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Trication species stabilized by heteroazulenes: synthesis and properties of 1,3,5-tris[bis(heteroazulen-3-yl)methyliumyl]benzenes

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A general synthesis and properties of a novel type of heteroazulene analogues of fairly stable trimethyliumylbenzenes (**14a**–**i**·**3BF$_4^-$**) bearing 1,3,5-trimethyliumyl groups substituted with six 2*H*-cyclohepta[*b*]furan-2-one **8a**, six 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **8b**, six 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **8c**, and their related compounds are reported. The synthetic method is based on a single and stepwise TFA-catalyzed electrophilic aromatic substitution on the heteroazulenes **8a**, **8b**, and **8c** with 1,3,5-triformylbenzene **9**, mono- and diformylbenzene having di-and monoheteroazulene-substituted methyl groups to afford the corresponding 1,3,5-trimethylbenzene derivatives, followed by oxidative hydrogen abstraction with DDQ, and subsequent exchange of the counter-anion by using aq. HBF_4 solution in Ac_2O. In spite of their tricationic nature, **14a**–**i** exhibited high stability with large [pK_{R+}] values due to the stabilizing effect of the heteroazulene units. In the case of trications **14b**, three methyliumyl-units were neutralized stepwise at the pH of 10.4, 11.5, and 13.0. However, we could not determine pK_{R+}, pK_{R++}, and pK_{R+++} values separately in the cases of other trications **14a** and **14c**–**i**. Thus, some [pK_{R+}] values were obtained as the average values of pK_{R+++} and pK_{R++} values as well as of pK_{R++} and pK_{R+} values. The electrochemical reduction of most of the trications exhibits irreversible waves and low reduction peak potentials upon cyclic voltammetry (CV); the values are discussed on the basis of a comparison with those of the related monocation and dication species to clarify the reduction process of trications **14a**–**i**. The reduction waves of **14a**–**e**,**h**,**i** were irreversible, while those of **14f**,**g** seem to be reversible; this feature would be ascribed to their large steric constraints.

Introduction

Since the aryl-stabilized carbotrication, 1,3,5-tris(diphenylmethyliumyl)benzene **1**, was reported by M. Leo,[1] much attention has been focused on the electrochemical properties of **1** (Fig. 1).[2–6] The 1,3,5-trimethyliumylbenzene **1** and its reduced molecule, trimethylenebenzene, have been studied theoretically and experimentally,[7,8] and thus, the incorporation of triradical building blocks based on **1** as the segments of a larger moleculer organic magnet has been investigated. On the other hand, it is noteworthy that T. Asao and coworkers have recently reported the synthesis and properties of an azulene analogue of **1**, *i.e.*, 1,3,5-tris[bis(3,6-di-*tert*-butylazulen-1-yl)methyliumyl]benzene **2**.[9,10] The trication **2** is extraordinarily stable with high pK_{R+++}, pK_{R++}, and pK_{R+} values of 9.1, 10.9, and 12.7, respectively. The values seem to be reasonable because azulene derivatives stabilize cations, *i.e.*, tri(azulen-1-yl)methyl,[11–20] di(azulen-1-yl)phenylmethyl,[11,14,16–20] and (azulen-1-yl)diphenylmethyl cations,[11,14,16,17,19] and their derivatives.

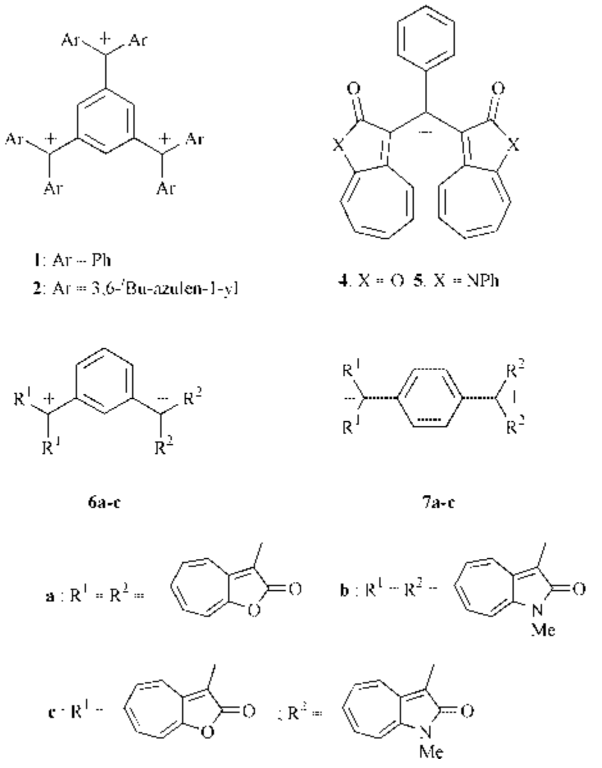

Fig. 1

On the other hand, we have previously studied the synthesis and properties of heteroazulene analogues of the triphenylmethyl cation, *i.e.*, tris(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl, tris(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl, and tris(1,2-dihydro-2-oxo-*N*-methylcyclohepta[*b*]pyrrol-3-yl)methyl cations, **3a**–**c**,[21] as well as bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)phenylmethyl and bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)phenylmethyl cations **4** and **5** and their derivatives.[22] Thus, heteroazulenes, such as **8a**–**c** (Scheme 1), are demonstrated to stabilize not only cations but also radical species and anions.[22] Based on these studies, we have also investigated the synthesis and properties of heteroazulene-substituted 1,3-dimethyliumylbenzenes **6a**–**c** and their 1,4-isomers **7a**–**c**.[23] The two methyliumyl-units in the dications **6a**–**c** and **7a**–**c** were neutralized simultaneously at pHs ranging from 9.0 to 12.7. The electrochemical reduction of **6a**–**c** and **7a**–**c** exhibits irreversible waves and low reduction peak potentials

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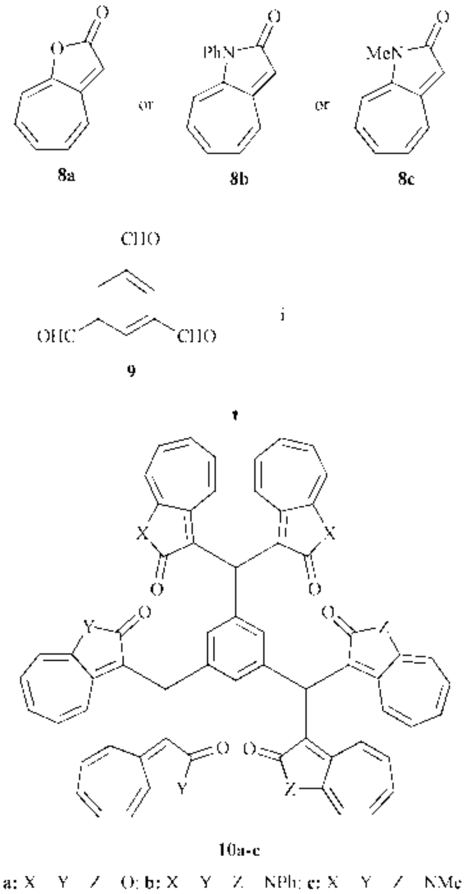
Table 1 Results for the preparation of 1,3,5-trismethylbenzene derivatives **10a–i**, and 1,3,5-tris(methyliumyl)benzenes **14a–i·3BF$_4^-$**

