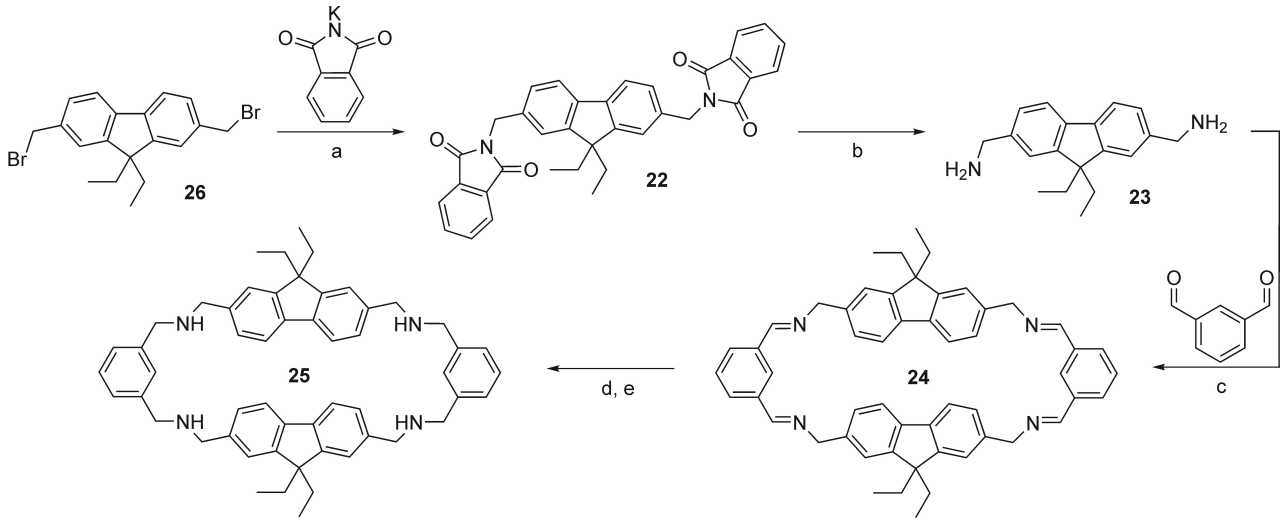
As already mentioned above, besides the acyclic 2,4,7-trisubstituted 9,9-diethylfluorenes, the fluorene-based macrocycles, such as **25**, have the potential to act as artificial receptors. In order to determine the best conditions for the macrocyclization reaction between 2,7-bis(aminomethyl)-9,9-diethylfluorene (**23**) and an aromatic bis-aldehyde, the first reactions have been carried out using the commercially available isophthalaldehyde. It should be noted that different factors influence the development of efficient syntheses of macrocyclic structures and such factors as well as the problems associated with the macrocyclization process have been often discussed in the literature.[21] The development of methods for the synthesis of various cyclophane tetraamines has been the subject of research for years and many interesting results have been published (for examples, see ref. [22]).

2,7-Bis(aminomethyl)-9,9-diethylfluorene (**23**) was prepared from **26**[23] via a *Gabriel synthesis*, including the preparation of the derivative **22** (67% yield, see Scheme 4) and its subsequent hydrazinolysis to **23** (97% yield).

The reaction of **23** with isophthalaldehyde was carried out in dry ethanol in the presence of a catalytic amount of acetic acid at 40 °C for 8 hours. As the mixture was heated, a solid was already formed, changing from sticky to finely dispersed over time. After the separation of this solid by using a centrifuge, the pure product could be obtained by thoroughly washing with ethanol. This procedure allowed the synthesis of **24** with excellent yield of 96%. It has to be pointed out, that the



Scheme 3. Syntheses of the imines **18** and **20** as well as the amines **19** and **21**. Reagents and conditions: (a) dry MeOH, cat. AcOH, 24 h, room temperature (74% of **18**, 24% of **20**); (b) dry MeOH, $(EtO)_3CH$, 4 h, reflux; (c) dry MeOH, $NaBH_4$, overnight, room temperature; (d) $MeOH/H_2O$, 2 h, room temperature (44% of **19**); (e) dry CH_2Cl_2, molecular sieves (4 Å), 8 h, reflux; (f) dry CH_2Cl_2/MeOH, $NaBH_4$, overnight, room temperature; (g) CH_2Cl_2/MeOH/H_2O, 2 h, room temperature (20% of **21**).



Scheme 4. Syntheses of the 2,7-disubstituted derivatives **22** and **23** as well as of the fluorene-based macrocycles **24** and **25**. Reagents and conditions: (a) DMSO, 4 h, 80 °C (67% of **22**); (b) EtOH/Toluene, N_2H_4 (64% aq. solution), 8 h, reflux (97% of **23**); (c) dry EtOH, AcOH (cat. amount), 8 h, 40 °C (96% of **24**); (d) dry MeOH/CH_2Cl_2, $NaBH_4$, overnight, room temperature; (e) CH_2Cl_2/MeOH/H_2O, 2 h, room temperature (83% of **25**).

starting materials have to be fully free of impurities or water, that impede a clean precipitation of the imine derivative or promoting the formation of open chained side products, respectively. The subsequent reduction of **24** with sodium borohydride in a mixture of dry methylene chloride and methanol (1 : 1, *v/v*) gave **25** with 83% yield.

Conclusion

2,4,7-Tris(bromomethyl)-9,9-diethylfluorene (**2**) has been successfully used for the syntheses of seventeen 9,9-diethylfluorenes consisting of three side-arms each bearing a heterocyclic, bis(carboxymethyl)amino, bis(carbamoylmethyl)amino, bis(ethoxycarbonylmethyl)amino or an amino group (compounds **5**–

21; see Figure 2). Imidazolyl, benzimidazolyl, pyrazolyl, pyrrolyl, 1,3-dioxoisoindolyl and pyridinium groups were taken into account as heterocyclic units, attached to the aromatic skeleton via $-CH_2-$, $-CH_2NHCH_2-$ or $-CH_2N{=}CH-$ linkers. It is worth noting that elegant methods have been developed to avoid the problematic isolation of some target compounds. For example, the ester-functionalized derivative **13** could be obtained in very good yield by converting the bromomethyl substituted fluorenes, which are present in the crude mixture, into the corresponding pyridinium derivatives. These could easily be separated from the desired product.

Based on the knowledge gained from this study, the syntheses of compounds displaying not identically substituted side-arms are now in progress (for examples, see Figure 4). Both the compounds **5**–**21** as well as the derivatives of the type shown in Figure 4 are all potentially suitable to act as artificial receptors. The design of the fluorene derivatives bearing different functional groups is inspired by the results of binding studies with benzene-based receptor molecules. These studies revealed that compounds consisting of side-arms bearing different types of functional groups (acting as recognition units) are often more selective receptors than those that consist of identical recognition units.

The fluorene-based macrocycles[24] **24** and **25** have been successfully synthesized through the reaction of 2,7-bis (aminomethyl)-9,9-diethylfluorene (**23**) with isophthalaldehyde. The excellent yield of the macrocyclization reaction (96%) is worth a special mention. The syntheses of further macrocycles are now in progress and involve the preparation of compounds with different substituents in the 9 position of the fluorene ring (units X in the Figure 5a) as well as with different bridge units (units Y). Such macrocycles are designed to recognize disaccharides like β-maltoside, as shown in Figure 5b (in analogy to the effective recognition of monosaccharides by benzene-based macrocycles[14]).

Experimental Section

Melting points (uncorrected) were measured on a hot stage microscope (Büchi 510). FT-IR spectra were obtained from a Perkin Elmer FT-IR 1600 spectrometer as KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III-500 MHz spectrometer using Me_4Si as internal standard. Mass spectra were recorded on a solariX 15T FT-ICR-MS (Bruker Daltonic). 1*H*-imidazole, 1*H*-benzimidazole, 2-bromo-1*H*-benzimidazole 3,5-dimethyl-1*H*-pyrazole, 4-bromo-1*H*-pyrazole, 4-bromo-3,5-dimethyl-1*H*-pyrazole, potassium 1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl, diethyl iminodiacetate, 1*H*-imidazole-2-carbaldehyde, 1*H*-pyrrole-2-carbaldehyde and isophthalaldehyde are commercially available. 2,4,7-Tris(bromomethyl)-9,9-diethylfluorene (**2**)[9] (for prior synthesis see ref [23]), 2,7-bis (bromomethyl)-9,9-diethylfluorene (**26**)[23] and 4-iodo-3,5-dimethyl-1*H*-pyrazole[25] were synthesized according to literature procedures.

General procedure for the synthesis of compounds 5–11

Route A: Compound **2**, the corresponding heterocyclic compound and *N,N*-diisopropylethylamine (DIPEA) were dissolved in THF and the mixture was stirred at room temperature or refluxed. The progress of the reaction was monitored by thin layer chromatography (TLC). The formed salts were filtered off and the solvent was evaporated. The product was isolated by column chromatography, using silica gel as stationary phase and $CHCl_3$/MeOH (7N NH_3) as mobile phase.

Route B: The corresponding heterocyclic compound was dissolved in dry THF under nitrogen atmosphere and NaH (60% dispersion in mineral oil) was added in portions. The mixture was stirred for 30 min at room temperature. Compound **2** was dissolved in dry THF and added dropwise to the reaction over a period of 15 min. The reaction mixture was stirred at room temperature for 24 h or refluxed for 8 h, cooled down and poured into water (20 ml). The resulting slurry was extracted with $CHCl_3$ (3×20 ml). The combined organic layers were dried over Na_2SO_4. The solvent was evaporated and the raw product purified by column chromatography, using silica gel as stationary and $CHCl_3$/EtOAc 5:1 (v/v) as mobile phase.

2,4,7-Tris[(1*H*-imidazol-1-yl)methyl]-9,9-diethylfluorene (5). Route A: Compound **2** (300 mg, 0.60 mmol), 1*H*-imidazol (163 mg, 2.39 mmol) and DIPEA (310 mg, 2.40 mmol) were dissolved in THF (5 ml) and reacted at room temperature over 24 h. Purification by column chromatography [$CHCl_3$/MeOH (7N NH_3) 25:1 (*v/v*), R_f = 0.43] yielded 43% of **5** (118 mg, 0.255 mmol); **Route B**: Prepared from 1*H*-imidazol (163 mg, 2.39 mmol), NaH (60% dispersion in mineral oil; 96 mg, 2.40 mmol) in 5 ml dry THF and **2** (300 mg, 0.60 mmol; dissolved in 2 ml dry THF), stirred at room temperature. Purification by column chromatography [$CHCl_3$/MeOH (7N NH_3) 25:1 (*v/v*), R_f = 0.43] yielded 80% of **5** (222 mg, 0.48 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.22 (t, *J* = 7.3 Hz, 6H), 1.97 (q, *J* = 7.3 Hz, 4H), 5.13 (s, 2H), 5.20 (s, 2H), 5.55 (s, 2H), 6.62 (s, 1H), 6.85–6.88 (m, 1H),

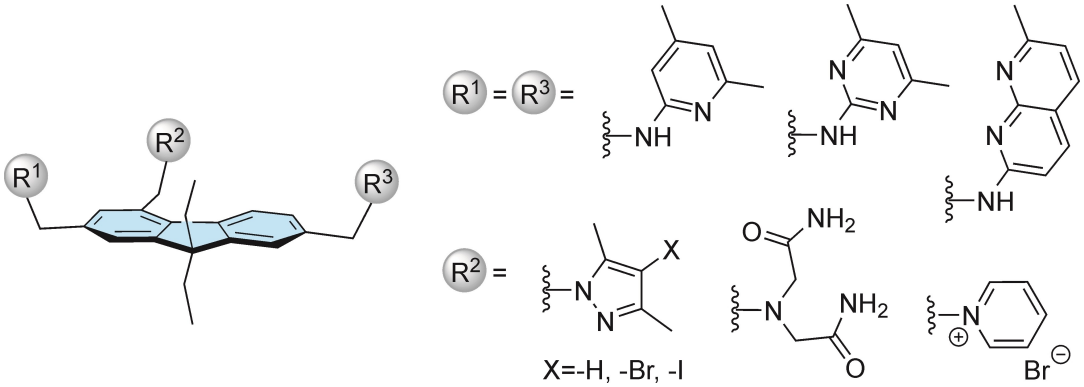


Figure 4. Exemplary structures of 2,4,7-trisubstituted-9,9-diethylfluorenes with side-arms bearing different functional groups, which can be easily prepared based on the knowledge gained from this study.

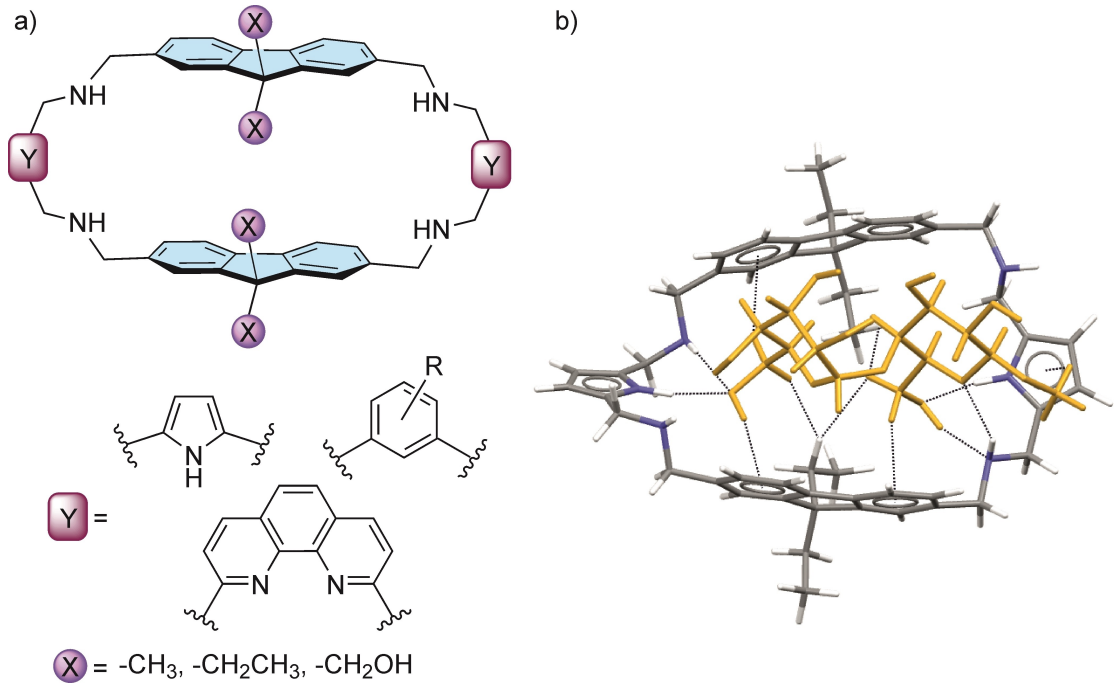


Figure 5. a) Schematic illustration of some planned fluorene-based macrocycles; b) Energy-minimized structure of a 1:1 complex formed between methyl β-maltoside and a fluorene-based macrocycle (Y = pyrrole-based bridge). MacroModel V.8.5, OPLS 2001 force field, MCMM, 50000 steps. Color code: receptor N, blue; receptor C, gray; the sugar molecule is highlighted in orange, short contacts are represented as dashed lines.

6.90–6.93 (m, 1H), 6.94–6.97 (m, 1H), 7.05–7.08 (m, 1H), 7.09–7.12 (m, 3H), 7.13–7.15 (m, 2H), 7.49–7.50 (m, 1H), 7.50–7.54 (m, 2H), 7.56–7.58 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 8.4, 32.8, 49.0, 50.7, 50.8, 56.0, 119.1, 119.2, 119.4, 121.6, 122.0, 122.8, 125.9, 126.6, 130.0, 130.1, 131.0, 135.7, 136.0, 137.3, 137.5, 138.5, 140.2, 151.7, 152.5 ppm. IR (KBr): $\tilde{\upsilon}$ = 3356, 3106, 2961, 2928, 2873, 2851, 1613, 1503, 1440, 1391, 1347, 1282, 1225, 1106, 1074, 1028, 1004, 906, 815, 733, 660, 616, 480 cm^{-1}. HRMS-ESI: $C_{29}H_{30}N_6$ calcd. for $[M+H]^+$: 463.260471, found: 463.260452.