Run	Heteroazulene	Aldehyde	Condensation product (yield/%)	Hydride abstraction product (yield/%)
1	**8a**[a]	**9**	**10a** (68)	**14a·3BF$_4^-$** (89)
2	**8b**[a]	**9**	**10b** (90)	**14b·3BF$_4^-$** (89)
3	**8c**[a]	**9**	**10c** (94)	**14c·3BF$_4^-$** (98)
4	**8a**[b]	**9**	**11a** (39), **12a** (31), **9** (21)	—
5	**8c**[b]	**9**	**11c** (45), **12c** (27), **9** (16)	—
6	**8b**[c]	**11a**	**10d** (94)	**14d·3BF$_4^-$** (87)
7	**8b**[b]	**12a**	**10e** (100)	**14e·3BF$_4^-$** (83)
8	**8c**[c]	**11a**	**10f** (74)	**14f·3BF$_4^-$** (87)
9	**8c**[b]	**12a**	**10g** (80)	**14g·3BF$_4^-$** (91)
10	**8b**[b]	**12c**	**10h** (100)	**14h·3BF$_4^-$** (100)
11	**8b**[d]	**11c**	**13** (25), **11c** (34)	—
12	**8a**[b]	**13**	**10i** (97)	**14i·3BF$_4^-$** (87)

[a] Six equiv. heteroazulene. [b] Two equiv. heteroazulene. [c] Four equiv. heteroazulene. [d] One equiv. heteroazulene.

upon cyclic voltammetry (CV).[23] The reduction processes of **6c**, which has two different methyliumyl-units, and **7a–c** proceed *via* four one-electron reduction steps. In contrast, dications **6a**,**b**, which have two identical methyliumyl-units, exhibited two two-electron reduction steps.[23] Thus, in connection with our previous studies of heteroazulene-substituted methylium ions,[21–24] we embarked on the synthesis and clarification of the properties of heteroazulene-substituted trications **14a–i**. The trications have been found to be fairly stable with large [pK_{R+}] values and low reduction potentials. We report herein the results in detail.

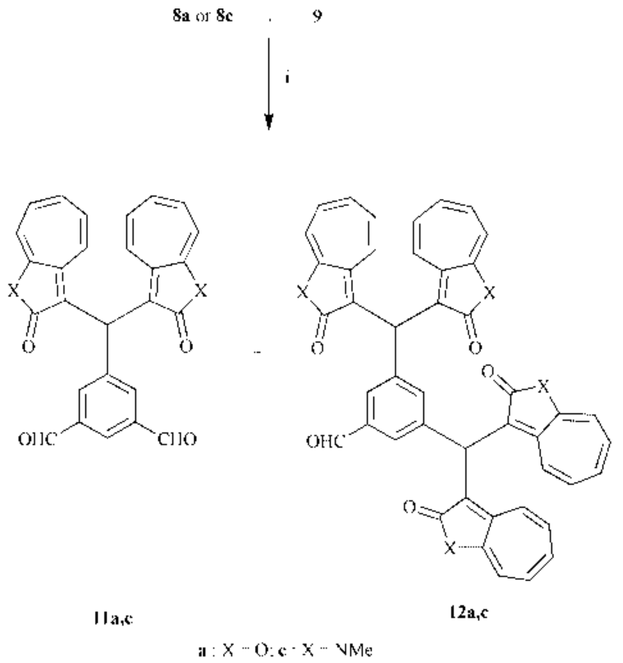


Scheme 1 *Reagents and conditions*: i, CH_2Cl_2–TFA (5 : 1), rt, 48 h.

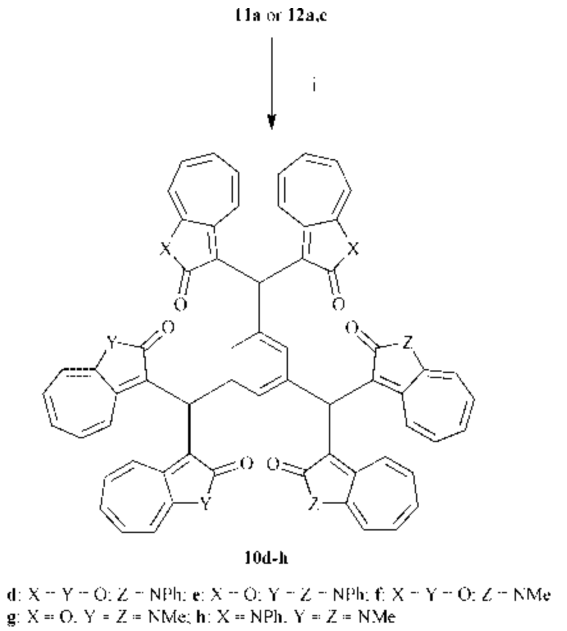
Results and discussion

Synthesis

Preparation of various trication species was easily accomplished by the TFA-catalyzed condensation of aldehydes with heteroazulenes and subsequent oxidative hydrogen abstraction. The reactions of 1,3,5-triformylbenzene **9** with six molar equivalent amounts of 2*H*-cyclohepta[*b*]furan-2-one **8a**,[25] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **8b**,[26] and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **8c**[27,28] in CH_2Cl_2–TFA (5 : 1) at rt for 48 h afforded three types of six-heteroazulene-substituted 1,3,5-trimethylbenzene, 1,3,5-tris[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]benzene **10a**, 1,3,5-tris[bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl]benzene **10b**, and 1,3,5-tris[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl]benzene **10c** in moderate to good yields (Scheme 1, Table 1, Runs 1–3, respectively). On the other hand, preparation of heteroazulene analogues of 1,3,5-trimethylbenzene having two or three types of heteroazulene-substituted methyl groups was successfully accomplished by stepwise condensation reaction of **9** with heteroazulenes. Controlled reaction of 1,3,5-triformylbenzene **9** with two molar equivalent amounts of **8a** in CH_2Cl_2–TFA (5 : 1) at rt afforded the expected 5-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]-1,3-diformylbenzene **11a** and 3,5-bis[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]benzaldehyde **12a**, as well as recovery of unreacted **9** (Scheme 2, Table 1, Run 4). Similarly, reaction of 1,3,5-triformylbenzene **9** with **8c** afforded 5-[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl]-1,3-diformylbenzene **11c** and 3,5-bis[bis-(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl]-benzaldehyde **12c**, as well as recovery of unreacted **9** (Table 1, Run 5). The aldehydes **11a**, **12a**, and **12c** reacted with heteroazulene **8b** in a similar fashion to afford 3,5-bis[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]-1-[bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl]benzene **10d**, 1,3-bis[bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl]-5-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]-benzene **10e**, and 1,3-bis[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl]-5-[bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl]benzene **10h**, respectively, in excellent yields (Scheme 3, Table 1, Runs 6, 7, and 10). Similarly, the aldehydes **11a** and **12a** were allowed to react with heteroazulene **8c** to give 3,5-bis[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]-1-[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl)methyl]benzene **10f** and 1,3-bis[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl]-5-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]benzene **10g**, respectively, in moderate yields (Table 1, Runs 8 and 9). Treatment of **11c** with an equivalent amount of heteroazulene **8b** in a similar fashion afforded 3-[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl]-5-[bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl]benzaldehyde **13**, as well as recovery of unreacted **11c** (Scheme 4, Table 1, Run 11). Similarly, aldehyde **13** reacted with heteroazulene **8a** to yield a product having three different heteroazulene-substituted methyl groups, 5-[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl)methyl]-3-[bis(1,2-dihydro-2-oxo-*N*-phenylcyclo-