2,4,7-Tris[(1*H*-benzimidazol-1-yl)methyl]-9,9-diethylfluorene (6). Route A: Compound **2** (300 mg, 0.60 mmol), 1*H*-benzimidazol (280 mg, 2.37 mmol) and DIPEA (310 mg, 2.40 mmol) were dissolved in THF (5 ml) and reacted under reflux conditions over 8 h. Purification by column chromatography [$CHCl_3$/MeOH (7N NH_3) 50:1 (*v/v*), R_f = 0.53] yielded 36% of **6** (132 mg, 0.215 mmol); **Route B**: Prepared from 1*H*-benzimidazol (280 mg, 2.37 mmol), NaH (60% dispersion in mineral oil; 95 mg, 2.38 mmol) in 5 ml dry THF and **2** (300 mg, 0.60 mmol; dissolved in 2 ml dry THF), under reflux conditions. Purification by column chromatography [$CHCl_3$/MeOH (7N NH_3) 50:1 (*v/v*), R_f = 0.53] yielded 87% of **6** (318 mg, 0.52 mmol); M.p. 160–162 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.17 (t, *J* = 7.3 Hz, 6H), 1.85–1.92 (m, 4H), 5.28 (s, 2H), 5.42 (s, 2H), 5.70 (s, 2H), 6.69 (s, 1H), 7.05–7.09 (m, 3H), 7.15–7.19 (m, 2H), 7.22–7.24 (m, 2H), 7.25–7.30 (m, 4H), 7.32–7.37 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.79–7.81 (m, 1H), 7.82–7.84 (m, 1H), 7.85–7.88 (m, 2H), 7.95 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.3, 32.8, 47.1, 48.9, 49.0, 56.0, 109.7, 109.9, 110.1, 120.5, 120.7, 121.7, 122.0, 122.4, 122.7, 123.0, 123.1, 123.4, 125.8, 126.6, 130.0, 133.7, 133.8, 133.9, 134.9, 135.2, 138.7, 140.2, 142.6, 142.9, 143.1, 143.9, 144.0, 151.8, 152.7 ppm. IR (KBr): $\tilde{\upsilon}$ = 3083, 3053, 2960, 2925, 2872, 2852, 1613, 1585, 1492, 1456, 1361, 1330, 1284, 1261, 1200, 1177, 1005, 966, 929, 887, 862, 737, 621,582, 470, 424 cm^{-1}. HRMS-ESI: $C_{41}H_{36}N_6$ calcd. for $[M+H]^+$: 613.307422, found: 613.307435.

2,4,7-Tris[(2-bromo-1*H*-benzimidazol-1-yl)methyl]-9,9-diethylfluorene (7). Route B: Prepared from 2-bromo-1*H*-benzimidazol (1000 mg, 5.08 mmol), NaH (60% dispersion in mineral oil; 204 mg, 5.10 mmol) in 20 ml dry THF and **2** (770 mg, 1.54 mmol; dissolved in 2 ml dry THF). Purification by column chromatography [chloroform/ethyl acetate 5:1 (*v/v*), R_f = 0.32] yielded 94% of **7** (1231 mg, 1.45 mmol); M.p. 222–224 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.20 (t, *J* = 7.2 Hz, 6H), 1.83–1.95 (m, 4H), 5.17 (s, 2H), 5.51 (s, 2H), 5.77 (s, 2H), 6.26 (s, 1H), 6.91–6.94 (m, 1H), 6.99–7.01 (m, 1H), 7.03 (s, 1H), 7.06–7.10 (m, 1H), 7.12–7.16 (m, 1H), 7.17–7.21 (m, 2H), 7.22–7.27 (m, 3H), 7.28–7.31 (m, 1H), 7.63–7.65 (m, 1H), 7.71–7.76 (m, 2H), 7.78–7.80 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.3, 32.7, 46.8, 48.9, 49.2, 55.9, 109.5, 109.7, 109.9, 119.5, 119.6, 119.7, 121.0, 122.0, 122.7, 122.9, 123.1, 123.3, 123.4, 123.6, 126.0, 129.8, 130.3, 130.4, 130.6, 134.5, 134.9, 135.3, 135.6, 137.5, 140.3, 143.1, 143.2, 143.4, 151.9, 152.4 ppm. IR (KBr): $\tilde{\upsilon}$ = 3053, 2960, 2927, 2873, 2852, 1613, 1587, 1451, 1435, 1358, 1328, 1278, 1237, 1182, 1150, 1129, 1096, 1006, 984, 929, 862, 804, 736, 663, 569, 525, 474, 428 cm^{-1}. HRMS-ESI: $C_{41}H_{33}Br_3N_6$ calcd. for $[M+H]^+$: 847.038959, found: 847.039265.

2,4,7-Tris[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-9,9-diethylfluorene (8). Route A: Compound **2** (300 mg, 0.60 mmol), 3,5-dimethyl-1*H*-pyrazol (230 mg, 2.39 mmol) and DIPEA (310 mg, 2.40 mmol) were dissolved in THF (5 ml) and reacted under reflux conditions over 16 h. Purification by column chromatography [$CHCl_3$/MeOH (7N NH_3) 50:1 (*v/v*), R_f = 0.57] yielded 67% of **8** (220 mg, 0.40 mmol). **Route B**: Prepared from 3,5-dimethyl-1*H*-pyrazol (230 mg, 2.39 mmol), NaH (60% dispersion in mineral oil; 96 mg, 2.40 mmol) in 5 ml dry THF and **2** (300 mg, 0.60 mmol; dissolved in 2 ml dry THF). Purification by column chromatography [chloroform/ethyl acetate 5:1 (*v/v*), R_f = 0.32] yielded 82% of **8** (267 mg, 0.49 mmol); M.p. 159–161 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.20 (t, *J* = 7.3 Hz, 6H), 1.86–1.97 (m, 4H), 2.01 (s, 3H), 2.05 (s, 3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.27 (s, 6H), 5.14 (s, 2H), 5.30 (s, 2H), 5.59 (s, 2H), 5.71 (s, 1H), 5.78 (s, 1H), 5.87 (s, 1H), 5.89 (s, 1H), 6.89 (s, 1H), 6.99–

7.03 (m, 1H), 7.06–7.09 (m, 1H), 7.60 (d, $J=8.0$ Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.3, 10.9, 11.2, 13.5, 13.6, 32.8, 50.9, 52.8, 53.0, 55.6, 105.5, 105.6, 105.7, 119.6, 121.3, 121.8, 122.8, 125.4, 133.0, 136.1, 136.5, 136.9, 139.2, 139.9, 140.5, 147.4, 147.5, 147.9, 151.2, 151.3 ppm. IR (KBr): $\tilde{\nu}$ = 2972, 2935, 2916, 2875, 2854, 1610, 1552, 1485, 1460, 1445, 1419, 1381, 1337, 1315, 1300, 1276, 1232, 1175, 1146, 1115, 1028, 1005, 974, 906, 880, 853, 836, 776, 742, 720, 701, 686, 665, 629, 594, 565, 484, 465 cm^{-1}. HRMS-ESI: $C_{35}H_{42}N_6$ calcd. for $[M+H]^+$: 547.354372, found: 547.354384.

2,4,7-Tris[(4-bromo-1*H*-pyrazol-1-yl)methyl]-9,9-diethylfluorene (9). Route B: Prepared from 4-bromo-1*H*-pyrazol (968 mg, 6.59 mmol), NaH (60% dispersion in mineral oil; 264 mg, 6.60 mmol) in 20 ml dry THF and **2** (1000 mg, 2.00 mmol; dissolved in 5 ml dry THF). Purification by column chromatography [chloroform/ethyl acetate 5:1 (*v/v*), R_f = 0.81] yielded 77% of **9** (1070 mg, 1.530 mmol); M.p. 127–128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.24 (t, $J=7.3$ Hz, 6H), 1.98 (q, $J=7.3$ Hz, 4H), 5.32 (s, 2H), 5.33 (s, 2H), 5.66 (s, 2H), 6.62 (s, 1H), 7.13 (dd, $J=8.0/1.5$ Hz, 1H), 7.18 (d, $J=1.5$ Hz, 1H), 7.20–7.22 (m, 2H), 7.38–7.40 (m, 2H), 7.51–7.52 (m, 2H), 7.54 (d, $J=8.0$ Hz, 1H), 7.56–7.57 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.5, 32.7, 54.9, 55.9, 56.4, 56.7, 93.5, 93.6, 122.2, 122.4, 123.0, 126.9, 127.1, 129.4, 129.5, 130.2, 135.1, 135.6, 139.0, 140.1, 140.2, 140.3, 140.4, 151.5, 152.5 ppm. IR (KBr): $\tilde{\nu}$ = 3121, 2960, 2927, 2871, 2850, 1613, 1587, 1517, 1441, 1421, 1377, 1303, 1192, 1150, 1156, 1108, 1034, 989, 950, 883, 839, 794, 758, 727, 706, 677, 645, 603, 482 cm^{-1}. HRMS-ESI: $C_{29}H_{27}Br_3N_6$ calcd. for $[M+H]^+$: 696.992009, found: 696.992012.

2,4,7-Tris[(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-9,9-diethylfluorene (10). Route B: Prepared from 4-bromo-3,5-dimethyl-1*H*-pyrazol (880 mg, 5.03 mmol), NaH (60% dispersion in mineral oil; 203 mg, 5.08 mmol) in 20 ml dry THF and **2** (770 mg, 1.54 mmol; dissolved in 2 ml dry THF). Purification by column chromatography [chloroform/ethyl acetate 5:1 (*v/v*), R_f = 0.60] yielded 83% of **10** (996 mg, 1.271 mmol); M.p. 146–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.22 (t, $J=7.3$ Hz, 6H), 1.95 (q, $J=7.3$ Hz, 4H), 2.03 (s, 3H), 2.04 (s, 3H), 2.15 (s, 3H), 2.23 (s, 3H), 2.26 (s, 3H), 2.27 (s, 3H), 5.18 (s, 2H), 5.32 (s, 2H), 5.62 (s, 2H), 5.71 (s, 1H), 6.98 (s, 1H), 7.02–7.05 (m, 1H), 7.11–7.13 (m, 1H), 7.60 (d, $J=7.9$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.4, 10.1, 10.2, 10.5, 12.3, 12.4, 32.8, 52.0, 53.9, 54.3, 55.7, 94.5, 94.6, 94.7, 120.0, 121.6, 123.0, 125.7, 132.5, 135.5, 136.3, 136.8, 137.2, 137.3, 138.0, 140.4, 146.2, 146.7, 151.4, 151.6 ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2918, 2874, 2852, 1613, 1548, 1473, 1421, 1378, 1310, 1212, 1122, 1067, 1037, 1003, 844, 818, 796, 744, 710, 694, 658, 590, 515, 478 cm^{-1}. HRMS-ESI: $C_{35}H_{39}Br_3N_6$ calcd. for $[M+H]^+$: 781.085909, found: 781.086168.

2,4,7-Tris[(4-iodo-3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-9,9-diethylfluorene (11). Route B: Synthesis and purification were carried out under the absence of light. Prepared from 4-iodo-3,5-dimethyl-1*H*-pyrazole[24] (4240 mg, 19.1 mmol), NaH (60% dispersion in mineral oil; 780 mg, 19.5 mmol) in 25 ml dry THF and **2** (2900 mg, 5.79 mmol; dissolved in 6 ml dry THF). Purification by column chromatography [chloroform/ethyl acetate 5:1 (*v/v*), R_f = 0.60] yielded 97% of **11** (5220 mg, 5.64 mmol); M.p. 174–176 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.22 (t, $J=7.3$ Hz, 6H), 1.95 (q, $J=7.3$ Hz, 4H), 2.06 (s, 3H), 2.09 (s, 3H), 2.19 (s, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 2.29 (s, 3H), 5.22 (s, 2H), 5.36 (s, 2H), 5.66 (s, 2H), 5.78 (s, 1H), 6.98 (s, 1H), 7.03 (dd, $J=7.9/1.5$ Hz, 1H), 7.12 (d, $J=1.5$ Hz, 1H), 7.60 (d, $J=7.9$ Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.4, 11.8, 11.9, 12.1, 14.1, 14.2, 32.8, 52.1, 54.1, 54.3, 55.7, 63.1, 63.4, 120.0, 121.6, 121.7, 123.0, 125.7, 132.5, 135.6, 136.3, 136.7, 140.4, 140.6, 140.7, 141.4, 149.4, 149.5, 150.0, 151.3, 151.6 ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2920, 2872, 2851, 1614, 1537, 1456, 1417, 1377, 1359, 1310, 1242, 1209, 1172, 1121, 1055, 1003, 882, 839, 817, 796, 746, 710, 694, 658, 588, 508, 478 cm^{-1}. HRMS-ESI: $C_{35}H_{39}I_3N_6$ calcd. for $[M+H]^+$: 925.044312, found: 925.044349.

Syntheses of compounds 12–17

2,4,7-Tris(pyridiniummethyl)-9,9-diethylfluorene tribromide (12). Compound **2** (250 mg, 0.50 mmol) and pyridine (0.12 ml, 118 mg, 1.49 mmol) were refluxed in $CHCl_3$ (30 ml) for 4 h. The formed oil was separated and washed with $CHCl_3$. The residue was transferred into a crystalline solid by dissolving in MeOH and removing the solvent again. Recrystallisation from acetone yielded 92% of **12** (338 mg, 0.46 mmol); M.p. 185–187 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 0.21 (t, $J=7.4$ Hz, 6H), 2.19 (q, $J=7.4$ Hz, 4H), 6.05 (s, 4H), 6.55 (s, 2H), 7.31 (s, 1H), 7.64 (dd, $J=8.0/1.3$ Hz, 1H), 7.85 (s, 1H), 7.91 (s, 1H), 7.94 (d, $J=8.0$ Hz, 1H), 8.17–8.22 (m, 4H), 8.22–8.25 (m, 2H), 8.64–8.70 (m, 2H), 8.70–8.74 (m, 1H), 9.12 (d, $J=5.8$ Hz, 2H), 9.25 (d, $J=6.3$ Hz, 4H) ppm. ^{13}C-NMR (125 MHz, CD_3OD): δ = 8.8, 33.5, 57.9, 63.2, 64.9, 65.5, 124.9, 125.5, 126.4, 129.6, 129.8, 129.9, 130.0, 130.1, 135.0, 135.2, 141.3, 141.8, 146.0, 146.1, 146.3, 147.5, 147.8, 153.9, 155.1 ppm. IR (KBr): $\tilde{\nu}$ = 3434, 3409, 3376, 3344, 3261, 3048, 3022, 2958, 2931, 2870, 1645, 1626, 1577, 1487, 1474, 1461, 1445, 1422, 1378, 1361, 1344, 1318, 1253, 1213, 1200, 1190, 1164, 1147, 1101, 1047, 1025, 1003, 957, 889, 862, 834, 811, 793, 768, 747, 735, 708, 690, 663, 623, 573, 481, 472, 446 cm^{-1}. HRMS-ESI: $C_{35}H_{36}Br_3N_3$ calcd. for $[M+Na]^+$: 758.035157, found: 758.035536.

2,4,7-tris[*N*,*N*-bis(ethoxycarbonylmethyl)aminomethyl]-9,9-diethylfluorene (13). Compound **2** (2000 mg, 3.99 mmol) and diethyl iminodiacetate were dissolved in a THF/MeCN (10:15 ml) mixture and K_2CO_3 (1840 mg, 13.3 mmol) was added. After refluxing for 8 h and subsequent cooling to room temperature the solid was filtered off and the solvent was removed under reduced pressure. The residue was dissolved in 25 ml acetone and refluxed with pyridine (1.0 ml, 980 mg, 12.4 mmol) for 4 h. The solvent was removed and the residue dissolved in 25 ml $CHCl_3$. The organic layer was washed with water (3×15 ml), dried over Na_2SO_4 and concentrated in vacuum. The raw product was eluted over a short column packed with silica gel using $CHCl_3$/EtOAc [5:1 (v/v), R_f = 0.69) as eluent system. Yield 88% of **13** (2915 mg, 3.53 mmol) as a sticky oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.22 (t, $J=7.2$ Hz, 6H), 1.23 (t, $J=7.1$ Hz, 6H), 1.27 (t, $J=7.1$ Hz, 6H), 1.28 (t, $J=7.1$ Hz, 6H), 2.00 (q, $J=7.3$ Hz, 4H), 3.55 (s, 4H), 3.57 (s, 4H), 3.60 (s, 4H), 3.98 (s, 2H), 4.00 (s, 2H), 4.14 (q, $J=7.2$ Hz, 4H), 4.17 (q, $J=7.2$ Hz, 4H), 4.18 (q, $J=7.2$ Hz, 4H), 4.37 (s, 2H), 7.29–7.32 (m, 3H), 7.34 (s, 1H), 7.95 (d, $J=7.9$ Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.4, 14.3, 33.0, 54.1, 54.2, 55.3, 56.1, 58.0, 60.4, 122.5, 123.0, 123.9, 127.9, 130.0, 132.2, 136.5, 136.6, 139.6, 140.8, 150.7, 151.4, 171.2, 171.3 ppm. IR (KBr): $\tilde{\nu}$ = 2979, 2962, 2931, 2916, 2908, 2874, 2851, 1729, 1446, 1413, 1394, 1369, 1346, 1297, 1261, 1184, 1149, 1095, 1027, 987, 918, 873, 844, 825, 800, 750, 665, 588, 490 cm^{-1}. HRMS-ESI: $C_{44}H_{63}N_3O_{12}$ calcd. for $[M+H]^+$: 826.448451, found: 826.448502.

2,4,7-tris[*N*,*N*-bis(carbamoylmethyl)aminomethyl]-9,9-diethylfluorene (14). Compound **13** (900 mg, 1.09 mmol) was stirred in a 7N methanolic ammonia solution (15 ml) for 7 d. The mixture was poured into ether (30 ml), the precipitate was filtered off and repeatedly washed with ether. Yield 71% of **14** (505 mg, 0.78 mmol); M.p. 124–126 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 0.18 (t, $J=7.3$ Hz, 6H), 2.04–2.12 (m, 4H), 3.23 (s + s, 8H), 3.39 (s, 4H), 3.82 (s, 4H), 4.26 (s, 2H), 7.35 (d, $J=1.5$ Hz, 1H), 7.38 (dd, $J=8.0/1.7$ Hz, 1H), 7.40 (d, $J=1.5$ Hz, 1H), 7.45 (d, $J=1.7$ Hz, 1H), 7.94 (d, $J=8.0$ Hz, 1H) ppm. ^{13}C-NMR (125 MHz, CD_3OD): δ = 8.8, 34.0, 56.7, 58.4, 58.6, 58.7, 60.2, 60.4, 124.5, 125.1, 129.6, 131.7, 133.5, 137.4, 141.1, 142.3, 152.3, 152.9, 176.3, 176.4 ppm. IR (KBr): $\tilde{\nu}$ = 3550-3000, 2961, 2916, 2871, 2847, 1651, 1444, 1394, 1373, 1335, 1298, 1119, 1097, 978, 868, 825, 498 cm^{-1}. HRMS-ESI: $C_{32}H_{45}N_9O_6$ calcd. for $[M+H]^+$: 652.356557, found: 652.356567.