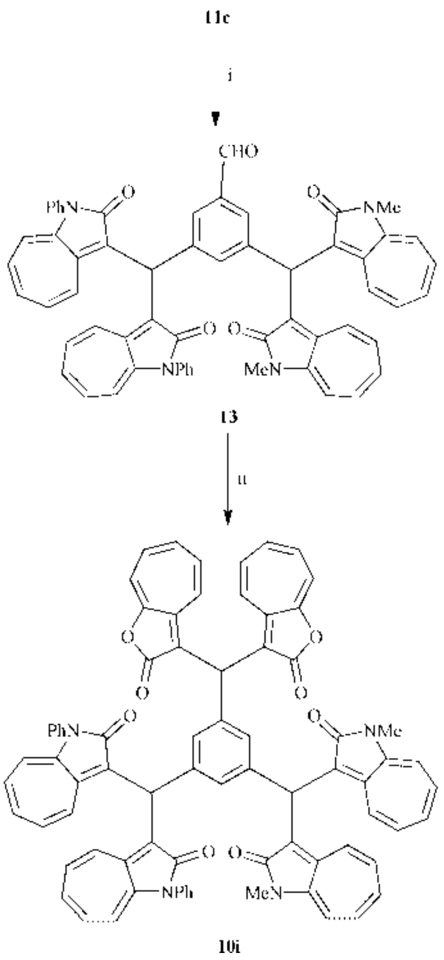


Scheme 2 *Reagents and conditions*: i, CH_2Cl_2–TFA (5 : 1), rt, 48 h.



Scheme 3 *Reagents and conditions*: i, **8b** or **8c**, CH_2Cl_2–TFA (5 : 1), rt, 48 h.

hepta[*b*]pyrrol-3-yl)methyl]-1-[bis(2-oxo-2*H*-cyclohepta[*b*]-furan-3-yl)methyl]benzene **10i** in good yield (Table 1, Run 12). The compounds **10a–i** formed powdery orange or yellow crystals, and their structures were assigned on the basis of their IR, ^1H and ^{13}C NMR spectral data, as well as elemental analyses and mass spectral data. The oxidative hydrogen abstraction of **10a–i** with DDQ in CH_2Cl_2 at rt for 1 h, followed by treatment with aqueous 42% HBF_4 in Ac_2O, afforded crystals of stable tricationic salts, 1,3,5-tris[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyliumyl]benzene tris(tetrafluoroborate) **14a·3BF$_4^-$** and the corresponding pyrrole analogues **14b,c·3BF$_4^-$** and their related compounds **14d–i·3BF$_4^-$** in the yields listed also in Table 1 (Scheme 5).

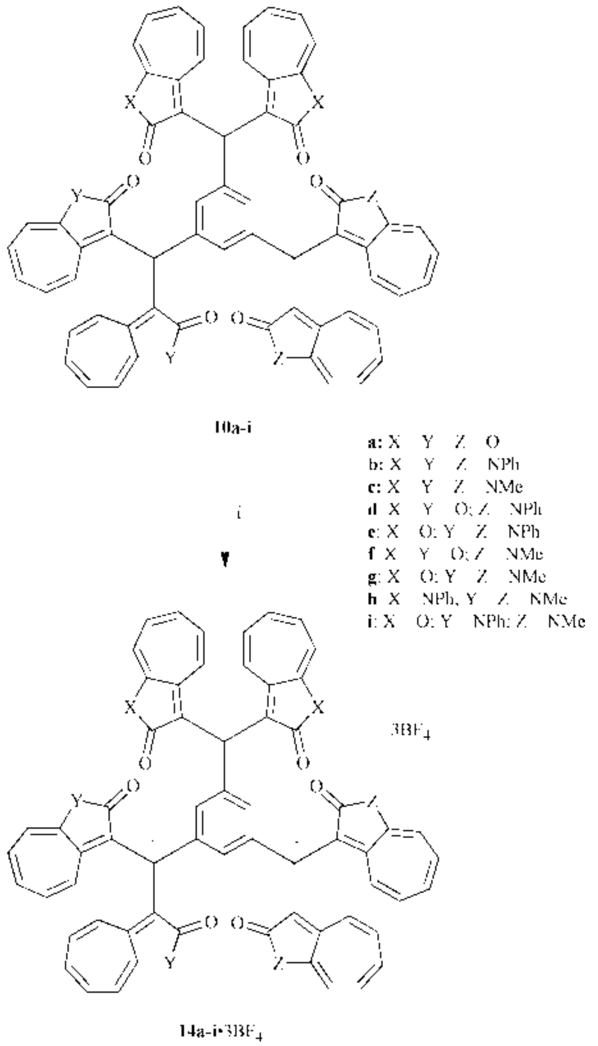


Scheme 4 *Reagents and conditions*: i, **8b** CH_2Cl_2–TFA (5 : 1), rt, 24 h.; ii, **8a** CH_2Cl_2–TFA (5 :1), rt, 24 h.

Spectroscopic properties

The abbreviations, Fn, PPn, and MPn, denote 2-oxo-2*H*-cyclohepta[*b*]furan-3-yl, 1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]-pyrrol-3-yl, and 1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl groups, respectively. In addition, the abbreviations, Fn-unit, PPn-unit, and MPn-unit, denote bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyliumyl, bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyliumyl, and bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyliumyl moieties, respectively. Tricationic species **14a–i·3BF$_4^-$** were fully characterized on the basis of their spectral data, as well as elemental analyses, as shown in the Experimental section. Several tricationic species were crystallized to give complexes containing HBF_4 molecules in the crystal lattice. Thus, some of the salts do not give satisfactory analytical data; however, the mass spectra of the salts **14a–i·3BF$_4^-$** ionized by FAB exhibited satisfactory ion peaks, $M^+ - 3BF_4$, $M^+ + 1 - 3BF_4$, or $M^+ + 2 - 3BF_4$ which are indicative of the tricationic structure of these compounds. The characteristic broad absorptions for the counter anion (BF_4^-) are observed at 1084 cm^{-1}in the IR spectra of **14a–i·3BF$_4^-$**. These features also support the tricationic nature of the compounds.

The signals of the methine protons of **10a–i** disappeared in the ^1H NMR spectra of **14a–i·3BF$_4^-$**. Thus, the ^1H NMR spectra also support the tricationic structure of these compounds. Proton signals on the seven-membered ring of **14a–i·3BF$_4^-$** appear as broad signals. Attempted measurement of the ^1H NMR spectra of **14a–i·3BF$_4^-$** at temperatures ranging from rt to 70 °C (in CD_3CN) exhibited no appreciable change in the broad signals. Thus, slow conformational change in the heteroazulene moieties of these cations occurs during ^1H NMR time scale at these temperatures. Several proton signals on the seven-membered ring of **10b**,**d–i** appear also as broad and complex signals. This feature is completely different from those of other heteroazulene-subtituted methane derivatives.[21–23] This feature would be ascribed to the very large steric hindrance experienced between one heteroazulene moiety and another



Scheme 5 *Reagents and conditions*: i, (a) DDQ in CH_2Cl_2, (b) 42% aq. HBF_4.

heteroazulene moiety in trimethylbenzene derivatives **10a**–**i** as well as in trications **14a**–**i**.

The UV–vis spectra of trications **14a**–**i** in CH_3CN are shown in Fig. 2 and Fig. 3. The longest wavelength absorption maxima of a series of trications **14a** (615 nm), **14b** (622 nm), **14c** (629 nm) **14d** (610 nm), **14e** (614 nm), **14f** (614 nm), **14g** (618 nm), **14h** (626 nm), and **14i** (617 nm) resemble each other. The longest wavelength absorption maxima of trications increase in the order **14a** (which has three Fn-units) < **14b** (which has three PPn-units) < **14c** (which has three MPn-units), and this feature shows that substitution of the heteroazulene induces a red-shift of the longest wavelength of trications in the order Fn < PPn < MPn. Thus, the longest wavelength of **14e** (which has one Fn-unit and two PPn-units) is longer than that of **14d** (which has two Fn-units and one PPn-unit), and the longest wavelength of **14g** (which has one Fn-unit and two MPn-units) is longer than that of **14f** (which has two Fn-units and one MPn-unit). Moreover, the longest wavelength increases in the order **14i** (which has an Fn-unit, a PPn-unit, and an MPn-unit) < **14h** (which has one PPn-unit and two MPn-units) < **14c** (which has three MPn-units). These features show that increasing the number of MPn-units induces a red-shift of the longest wavelengths of trications. The longest wavelength absorption maxima of trications **14a**,**d**,**e**,**f**,**g**,**i**, which have an Fn-unit, are even shorter than those of the related monocation **4** (621 nm), while those of **14b**,**c**,**h**, which have a PPn-unit, are shorter than those of the related monocation **5** (652 nm).[22] This feature seems to be reasonable based on our previous study considering the longest wavelength absorption maxima of **4** and **5** as well as the calculations of the stable conformations of **4** and **5**: the dihedral angles, θ_1, θ_2, and θ_3, which express deviation of the plane of the phenyl groups and heteroazulenes from the reference plane (the plane which is defined by the three arylic ipso carbons, Fig. 4).[22] Thus, the UV–vis spectra of trications **14a**–**i** suggest the absence of appreciable conjugation among the methyliumyl-units. Furthermore, this feature is similar to the cases of dications **6a**–**c**. The longest wavelength absorption maximum of trication **14a**, which has three Fn-units, is similar to those of related dication **6a**, which has two Fn-units. Similarly, the longest wavelength absorption maximum of trication **14c**, which has three MPn-units, is similar to those of the related dication **6b**, which has two MPn-units. Moreover, the longest wavelength absorption maxima of trications **14f**,**g**, which have two Fn-units and one MPn-unit and one Fn-unit and two MPn-units, respectively, are similar to those of the related dication **6c**, which has a Fn-unit and a MPn-unit.

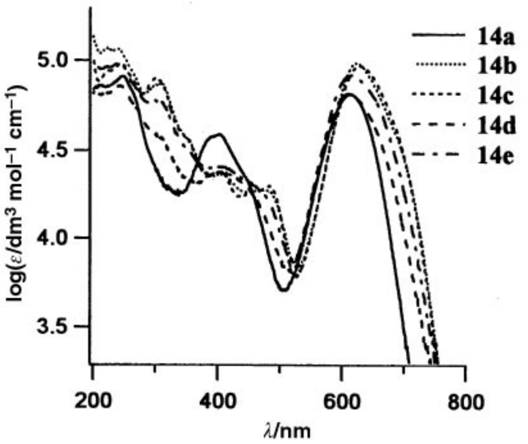


Fig. 2 UV–vis spectra of trications **14a**–**e** in CH_3CN.

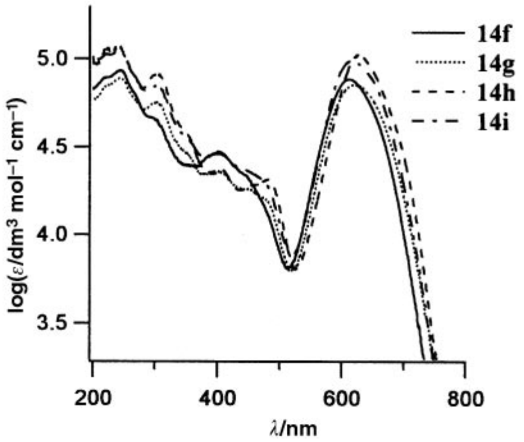
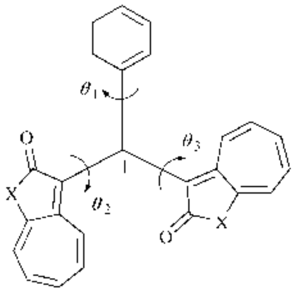


Fig. 3 UV–vis spectra of trications **14f**–**i** in CH_3CN.



4 X = O; 5: X = NPh

Fig. 4

Stability of the trications: [pK_{R+}] values and reduction potentials

The affinity of the carbocation toward the hydroxide ion,

Table 2 [pK_{R+}] values and reduction potentials[a] of trications **14a–i**[b], and reference compounds **2**, **4**, **5**, and **6a–c**