2,4,7-tris[*N*,*N*-bis(carboxylmethyl)aminomethyl]-9,9-diethylfluorene hexasodium salt (15a). Compound **13** (900 mg, 1.09 mmol) was dissolved in MeOH/THF (2:1 v/v, 6 mL) and a 1N aqueous

NaOH solution (10 ml) was added. The reaction was stirred at room temperature for 24 h. After removing the solvent under reduced pressure, the residue was extracted with cold ethanol. The solvent was removed and the obtained solid dried in vacuum. Yield 51% of **15a** (441 mg, 0.56 mmol); M.p. 150–152 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 0.18 (t, *J* = 7.3 Hz, 6H), 2.00–2.13 (m, 4H), 3.06 (s, 4H), 3.18 (s, 8H), 3.57 (s, 2H), 3.87 (s, 2H), 4.03 (s, 2H), 7.13 (s, 1H), 7.34 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.88 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, CD_3OD): δ = 8.8, 34.1, 56.5, 56.6, 59.4, 59.8, 60.2, 60.7, 123.8, 124.3, 125.9, 130.1, 132.2, 135.6, 136.3, 139.4, 139.9, 142.7, 151.8, 152.1, 177.5, 178.7, 179.1 ppm. IR (KBr): $\tilde{\nu}$ = 3550-3000 (H_2O), 2965, 2923, 2876, 1557, 1397, 1331, 1249, 1116, 1047, 1013, 995, 830, 701, 645, 619, 464 cm^{-1}. HRMS-ESI: $C_{32}H_{33}N_3Na_6O_{12}$ calcd. for $[M-Na]^-$: 766.155820, found: 766.160412.

2,4,7-Tris[*N*,*N*-bis(carboxylmethyl)aminomethyl]-9,9-diethylfluorene (15b). Compound **13** (250 mg, 0.30 mmol) was dissolved in dry MeOH (5 ml) and a solution of KOH (200 mg, 3.56 mmol) in dry MeOH (5 ml) was added dropwise to the reaction over the course of 15 minutes. The mixture was stirred at 40 °C for 8 h and then the solvent was removed under reduced pressure. The residue was treated with 2N HCl (10 ml) at room temperature for 60 min. The aqueous phase was concentrated to about a third of the volume and then poured into acetone. The precipitate was filtered off and dried under vacuum. The solid was then extracted with dry DMSO. After removal of the solvent and long drying under high vacuum, the product was obtained from the organic phase as a white solid. Yield 72% of **15b** (143 mg, 0.22 mmol); M.p. 165–167 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 0.18 (t, *J* = 7.3 Hz, 6H), 1.98–2.05 (m, 4H), 3.84 (s, 4H), 4.13 (s, 4H), 4.14 (s, 2H), 4.52 (s, 2H), 4.60 (s,2H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.64 (s, 1H), 7.66 (s, 2H), 8.19 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 8.3, 32.2, 53.5, 53.6, 53.7, 55.2, 58.7, 124.2, 124.3, 126.0, 126.1, 129.0, 130.7, 133.8, 140.8, 141.0, 150.9, 151.7, 167.5, 170.3 ppm. IR (KBr): $\tilde{\nu}$ = 3550–3000 (H_2O), 3000–2300, 2962, 2931, 2874, 2856, 1732, 1622, 1398, 1360, 1193, 1080, 1047, 1023, 941, 872, 822, 802, 752, 710, 652, 625, 530, 490, 465 cm^{-1}. HRMS-ESI: $C_{32}H_{39}N_3O_{12}$ calcd. for $[M-H]^-$: 656.245000, found: 656.247831.

2,4,7-Tris[(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)methyl]-9,9-diethylfluorene (16). Potassium phthalimide (4000 mg, 21.6 mmol) was suspended in DMSO (15 ml) and heated to 80 °C. Compound **2** (3000 mg, 5.99 mmol) was added in portions over a period of 15 min. After stirring for 4 h at 80 °C the mixture was poured into water (50 ml). The precipitate was filtered off, washed with water and dissolved in chloroform. Again the organic phase was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the raw product was recrystallized from THF/$CHCl_3$. Yield 91% of **16** (3810 mg, 5.45 mmol); M.p. 240 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.27 (t, *J* = 7.3 Hz, 6H), 1.94–2.02 (m, 4H), 4.77 (s, 2H), 4.92 (s, 2H), 5.29 (s, 2H), 7.03 (s, 1H), 7.27 (s, 1H), 7.42–7.46 (m, 2H), 7.64–7.68 (m, 2 H), 7.69–7.73 (m, 2H), 7.73–7.77 (m, 2H), 7.77–7.80 (m, 2H), 7.80–7.82 (m, 1H), 7.84–7.88 (m, 2H), 7.89–7.93 (m, 2H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 8.6, 32.7, 39.7, 41.7, 41.8, 55.6, 122.1, 123.3, 123.4, 123.6, 124.6, 127.5, 130.8, 132.1, 132.2, 133.8, 134.0, 134.1, 135.0, 135.3, 137.5, 140.6, 151.4, 152.0, 167.9, 168.1, 168.2 ppm. IR (KBr): $\tilde{\nu}$ = 3460, 3063, 2960, 2932, 2871, 2858, 1765, 1709, 1613, 1465, 1426, 1389, 1332, 1238, 1212, 1186, 1170, 1108, 1097, 1084, 1072, 1047, 1038, 1004, 991, 958, 952, 935, 929, 898, 889, 874, 846, 823, 794, 767, 744, 721, 707, 680, 659, 640, 622, 605, 563, 529, 513, 464, 422, 409 cm^{-1}. HRMS-ESI: calcd. for $C_{44}H_{33}N_3O_6$ $[M+H]^+$: 700.244212, found: 700.244210.

2,4,7-Tris(aminomethyl)-9,9-diethylfluorene (17). Compound **16** (1000 mg, 1.43 mmol) was suspended in a 2:1 (v/v) mixture of ethanol/toluene (2:1 v/v, 60 ml) and hydrazine (64% solution in water, 1 ml, 640 mg, 20.0 mmol) was added. After refluxing for 8 h the solvent was removed under reduced pressure and the remaining solid dissolved in 2 N KOH solution. The aqueous phase was extracted with CH_2Cl_2 (20 ml). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuum, yielding the product in pure form. Yield 84% of **17** (370 mg, 1.20 mmol); M.p. 93–94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.27 (t, *J* = 7.3 Hz, 6H), 2.02 (q, *J* = 7.3 Hz, 4H), 3.95 (s, 4H), 4.28 (s, 2H), 7.18 (s, 1H), 7.24 (s, 1H), 7.27–7.30 (m, 2H), 7.72–7.76 (m, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 8.5, 33.0, 44.9, 46.7, 55.5, 119.9, 121.5, 122.4, 125.1, 126.0, 137.2, 137.7, 140.1, 141.8, 142.2, 151.0, 151.4 ppm. IR (KBr): $\tilde{\nu}$ = 3356, 3279, 3181, 2960, 2914, 2872, 2850, 1591, 1452, 1417, 1375, 1340, 1169, 1051, 1003, 989, 955, 866, 822, 744, 690, 558, 486 cm^{-1}. HRMS-LDI: $C_{20}H_{27}N_3$ calcd. for $[M\cdot]^+$: 309.219949, found: 309.219950.

Synthesis of compounds 18–21

2,4,7-Tris[*N*-(1*H*-imidazol-2-yl-methylidene)aminomethyl]-9,9-diethylfluorene (18). Under N_2-atmosphere compound **17** (200 mg, 0.65 mmol) and imidazole-2-carbaldehyde (205 mg, 2.13 mmol) were dissolved in dry methanol (1 ml). A catalytic amount of acetic acid was added and the mixture stirred for 24 h at room temperature. The solution was filtered, the solvent removed and the residue dissolved in dry $CHCl_3$. The solution was poured into diethylether and the precipitate was filtered off. Dissolving in $CHCl_3$ and repeated precipitation yielded 74% of **18** (260 mg, 0.48 mmol) as a white solid. M.p. 146–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.16 (t, *J* = 7.3 Hz, 6H), 1.88 (q, *J* = 7.3 Hz, 4H), 4.71 (s, 2H), 4.80 (s, 2H), 5.02 (s, 2H), 6.93–7.18 (br s, 6H), 7.04–7.08 (m, 2H), 7.10 (s, 1H), 7.16 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 8.33 (s, 1H), 8.35 (s, 1H), 8.39 (s, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 8.6, 32.8, 55.6, 61.8, 64.5, 64.7, 118.9, 121.7, 122.5, 123.0, 126.9, 127.6, 130.5, 132.8, 136.9, 137.2, 138.0, 140.2, 144.7, 151.1, 151.6, 153.2, 153.8 ppm. IR (KBr): $\tilde{\nu}$ = 3500–2500, 3110, 3030, 2963, 2914, 2875, 2850, 2821, 1645, 1543, 1442, 1394, 1344, 1301, 1155, 1106, 1034, 998, 922, 873, 823, 759, 709, 659, 613, 505, 470 cm^{-1}. HRMS-ESI: $C_{32}H_{33}N_9$ calcd. for $[M+H]^+$: 544.293169, found: 544.293165.

2,4,7-Tris[*N*-(1*H*-imidazol-2-yl-methyl)aminomethyl]-9,9-diethylfluorene (19). Under N_2-atmosphere compound **17** (200 mg, 0.65 mmol) and imidazole-2-carbaldehyde (248 mg, 2.59 mmol) were dissolved in dry methanol (5 ml). Triethyl orthoformate (5 ml, 4455 mg, 30.1 mmol) was added and the reaction refluxed for 4 h. After cooling down to room temperature, $NaBH_4$ (130 mg, 3.45 mmol) was added in portions. The mixture was stirred overnight at room temperature. Water (20 ml) was added afterwards and stirring continued for another 2 h. The precipitated organic phase was separated and dried in vacuo. The product was isolated by column chromatography [chloroform/methanol 2:1 (*v/v*) + 2.0% NH_3, R_f = 0.35]. Yield 44% of **19** (158 mg, 0.29 mmol); M.p. 100–102 °C. ^{1}H NMR (500 MHz, CD_3OD): δ = 0.19 (t, *J* = 7.3 Hz, 6H), 2.05 (q, *J* = 7.3 Hz, 4H), 3.81 (s, 2H), 3.82 (s, 2H), 3.87 (s, 4H), 4.00 (s, 2H), 4.13 (s, 2H), 7.00 (s + s, 4H), 7.05 (s, 2H), 7.24–7.27 (m, 1H), 7.28 (s, 1H), 7.29 (s, 1H), 7.37 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 8.8, 34.0, 46.3, 46.4, 46.7, 51.8, 54.0, 56.8, 122.7, 122.9, 123.9, 128.6, 129.4, 135.0, 139.1, 139.3, 139.7, 141.8, 147.9, 148.0, 152.1, 152.5 ppm. IR (KBr): $\tilde{\nu}$ = 3144, 3043, 2961, 2912, 2873, 2844, 2821, 2663, 1666, 1556, 1448, 1375, 1338, 1213, 1155, 1097, 986, 858, 822, 797, 739, 663, 481 cm^{-1}. HRMS-ESI: $C_{32}H_{39}N_9$ calcd. for $[M+H]^+$: 550.340119, found: 550.340119.

2,4,7-Tris[*N*-(1*H*-pyrrol-2-yl-methylidene)aminomethyl]-9,9-diethylfluorene (20). Under N_2-atmosphere compound **17** (200 mg, 0.65 mmol) and pyrrole-2-carbaldehyde (200 mg, 2.10 mmol) were dissolved in dry degassed methanol (1 ml). A catalytic amount of acetic acid was added and the mixture stirred for 24 h at room temperature. The precipitate was filtered off. Dissolving in $CHCl_3$ and precipitation from ether yielded 24% of **20** (84 mg, 0.16 mmol)

as a white solid. M.p. >202 °C decomposition. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.27 (t, *J* = 7.3 Hz, 6H), 1.98 (q, *J* = 7.3 Hz, 4H), 4.76 (s, 2H), 4.79 (s, 2H), 5.09 (s, 2H), 6.10–6.12 (m, 1H), 6.17–6.19 (m, 1H), 6.20–6.23 (m, 1H), 6.39–6.42 (m, 1H), 6.48–6.50 (m, 1 H), 6.52–6.54 (m, 1 H), 6.58–6.60 (m, 1 H), 6.76–6.78 (m, 1 H), 6.81–6.83 (m, 1 H), 7.13 (s, 1H), 7.21–7.25 (m, 2 H), 7.27 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 8.02 (s, 1H), 8.15 (s, 1H), 8.18 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.6, 33.0, 55.6, 61.5, 64.5, 64.8, 109.4, 109.6, 109.7, 114.8, 114.9, 115.0, 121.0, 122.2, 122.3, 122.4, 123.0, 126.7, 127.1, 130.0, 130.1, 134.1, 137.8, 138.1, 140.5, 151.0, 151.1, 152.7, 153.0 ppm. IR (KBr): $\tilde{\nu}$ = 3500–2500, 3110, 3030, 2963, 2914, 2875, 2850, 2821, 1645, 1543, 1442, 1394, 1344, 1301, 1155, 1106, 1034, 998, 922, 873, 823, 759, 709, 659, 613, 505, 470 cm^{-1}. HRMS-ESI: $C_{35}H_{36}N_6$ calcd. for $[M+H]^+$: 541.307422, found: 541.307426.

2,4,7-Tris[*N*-(1*H*-pyrrol-2-yl-methyl)aminomethyl]-9,9-diethylfluorene (21). Under N_2-atmosphere compound **17** (200 mg, 0.65 mmol) and pyrrole-2-carbaldehyde (203 mg, 2.15 mmol) were dissolved in dry CH_2Cl_2 (5 ml). Molecular sieves (4 Å) were added and the reaction refluxed for 8 h. After cooling down to room temperature the drying agent was filtered off and dry methanol (2 ml) added. $NaBH_4$ (410 mg, 10.84 mmol) was added in portions and the mixture stirred overnight at room temperature. Water (20 ml) was added afterwards and stirring continued for another 2 h. The precipitated organic phase was separated and dried in vacuo. The product was isolated by column chromatography [$CHCl_3$/MeOH (7N NH_3) 25:1 (*v/v*), R_f = 0.18]. Yield 20% of **21** (72 mg, 0.13 mmol); M.p. 110–112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.24 (t, *J* = 7.3 Hz, 6H), 1.98 (q, *J* = 7.3 Hz, 4H), 3.80 (s, 2H), 3.81 (s, 2H), 3.82 (s, 2H), 3.84 (s, 2H), 3.90 (s, 2H), 4.13 (s, 2H), 6.02–6.05 (m, 2H), 6.07–6.10 (m, 1H), 6.11–6.15 (m, 3H), 6.67–6.69 (m, 2H), 6.69–6.71 (m, 1 H), 7.14 (s, 1H), 7.18 (s, 1H), 7.19–7.23 (m, 1 H), 7.24 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 8.94 (br s, 2H), 8.98 (br s, 1H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 8.6, 33.0, 45.8, 45.9, 46.4, 51.5, 53.3, 55.5, 106.5, 106.6, 106.8, 108.0, 117.5, 121.5, 122.5, 122.6, 127.2, 128.0, 130.2, 130.3, 134.2, 138.1, 138.4, 138.5, 140.3, 150.9, 151.4 ppm. IR (KBr): $\tilde{\nu}$ = 3361, 3196, 3097, 2962, 2922, 2872, 2850, 1568, 1446, 1344, 1293, 1238, 1165, 1095, 1024, 957, 883, 797, 716, 560 cm^{-1}. HRMS-ESI: $C_{35}H_{42}N_6$ calcd. for $[M+H]^+$: 547.354372, found: 547.354367.

Synthesis of compounds 22–25

2,7-Bis[(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)methyl]-9,9-diethylfluorene (22). Potassium phthalimide (1700 mg, 9.18 mmol) was suspended in DMSO (15 ml) and heated to 80 °C. Compound **26** (1500 mg, 3.67 mmol) was added in portions over a period of 15 min. After stirring for 4 h at 80 °C the mixture was poured into water (50 ml). The precipitate was filtered off, washed with water and dissolved in chloroform. Again the organic phase was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the raw product was recrystallized from THF/$CHCl_3$. Yield 67% of **22** (1331 mg, 2.46 mmol); M.p. 280–281 °C.^{1}H NMR (500 MHz, $CDCl_3$): 0.29 (t, *J* = 7.3 Hz, 6H), 1.98 (q, *J* = 7.3 Hz, 4H), 4.89 (s, 4H), 7.36–7.40 (m, 4H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.68–7.72 (m, 4H), 7.83–7.87 (m, 4H) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 8.6, 32.4, 42.0, 56.0, 119.8, 123.4, 123.6, 127.5, 132.2, 134.0, 135.2, 140.7, 150.8, 168.1 ppm. IR (KBr): $\tilde{\nu}$ = 3460, 3063, 2960, 2932, 2871, 2858, 1765, 1709, 1613, 1465, 1426, 1389, 1332, 1316, 1276, 1263, 1212, 1186, 1162, 1084, 1008, 943, 929, 896, 842, 812, 798, 750, 733, 719, 709, 690, 661, 600, 566, 529, 521, 464, 434, 404 cm^{-1}. HRMS-ESI: $C_{35}H_{28}N_2O_4$ calcd. for $[M+H]^+$: 541.212184, found: 541.212185.