<table>
<tr><th rowspan="2">Compd.</th><th colspan="3">[pK_{R+}]</th><th colspan="6">Reduction potentials</th></tr>
<tr><th>pK_{R+++}</th><th>pK_{R++}</th><th>pK_{R+}</th><th>$E1_{red}$</th><th>$E2_{red}$</th><th>$E3_{red}$</th><th>$E4_{red}$</th><th>$E5_{red}$</th><th>$E6_{red}$</th></tr>
<tr><td>14a</td><td>6.4</td><td colspan="2">9.0</td><td></td><td></td><td>−0.30</td><td></td><td></td><td>−1.13</td></tr>
<tr><td>14b</td><td>10.4</td><td>11.5</td><td>13.0</td><td></td><td></td><td>−0.56</td><td></td><td></td><td>−1.30</td></tr>
<tr><td>14c</td><td>10.5</td><td colspan="2">11.6</td><td></td><td></td><td>−0.60</td><td></td><td></td><td>−1.36</td></tr>
<tr><td>14d</td><td colspan="2">8.2</td><td>12.3</td><td></td><td>−0.32</td><td>−0.53</td><td></td><td>−1.03</td><td>−1.32</td></tr>
<tr><td>14e</td><td>6.7</td><td colspan="2">11.4</td><td>−0.30</td><td></td><td>−0.55</td><td>−1.10</td><td></td><td>−1.32</td></tr>
<tr><td>14f</td><td colspan="2">7.5</td><td>12.0</td><td></td><td>−0.34</td><td>−0.62</td><td></td><td>−1.05</td><td>−1.33</td></tr>
<tr><td>14g</td><td>6.6</td><td colspan="2">11.5</td><td>−0.29</td><td></td><td>−0.59</td><td>−1.06</td><td></td><td>−1.32</td></tr>
<tr><td>14h</td><td>9.4</td><td colspan="2">11.2</td><td></td><td></td><td>−0.59</td><td>−1.34</td><td></td><td>−1.49</td></tr>
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<tr><td>6a[c]</td><td></td><td>9.0</td><td></td><td></td><td>−0.33</td><td></td><td>−1.05</td><td></td><td></td></tr>
<tr><td>6b[c]</td><td></td><td>12.1</td><td></td><td></td><td>−0.60</td><td></td><td>−1.37</td><td></td><td></td></tr>
<tr><td>6c[c]</td><td></td><td>12.7</td><td></td><td>−0.34</td><td>−0.62</td><td>−0.96</td><td>−1.37</td><td></td><td></td></tr>
<tr><td>2[d]</td><td>9.1 ± 0.2</td><td>10.9 ± 0.2</td><td>12.7 ± 0.2</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>4[e]</td><td></td><td></td><td>9.3</td><td>(−0.31)</td><td>(−1.03)</td><td></td><td></td><td></td><td></td></tr>
<tr><td>5[e]</td><td></td><td></td><td>12.0</td><td>(−0.53)</td><td>(−1.29)</td><td></td><td></td><td></td><td></td></tr>
</table>

[a] Peak potentials in V *vs.* Ag/Ag$^+$. Reversible processes are shown in parentheses. [b] **14a–i·3BF$_4^-$** were used for the measurement. [c] Ref. 23. [d] Ref. 9. [e] Ref. 22.

expressed by the [pK_{R+}] values (*cf.* Table 2), is the most common criterion of carbocation stability.[29] The [pK_{R+}] values of the trications **14a–i** were determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH_3CN and are summarized in Table 2, along with those of the reference compounds **4**, **5**, and **6a–c**.[22,23] In the case of trications **14b**, three methyliumyl-units were neutralized stepwise at the pH of 10.4, 11.5, and 13.0, which correspond to pK_{R+++}, pK_{R++}, and pK_{R+}, respectively. Since sharp titration curves for stepwise neutralization of trications **14a** and **14c–i** are not obtained, we could not determine pK_{R+}, pK_{R++}, and pK_{R+++} values separately for these trications. This feature suggests that the two of the three methyliumyl-units in the trications **14a** and **14c–i** are neutralized simultaneously. The neutralization of the trications **14a–i** is not completely reversible. This feature may be ascribed to the instability of the neutralized products under the conditions of the pK_{R+} measurement. Immediate (after *ca.* 5 s) acidification of an alkaline solution (*ca.* pH 14) of **14a–i** with TFA regenerated the absorption maxima of the cations in the visible regions in 40–50%. As expected, the heteroazulenes effectively stabilize the trications, and the [pK_{R+}] values of **14a–i** are extremely high. On the basis of our previous studies of tris(heteroazulen-3-yl)methyl cations **3a–c**[21] and heteroazulene-substituted tropylium ions,[24] the stabilizing ability of heteroazulenes for these cations has been clarified to be in the order Fn < PPn < MPn. Consequently, the [pK_{R+}] values of heteroazulene-substituted methyl cations and tropylium ions increase in the order with the substituent Fn < PPn < MPn. The first [pK_{R+}] values of **14a**,**e**,**g** and **14i** (6.4, 6.7, 6.6, and 6.6), which have one Fn-unit, are similar to each other. In addition, the second [pK_{R+}] values of **14a**,**e**,**g**,**i** (9.0 and 11.4–11.8) are close to those of **6a**,**b** (9.0 and 12.1), respectively. Since the [pK_{R+}] values of **6a**,**b** are considered to be the average values of pK_{R++} and pK_{R+} values, the second [pK_{R+}] values of **14a**,**e**,**g**,**i** would correspond to the average values of pK_{R++} and pK_{R+} values. Thus, the first [pK_{R+}] values of **14a**,**e**,**g**,**i** are considered to be pK_{R+++} values, and an Fn-unit may be neutralized at first. On the other hand, the first [pK_{R+}] values of **14d**,**f** (8.2 and 7.5), which have two Fn-units and a PPn-or an MPn-unit, are larger than those of **14a**,**e**,**g**,**i**, and the second [pK_{R+}] values of **14d**,**f** (12.3 and 12.0) are larger than those of **14a**,**e**,**g**,**i**. In addition, the second [pK_{R+}] values of **14d**,**f** are similar to that of **5**. Thus, the first [pK_{R+}] values of **14d**,**f** probably correspond to the average values of pK_{R+++} and pK_{R++} values, and two Fn-units of **14d**,**f** are neutralized simultaneously at these pH units. Consequently, the second [pK_{R+}] values of **14d**,**f** would be pK_{R+} values of these trications, and the PPn-unit or the MPn-unit is neutralized at these pH units, respectively. The second [pK_{R+}] values of **14c**,**h** are similar to the average values of pK_{R++} and pK_{R+} values of **14b** and **14e**; thus, two MPn-units and a PPn-unit and an MPn-unit are neutralized simultaneously at these pH units. Thus, the first [pK_{R+}] values of **14c**,**h** (10.5, 9.4) are considered to correspond to the pK_{R+++} value. Simultaneous neutralization of two methyliumyl-units suggests the absence of conjugation among the methyliumyl-units.

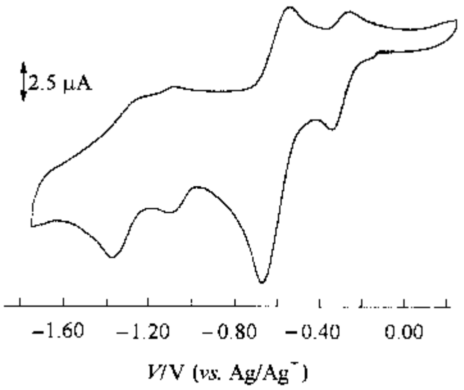
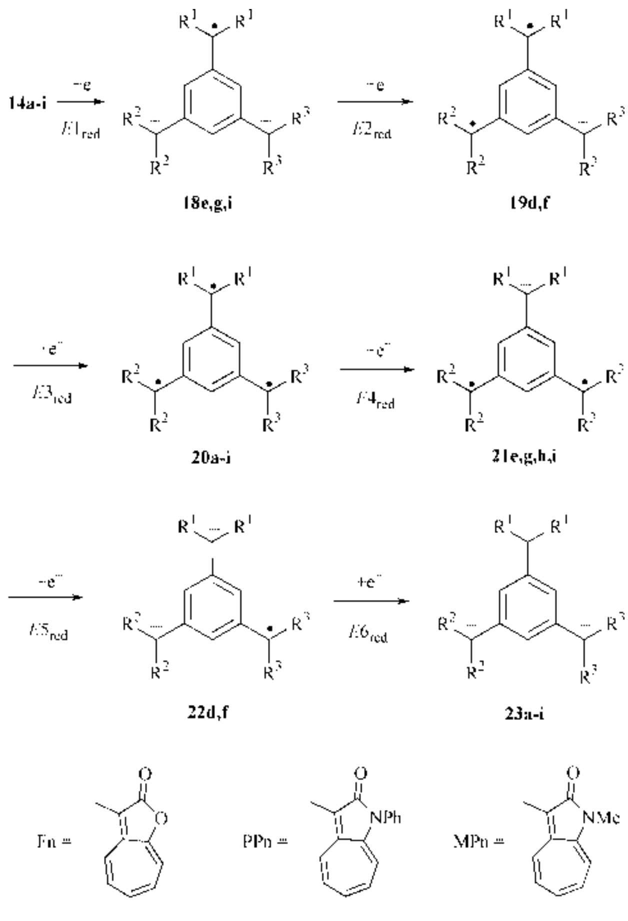


Fig. 5 Cyclic voltammogram of **14g** in MeCN.

The reduction potentials of trications **14a–i** were determined by cyclic voltammetry (CV) in CH_3CN. Most of the reduction waves of **14a–i** were irreversible except **14f**,**g** under the conditions of CV measurements, and thus, the peak potentials are summarized in Table 2 together with those of the reference cations **4**, **5** and **6a–c**.[22,23] The reversibility of the reduction waves of **14f**,**g** seemed to be enhanced, and thus, the CV of **14g** is shown as an example (Fig. 5). This feature suggests that the methyliumyl-units of trications and their reduced methyl-radical-units are stabilized sterically. The reduction behavior of trications is affected by the methyliumyl-units: the reduction potentials depend on the kind of substituted methyliumyl-units. The reduction of trications **14a–i** is expected to give a non-Kekulé-type electronic structure upon reduction. Since the stabilizing ability of heteroazulenes toward cations is in the order Fn < PPn < MPn (*vide supra*), reduction potentials of heteroazulene-substituted methyl cations and tropylium ions are more negative in the order of the substituents Fn < PPn < MPn.[21,24] As seen in the cations **6a–c**, **4**, and **5**, the reduction potentials of the Fn-unit, PPn-unit, and MPn-unit to give radical species are *ca.* −0.33, −0.53, and −0.60 V *vs.* Ag/Ag$^+$, respectively, and those of the Fn-unit, PPn-unit, and MPn-unit to give anion species are *ca.* −1.05, −1.29, and −1.37 V *vs.* Ag/Ag$^+$, respectively. On the basis of these facts, plausible



a: $R^1 = R^2 = R^3 =$ Fn; **b**: $R^1 = R^2 = R^3 =$ PPn; **c**: $R^1 = R^2 = R^3 =$ MPn
d: $R^1 = R^2 =$ Fn, $R^3 =$ PPn; **e**: $R^1 =$ Fn, $R^2 = R^3 =$ PPn
f: $R^1 = R^2 =$ Fn, $R^3 =$ MPn; **g**: $R^1 =$ Fn, $R^2 = R^3 =$ MPn
h: $R^1 =$ PPn, $R^2 = R^3 =$ MPn; **i**: $R^1 =$ Fn, $R^2 =$ PPn, $R^3 =$ MPn

Scheme 6

reduction processes of trications **14a**–**i** are depicted in Scheme 6. Trications **14a**–**c**, all of which have the same three methyliumyl-units, exhibited two reduction peaks $E3_{red}$ and $E6_{red}$ at −0.30 and −1.13, −0.56 and −1.30, and −0.60 and −1.36 V *vs.* Ag/Ag$^+$, respectively; the values for **14a**, which has three Fn-units, are close to those of $E2_{red}$ and $E4_{red}$ of **6a**, which is the dication having two Fn-units. The values for **14c**, which has three MPn-units, are very similar to those of $E2_{red}$ and $E4_{red}$ of **6b**, which is the dication having two MPn-units. In the case of **6a**,**b**, two-electron reductions proceed at $E2_{red}$ and $E4_{red}$ to afford diradical and dianion species, respectively. Thus, the reduction process of **14a**–**c** is rationalized to proceed *via* two steps of three-electron reduction affording triradical species **20a**–**c** and their trianions **23a**–**c**, respectively. On the other hand, trications **14d**–**g**, which have two different methyliumyl-units, exhibited four reduction potentials among $E1_{red}$–$E6_{red}$ (Table 2). The first ($E2_{red}$) and third ($E5_{red}$) reduction potentials of **14d**,**f** (−0.32 and −1.03 V *vs.* Ag/Ag$^+$ for **14d**; −0.34 and −1.05 for **14f**), which have two Fn-units and a PPn-unit or an MPn-unit, are similar to $E2_{red}$ and $E4_{red}$ of **6a**, as well as $E1_{red}$ and $E2_{red}$ of **4**, respectively. In the cases of **6a** and **4**, Fn-units are reduced at those reduction potentials to give radical and, then, anion species in a step-wise fashion. Thus, two Fn-units of **14d**,**f** are considered to be reduced at the first and third reduction potentials. In addition, the second ($E3_{red}$) and fourth ($E6_{red}$) reduction potentials of **14d**,**f** (−0.53 and −1.32 V *vs.* Ag/Ag$^+$ for **14d**; −0.62 and −1.33 for **14f**) are similar to $E3_{red}$ and $E6_{red}$ of **14b**,**c**, respectively. Thus, a PPn-unit and an MPn-unit of **14d**,**f** are reduced at the second and fourth reduction potentials. Consequently, the reduction process of **14d**,**f** proceeds *via* two-electron reduction of two Fn-units at $E2_{red}$ to afford diradical-cation species **19d**,**f**, which undergo one-electron reduction of a PPn-unit and an MPn-unit at $E3_{red}$ to afford triradical species **20d**,**f**. Then, the two-electron reduction of two Fn-units at $E5_{red}$ affords radical-dianion species **22d**,**f**, which undergo the one-electron reduction of a PPn-unit or a MPn-unit at $E6_{red}$, to afford trianion species **23d**,**f**. On the other hand, the first ($E1_{red}$) and third ($E4_{red}$) reduction potentials of **14e**,**g** (−0.30 and −1.10 V *vs.* Ag/Ag$^+$ for **14e**; −0.29 and −1.06 for **14g**), which have Fn-unit and two PPn-units or two MPn-units, are similar to $E2_{red}$ and $E4_{red}$ of **6a**, as well as $E1_{red}$ and $E2_{red}$ of **4**, respectively. Thus, the Fn-unit of **14e**,**g** is probably reduced at the first and third reduction potentials. In addition, the second ($E3_{red}$) and fourth ($E6_{red}$) reduction potentials of **14e**,**g** (−0.55 and −1.32 V *vs.* Ag/Ag$^+$ for **14e**; −0.59 and −1.32 for **14g**) are similar to those of $E3_{red}$ and $E6_{red}$ of **14b**,**c**, respectively. Thus, two PPn-units and two MPn-units of **14e**,**g** are probably reduced at the second and fourth reduction potentials. Consequently, the reduction process of **14e**,**g** proceeds *via* one-electron reduction of an Fn-unit at $E1_{red}$ to afford radical-dication species **18e**,**g**, and subsequent two-electron reduction of two PPn-units or two MPn-units occurs at $E3_{red}$ simultaneously to afford triradical species **20e**,**g**. Then, further one-electron reduction of an Fn-unit at $E4_{red}$ affords diradical-anion species **21e**,**g**, which undergo simultaneous two-electron reduction of two PPn-units or two MPn-units at $E6_{red}$ occurs to afford trianion species **23e**,**g**. Although a similar feature was expected for **14h**, it exhibited only three reduction potentials (Table 2). Since the difference between the reduction potentials of one-electron reduction of a PPn- and an MPn-unit (*cf.* $E1_{red}$ of **5** and $E2_{red}$ of **6b**) would be small, the reductions of these units occur simultaneously to give **20h**. Then, further one-electron reduction occurs to give **21h** in a step-wise fashion, which undergoes two-electron reduction to formation of **23h**. In a similar manner, trication **14i**, which has three different methyliumyl-units, exhibited also four reduction potentials between $E1_{red}$–$E6_{red}$ (Table 2). In this case, the $E2_{red}$ and $E3_{red}$, which correspond to one-electron reduction of a PPn-and an MPn-unit, respectively, are similar, and thus, the reduction of these units in **18i** to give **20i** occurs simultaneously. After reduction of an Fn-unit in **20i** at $E4_{red}$ to afford **21i**, since the $E5_{red}$ and $E6_{red}$, which correspond to one-electron reduction of a PPn-and an MPn-unit, respectively, are also similar, two-electron reduction of **21i** occurs to give **24i**. The reduction properties of **14a**–**i** described above clearly show the absence of conjugation among three methyliumyl-units, and the existence of triradical species **20a**–**i** and trianion species **23a**–**i**. This feature is similar to the cases of non-Kekulé-type dications **6a**–**c** and is completely different from the cases of Kekulé-type dications **7a**–**c**, which involve conjugation among two methyliumyl-units.