2,7-Bis(aminomethyl)-9,9-diethylfluorene (23). Compound **22** (2000 mg, 3.70 mmol) was suspended in a 2:1 (v/v) mixture of ethanol/toluene (2:1 v/v, 150 ml) and hydrazine (64% solution in water, 1 ml, 640 mg, 20.0 mmol) was added. After refluxing for 8 h the solvent was removed under reduced pressure and the remaining solid dissolved in 2 N KOH solution. The aqueuos phase was extracted with toluene (3×20 ml). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuum. The product was obtained as a pale yellow solid. Yield 97% of **23** (1.01 g, 3.60 mmol); M.p. 34–35 °C.^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.31 (t, *J* = 7.4 Hz, 6H), 2.02 (q, *J* = 7.4 Hz, 4H), 3.93 (s, 4H), 7.23–7.27 (m, 4H), 7.63 (d, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.6, 32.7, 46.8, 56.0, 119.4, 121.5, 125.8, 140.2, 142.2, 150.4 ppm. IR (KBr): $\tilde{\nu}$ = 3342, 3267, 3183, 3061, 3042, 2995, 2963, 2913, 2873, 2850, 1606, 1458, 1417, 1375, 1328, 1317, 1299, 1214, 1159, 1129, 1091, 1045, 1005, 967, 942, 885, 862, 839, 806, 744, 723, 688, 553, 541, 509, 468, 420 cm^{-1}. HRMS-LDI: $C_{19}H_{24}N_2$ calcd. for $[M\cdot]^+$: 280.193400, found: 280.193398.

Macrocycle 24. Amine **23** (100 mg, 0.36 mmol) was dissolved in dry ethanol (4 ml) and isophthalic aldehyde (48 mg, 0.36 mmol) added. A catalytic amount of acetic acid was added and the reaction mixture stirred for 8 h at 40 °C. The precipitated solid was filtered off, washed with dry ethanol and dried under vacuum. Yield 96% of **24** (129 mg, 0.17 mmol); M.p. 162–164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.33 (t, *J* = 7.1 Hz, 12H), 2.01 (q, *J* = 7.1 Hz, 8H), 4.90 (s, 8H), 7.26–7.28 (m, 8H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 4H), 7.90 (d, *J* = 7.6 Hz, 4H), 8.16 (s, 2H), 8.45 (s, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.8, 32.8, 56.2, 65.5, 119.7, 122.7, 126.9, 128.7, 129.1, 130.3, 136.8, 137.8, 140.5, 150.6, 161.4 ppm. IR (KBr): $\tilde{\nu}$ = 3055, 3034, 3007, 2961, 2928, 2915, 2871, 2847, 1641, 1604, 1583, 1463, 1448, 1417, 1373, 1317, 1290, 1265, 1205, 1154, 1084, 1033, 997, 939, 885, 812, 744, 688, 648, 546, 511, 474, 447, 422 cm^{-1}. HRMS-ESI: $C_{54}H_{52}N_4$ calcd. for $[M+H]^+$: 757.426474, found: 757.426477.

Macrocycle 25. Imine **24** (100 mg, 0.13 mmol) was dissolved in dry CH_2Cl_2 (2 ml) and dry methanol (2 ml) was added. $NaBH_4$ (100 mg, 2.64 mmol) was added in portions and the mixture stirred overnight at room temperature. Water (10 ml) was added afterwards and stirring continued for another 2 h. The organic layer was separated, washed with water (3×10 ml) and dried over Na_2SO_4. Removing the solvent under vacuum yielded 83% of **25** (84 mg, 0.11 mmol). M.p. 70–72 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.30 (t, *J* = 7.3 Hz, 12H), 2.01 (q, *J* = 7.3 Hz, 8H), 3.83 (s, 8H), 3.88 (s, 8H), 7.21–7.36 (m, 16H), 7.60–7.64 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.6, 32.8, 53.1, 53.6, 55.9, 119.4, 122.6, 126.9, 128.2, 128.5, 138.9, 140.4, 140.5, 150.2 ppm. IR (KBr): $\tilde{\nu}$ = 3306, 3184, 3053, 3026, 3003, 2960, 2915, 2871, 2848, 1606, 1449, 1417, 1373, 1311, 1210, 1160, 1105, 1086, 1034, 1006, 938, 887, 812, 786, 744, 696, 590, 494, 464, 424 cm^{-1}. HRMS-ESI: $C_{54}H_{60}N_4$ calcd. for $[M+H]^+$: 765.489074, found: 765.489081.

Supporting Information

Supporting Information available. ^{1}H und ^{13}C NMR spectra of compounds **5**–**25** (Figures S1–S54).

Acknowledgment

Financial support from the Federal German Ministry of Education and Research (BMBF, Bundesministerium für Bildung und Forschung) is gratefully acknowledged. Open access funding by the Publication Fund of the TU Bergakademie Freiberg. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: artificial receptors · fluorenophane · heterocycles · imines · macrocyclization

[1] a) T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker, J. Salbeck, *Chem. Rev.* **2007**, *107*, 1011–1065; b) M. Irfan, K. D. Belfield, A. Saeed, *RSC Adv.* **2015**, *5*, 48760–48768; c) Y. Ie, A. Uchida, N. Kawaguchi, M. Nitani, H. Tada, F. Kakiuchi, Y. Aso, *Org. Lett.* **2016**, *18*, 4320–4323; d) Y.-Y. Liu, J.-Y. Lin, Y.-F. Bo, L.-H. Xie, M.-D. Yi, X.-W. Zhang, H.-M. Zhang, T.-P. Loh, W. Huang, *Org. Lett.* **2016**, *18*, 172–175; e) C. Poriel, J. Rault-Berthelot, *J. Mater. Chem. C* **2017**, *5*, 3869–3897; f) L. Sicard, O. Jeannin, J. Rault-Berthelot, C. Quinton, C. Poriel, *ChemPlusChem* **2018**, *83*, 874–880; g) K. R. J. Thomas, A. Baheti, *Mater. Technol.* **2013**, *28*, 71–87; h) J. Shaya, F. Fontaine-Vive, B. Y. Michel, A. Burger, *Chem. Eur. J.* **2016**, *22*, 10627–10637; i) I. V. Kurdyukova, A. A. Ishechenko, *Russ. Chem. Rev.* **2012**, *81*, 258–290.

[2] a) X. Guo, M. Baumgarten, K. Müllen, *Prog. Polym. Sci.* **2013**, *38*, 1832–1908; b) R. Abbel, A. P. H. J. Schenning, E. W. Meier, *J. Polym. Sci. Part A* **2009**, *47*, 4215–4233; c) S.-A. Chen, H.-H. Lu, C. W. Huang, *Adv. Polym. Sci.* **2008**, *212*, 49–84; d) U. Scherf, E. J. W. List, *Adv. Mater.* **2002**, *14*, 477–487; e) Y. Wu, D. Wu, H. Zhao, J. Li, X. Li, Z. Wang, H. Wang, F. Zhu, B. Xu, *RSC Adv.* **2019**, *9*, 22176–22184; f) N. Giuseppone, G. Fuks, J.-M. Lehn, *Chem. Eur. J.* **2006**, *12*, 1723–1735.

[3] a) L. Zhu, J. Qin, C. Yang, *Chem. Commun.* **2010**, *46*, 8755–8757; b) C.-S. Wu, Y.-J. Lin, Y. Chen, *Org. Biomol. Chem.* **2014**, *12*, 1419–1429; c) S. W. Thomas, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339–1386; d) T. Yang, Y. Zuo, Y. Zhang, Z. Gou, X. Wang, W. Lin, *J. Mater. Chem. B* **2019**, *7*, 4649–4654.

[4] a) R. Hosseinzadeh, M. Mohadjerani, M. Pooryousef, *Anal. Bioanal. Chem.* **2016**, *408*, 1901–1908; b) A. S. Tanwar, S. Hussain, A. H. Malik, M. A. Afroz, P. K. Iyer, *ACS Sens.* **2016**, *1*, 1070–1077.