In summary, efficient synthesis of fairly stable trications **14a**–**i** having a variety of methyliumyl-units substituted with hetero-azulenes has been accomplished. The stability of **14a**–**i** was evaluated by the [pK_{R+}] values and the reduction potentials measured by CV. In the case of trications **14b**, three methyliumyl-units were neutralized stepwise at pH 10.4, 11.5, and 13.0. However, we could not determine pK_{R+}, pK_{R++}, and pK_{R+++} values separately in the cases of other trications **14a** and **14c**–**i**. This feature shows that two methyliumyl-units are neutralized simultaneously in these trications. The reduction potentials of trications **14a**–**i** are affected by the methyliumyl-units. Among different trications, the reduction potentials of the same methyliumyl-units are similar to each other. In addition, the same methyliumyl-units in one trication are reduced simultaneously. These features show that three methyliumyl-units of trications **14a**–**i** are twisted against the central phenyl group, and no conjugation among methyliumyl-units is suggested. Further studies concerning the synthesis and properties of stable heteroazulene-substituted polycations and radical species will be continued.

Experimental

IR spectra were recorded on a HORIBA FT-710 spectrometer. Mass spectra and high-resolution mass spectra were run on JMS-AUTOMASS 150 and JMS-SX102A spectrometers. Unless otherwise specified, ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a JNM-lambda 500 spectrometers using $CDCl_3$ as the solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard: *J*-values are given in Hz. The abbreviations, Fn, PPn, and MPn in the ^{1}H NMR data denote 2-oxo-2*H*-cyclohepta[*b*]furan-3-yl, 1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl, and 1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl moieties, respectively. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. The heteroazulenes, 2*H*-cyclohepta[*b*]furan-2-one **8a**,[25] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **8b**,[26] and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **8c**,[27,28] were prepared as described in the literature.

Preparation of 10a–c

A solution of **8a**–**c** (3 mmol) and **9** (0.5 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on SiO_2 by using hexane–AcOEt (1 : 1) as the eluent to give the products **10a**–**c** (Table 1, Runs 1, 2, and 3).

For 10a. Orange powder; mp 239–240 °C (decomp) (from CH_2Cl_2–EtOH); δ_H (500MHz) 5.54 (3H, s, Fn_2CH), 6.76 (6H, t, *J* 9.6, Fn-6), 6.85–6.94 (18H, m, Fn-5, Fn-7, Fn-8), 6.97 (3H, s, Ph-2, 4, 6), 7.38 (6H, d, *J* 11.6, Fn-4); δ_C (125.7 MHz) 35.4, 108.6, 113.9, 126.0, 128.1, 130.9, 132.1, 135.0, 138.5, 148.7, 157.5, 169.1; ν_{max} ($CHCl_3$)/cm^{-1} 1735 1261; *m*/*z* (FAB) 984 (M^+) (Found: C, 74.7; H, 3.8. $C_{63}H_{36}O_{12}$·1/2CH_2Cl_2 requires C, 74.23; H, 3.63%).

For 10b. Orange powder; mp 264–266 °C (from CH_2Cl_2–EtOH); δ_H (500MHz) 6.14 (3H, s, PPn_2CH), 6.56–6.63 (12H, m, PPn-6, 8), 6.70–6.75 (12H, m, PPn-5, 7), 7.16–7.17 (12H, m, NPh), 7.25–7.27 (3H, m, Ph-2, 4, 6), 7.33–7.38 (18H, m, NPh), 7.86 (6H, d, *J* 11.4, PPn-4); δ_C (125.7 MHz) 36.4, 112.3, 113.9, 126.5, 128.1, 129.0, 129.2, 129.7, 130.0, 130.7, 134.9, 140.3, 141.6, 145.6, 168.7 (one carbon overlapping); ν_{max} ($CHCl_3$)/cm^{-1} 1684; *m*/*z* (FAB) 1435 (M^+ + 1) (Found: C, 79.1; H, 4.4; N, 5.5. $C_{99}H_{66}N_6O_6$ requires C, 78.99; H, 4.51; N, 5.53%).

For 10c. Orange powder; mp 279–281 °C (decomp) (from CH_2Cl_2–EtOH); δ_H (500MHz) 3.32 (18H, s, Me), 5.91 (3H, s, MPn_2CH), 6.63 (6H, d, *J* 9.0, MPn-8), 6.65–6.72 (12H, m, MPn-5, 6), 6.88 (6H, dd, *J* 9.3, 9.0, MPn-7), 6.92 (3H, s, Ph-2, 4, 6), 7.64 (6H, d, *J* 11.2, MPn-4); δ_C (125.7 MHz, DMSO-d$_6$) 26.0, 35.4, 111.4, 113.4, 125.3, 127.2, 128.1, 130.0, 130.5, 139.7, 139.9, 143.7, 167.1; ν_{max} ($CHCl_3$)/cm^{-1} 1654; *m*/*z* (FAB) 1063 (M^+) (Found: C, 74.7; H, 5.1; N, 7.3. $C_{69}H_{54}N_6O_6$·2/3CH_2Cl_2 requires C, 74.72; H, 4.98; N, 7.50%).