[5] S. Oger, D. Schapman, R. Mougeot, S. Leleu, N. Lascoux, P. Baldeck, M. Bénard, T. Gallavardin, L. Galas, X. Franck, *Chemistry* **2019**, *25*, 10954–10964.

[6] a) N. Zehra, D. Dutta, A. H. Malik, S. S. Ghosh, P. K. Iyer, *ACS Appl. Mater. Interfaces* **2018**, *10*, 27603–27611; b) I. H. Bae, H. S. Kim, Y. You, C. Chough, W. Choe, M. K. Seon, S. G. Lee, G. Keum, S. K. Jang, B. Moon Kim, *Eur. J. Med. Chem.* **2015**, *101*, 163–178.

[7] a) L. Wang, T. Zhuang, F. Li, W. Wei, *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 27407–27413; b) E. M. Hussein, R. I. Alsantali, S. M. Abd El-Galil, R. J. Obaid, A. Alharbi, M. A. S. Abourehab, S. A. Ahmed, *Heliyon* **2019**, *5*, e01982.

[8] a) S. R. Chowdhury, S. Mondal, B. Muthuraj, S. N. Balaji, V. Trivedi, P. K. Iyer, *ACS Omega* **2018**, *3*, 8059–8066; b) M. T. Gabr, M. S. Abdel-Raziq, *Chem. Biodiversity* **2018**, *15*, e1800244.

[9] P. Seidel, A. Schwarzer, M. Mazik, *Eur. J. Org. Chem.* **2019**, 1493–1502.

[10] For examples of acyclic benzene-based carbohydrate receptors reported by our group, see: a) M. Stapf, W. Seichter, M. Mazik, *Eur. J. Org. Chem.* **2020**, 4900–4915; b) S. Kaiser, C. Geffert, M. Mazik, *Eur. J. Org. Chem.* **2019**, 7555–7562; c) N. Koch, W. Seichter, M. Mazik, *Synthesis* **2016**, *48*, 2757–2767; d) J. Lippe, W. Seichter, M. Mazik, *Org. Biomol. Chem.* **2015**, *13*, 11622–11632; e) C. Geffert, M. Mazik, *J. Org. Chem.* **2013**, *78*, 292–300; f) J.-R. Rosien, W. Seichter, M. Mazik, *Org. Biomol. Chem.* **2013**, *11*, 6569–6579; g) C. Sonnenberg, A. Hartmann, M. Mazik, *Nat. Prod. Commun.* **2012**, *7*, 321–326; h) M. Mazik, A. Hartmann, *Beilstein J. Org. Chem.* **2010**, *6*, No. 9; i) M. Mazik, M. Kuschel, *Chem. Eur. J.* **2008**, *14*, 2405–2419; j) M. Mazik, H. Cavga, *J. Org. Chem.* **2007**, *72*, 831–838; k) M. Mazik, C. Geffert, *Org. Biomol. Chem.* **2011**, *9*, 2319–2326; l) M. Mazik, W. Radunz, R. Boese, *J. Org. Chem.* **2004**, *69*, 7448–7462; m) M. Mazik, W. Sicking, *Chem. Eur. J.* **2001**, *7*, 664–670; n) M. Mazik, H. Bandmann, W. Sicking, *Angew. Chem. Int. Ed.* **2000**, *39*, 551–554; *Angew. Chem.* **2000**, *112*, 562–565; o) M. Mazik, W. Radunz, W. Sicking, *Org. Lett.* **2002**, *4*, 4579–4582; For reviews, see:; p) M. Mazik, *Chem. Soc. Rev.* **2009**, *38*, 935–956; q) M. Mazik, *RSC Adv.* **2012**, *2*, 2630–2642; r) L. Köhler, W. Seichter, M. Mazik, *Eur. J. Org. Chem.* **2020**, DOI: 10.1002/ejoc.202001101.

[11] For examples of tripodal and hexapodal benzene derivatives with the ability to complex ammonium ions, see: a) J. Chin, J. Oh, S. Y. Jon, S. H. Park, C. Walsdorff, B. Stranix, A. Ghoussoub, S. J. Lee, H. J. Chung, S.-M. Park, K. Kim, *J. Am. Chem. Soc.* **2002**, *124*, 5374–5379; b) M. Arunachalam, B. N. Ahamed, P. Ghosh, *Org. Lett.* **2010**, *12*, 2742–2745; c) N. Koch, W. Seichter, M. Mazik, *Tetrahedron* **2015**, *71*, 8965–8974; d) M. Schulze, N. Koch, W. Seichter, M. Mazik, *Eur. J. Org. Chem.* **2018**, 4317–4330; e) T. M. Jonah, L. Mathivathanan, A. N. Morozov, A. M. Mebel, R. G. Raptis, K. Kavallieratos, *New J. Chem.* **2017**, *41*, 14835–14838; f) K. H. Ahn, S.-G. Kim, J. Jung, K.-H. Kim, J. Kim, J. Chin, K. Kim, *Chem. Lett.* **2000**, *29*, 170–171; For a review on the recognition of organic ammonium ions, see: g) A. Späth, B. König, *Beilstein J. Org. Chem.* **2010**, *6*, No.32.

[12] For a unique hydrogen-bonded complex formed between a triethylbenzene derivative and hydronium and hydroxide ions, see: M. Stapf, W. Seichter, M. Mazik, *Chem. Eur. J.* **2015**, *21*, 6350–6354.

[13] For earlier examples of artificial receptors consisting of a triethylbenzene-based scaffold, see: a) A. Metzger, V. M. Lynch, E. V. Anslyn, *Angew. Chem. Int. Ed.* **1997**, *36*, 862–865; *Angew. Chem.* **1997**, *109*, 911–914; For a review on 1,3,5-substituted 2,4,6-triethylbenzene derivatives, see: b) G. Hennrich, E. V. Anslyn, *Chem. Eur. J.* **2002**, *8*, 2219–2224.

[14] For examples of macrocyclic carbohydrate receptors reported by our group, see: a) F. Amrhein, J. Lippe, M. Mazik, *Org. Biomol. Chem.* **2016**, *14*, 10648–10659; b) J. Lippe, M. Mazik, *J. Org. Chem.* **2015**, *80*, 1427–1439; c) J. Lippe, M. Mazik, *J. Org. Chem.* **2013**, *78*, 9013–9020.

[15] For examples of acyclic carbohydrate receptors consisting of a biphenyl-, diphenylmethane- or dimesitylmethane-based scaffold, see: a) M. Mazik, A. König, *J. Org. Chem.* **2006**, *71*, 7854–7857; b) M. Mazik, A. C. Buthe, *Org. Biomol. Chem.* **2009**, *7*, 2063–2071; c) N. Koch, J.-R. Rosien, M. Mazik, *Tetrahedron* **2014**, *70*, 8758–8767.

[16] V. Marks, H. E. Gottlieb, A. Melman, G. Byk, S. Cohen, S. E. Biali, *J. Org. Chem.* **2001**, *66*, 6711–6718.

[17] For other 2,4,7-trisubstituted fluorenes containing imidazolyl groups, see: D. Kumar, K. R. J. Thomas, Y.-L. Chen, Y.-C. Jou, J.-H. Jou, *Tetrahedron* **2013**, *69*, 2594–2602.

[18] J. M. Khurana, S. Chauhan, G. Bansal, *Monatsh. Chem.* **2004**, *135*, 83–87.

[19] N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, W. M. Weaver, *J. Am. Chem. Soc.* **1957**, *79*, 6562.

[20] H. R. Ing, R. H. F. Manske, *J. Chem. Soc.* **1926**, *129*, 2348–2351.

[21] For a review, see: V. Martí-Centelles, M. D. Pandey, M. I. Burguete, S. V. Luis, *Chem. Rev.* **2015**, *115*, 8736–8834.

[22] a) T. Shinmyozu, N. Shibakawa, K. Sugimoto, H. Sakane, H. Takemura, K. Sako, T. Inazu, *Synthesis* **1993**, 1257–1260; b) P. Rajakumar, R. Padmanabhan, *Tetrahedron* **2011**, *67*, 9669–9679; c) Y.-H. Chang, Y.-J. Lee, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu, *Org. Lett.* **2018**, *20*, 2416–2419.

[23] S. Yao, K. D. Belfield, *J. Org. Chem.* **2005**, *70*, 5126–5132.

[24] For examples of other fluorenophanes, see: a) P. Rajakumar, R. Kanagalatha, *Tetrahedron Lett.* **2007**, 2761–2764; b) P. Rajakumar, R. Anandhan, *Synth. Commun.* **2013**, *43*, 882–892.

[25] B. Kenda, Y. Quesnei, A. Ates, P. Michel, L. Turet, J. Mercifer, Patent WO2006128692 A2, **2006**.

Manuscript received: September 13, 2020
Revised manuscript received: October 17, 2020