Preparation of 11a, 12a, 11c, and 12c

A solution of **8a**,**c** (2 mmol) and **9** (1 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. The reaction mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on SiO_2 by using hexane–AcOEt (1 : 1) as the eluent to give the products **11a**,**c** and **12a**,**c**, and recovery **9** (Table 1, Runs 4 and 5).

For 11a. Orange powder; mp 150–151 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 5.81 (1H, s, Fn_2CH), 6.90 (2H, dd, *J* 9.5,8.6, Fn-6), 7.03–7.10 (6H, m, Fn-5, 7, 8), 7.58 (2H, d, *J* 11.4, Fn-4), 7.98 (2H, s, Ph-4, 6), 8.30 (1H, s, Ph-2), 10.06 (2H, s, CHO); δ_C (125.7 MHz) 34.7, 107.5, 115.1, 127.8, 129.8, 131.5, 132.9, 133.7, 135.8, 137.5, 140.0, 149.1, 157.7, 169.3, 190.9; ν_{max} (KBr)/cm^{-1} 1735, 1252; *m*/*z* (FAB) 436 (M^+) (Found: C, 68.5 H, 3.2. $C_{27}H_{16}O_6$·1/2CH_2Cl_2 requires C, 68.97; H, 3.58%).

For 12a. Yellow powder; mp 194–195 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 5.68 (2H, s, Fn_2CH), 6.82 (4H, dd, *J* 10.2, 8.1, Fn-6), 6.94–7.00 (12H, m, Fn-5, 7, 8), 7.32 (1H, s, Ph-4), 7.46 (4H, d, *J* 11.4, Fn-4), 7.64 (2H, s, Ph-2, 6), 9.91 (1H, s, CHO); δ_C (125.7 MHz) 35.0, 108.0, 114.4, 127.8, 127.9, 131.2, 132.5, 132.9, 135.4, 137.5, 139.2, 148.9, 157.6, 169.2, 192.0; ν_{max} (KBr)/cm^{-1} 1735, 1271; *m*/*z* (FAB) 711 (M^+ + 1) (Found: C, 71.3 H, 3.0. $C_{45}H_{26}O_9$·2/3CH_2Cl_2 requires C, 71.48; H, 3.59%).

For 11c. Yellow powder; mp 220–221 °C (from CH_2Cl_2–EtOH); δ_H (400 MHz) 3.56 (6H, s, Me), 6.28 (1H, s, MPn_2CH), 6.90 (2H, dd, *J* 10.0, 9.3, MPn-6), 6.94 (2H, d, *J* 9.3, MPn-8), 7.05 (2H, dd, *J* 11.2, 9.3, MPn-5), 7.10 (2H, dd, *J* 10.0, 9.3, MPn-7), 7.93 (2H, d, *J* 11.2, MPn-4), 7.97 (2H, s, Ph-4, 6), 8.24 (1H, s, Ph-2), 10.01 (2H, s, CHO); δ_C (125.7 MHz) 26.7, 35.3, 112.0, 112.8, 128.2, 129.1, 129.3, 130.7, 131.5, 134.5, 137.1, 141.6, 142.8, 144.8, 168.4, 191.4; ν_{max} ($CHCl_3$)/cm^{-1} 1700, 1684; *m*/*z* (FAB) 463 (M^+ + 1) (Found: C, 70.4 H, 4.5; N, 5.1. $C_{29}H_{22}N_2O_4$ requires C, 70.17; H, 4.59; N, 5.55%).

For 12c. Yellow powder; mp 250–251 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 3.44 (12H, s, Me), 6.09 (2H, s, MPn_2CH), 6.78 (4H, d, *J* 9.6, MPn-8), 6.79 (4H, dd, *J* 10.3, 8.6, MPn-6), 6.88 (4H, dd, *J* 11.0, 8.6, MPn-5), 6.99 (4H, dd, *J* 10.3, 9.6, MPn-7), 7.33 (1H, s, Ph-4), 7.58 (2H, s, Ph-2, 6), 7.76 (4H, d, *J* 11.0, MPn-4), 9.83 (1H, s, CHO); δ_C (125.7 MHz) 26.4, 35.5, 111.2, 113.5, 127.5, 128.5, 128.8, 130.0, 130.7, 134.3, 136.8, 141.2, 141.3, 144.7, 168.5, 192.8; ν_{max} ($CHCl_3$)/cm^{-1} 1669; *m*/*z* (FAB) 763 (M^++1) (Found: C, 70.9 H, 4.5; N, 6.3. $C_{49}H_{38}N_4O_5$ requires C, 70.84; H, 4.76; N, 6.61%).

Preparation of 10d,e

A solution of **11a** or **12a** (1 mmol) and **8b** (2 or 4 mmol) in a mixture of CH_2Cl_2 (20 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on SiO_2 by using hexane–AcOEt (1 : 1) as the eluent to give the product **10d** or **10e** (Table 1, Runs 6 and 7).

For 10d. Yellow powder; mp 225–226 °C (decomp) (from CH_2Cl_2–EtOH); δ_H (500 MHz) 5.55 (2H, s, Fn_2CH), 6.10 (1H, s, PPn_2CH), 6.63–6.88 (24H, m, Fn-5, 6, 7, 8, PPn-5, 6, 7, 8), 6.94 (1H, s, Ph-4), 7.11 (2H, s, Ph-2, 6), 7.15–7.23 (4H, m, NPh), 7.38 (4H, d, *J* 11.4, Fn-4), 7.39–7.50 (6H, m, NPh), 7.82 (2H, d, *J* 11.4, PPn-4); δ_C (150 MHz, DMSO-d$_6$) 35.4, 35.8, 108.7, 112.8, 113.2, 113.7, 125.3, 126.4, 128.4, 128.8, 129.0, 129.3, 129.4, 130.5, 130.8, 131.1, 131.9, 134.5, 134.7, 138.1, 141.2, 141.7, 145.3, 148.6, 157.5, 168.4, 169.2 (one carbon overlapping); ν_{max} (KBr)/cm^{-1} 1735, 1654, 1269; *m*/*z* (FAB) 1135 (M^+ + 1) (Found: C, 74.2; H, 3.9; N, 2.2. $C_{75}H_{46}N_2O_{10}$·CH_2Cl_2 requires C, 74.81; H, 3.97; N, 2.30%).

For 10e. Yellow powder; mp 233–235 °C (decomp) (from CH_2Cl_2–EtOH); δ_H (500 MHz) 5.54 (1H, s, Fn_2CH), 6.13 (2H, s, PPn_2CH), 6.62 (4H, d, *J* 8.9, PPn-8), 6.61–6.69 (6H, m, Fn-6, PPn-6), 6.73–6.83 (16H, m, Fn-5, 7, 8, PPn-5, 7), 7.08 (2H, s, Ph-4, 6), 7.15–7.22 (8H, m, NPh), 7.29 (1H, s, Ph-2), 7.36 (2H, d, *J* 11.2, Fn-4), 7.35–7.42 (12H, m, NPh), 7.85 (4H, d, *J* 11.6, PPn-4); δ_C (150 MHz, DMSO-d_6) 35.6, 36.0, 108.9, 112.6, 113.4, 113.5, 125.8, 127.0, 128.2, 128.5, 128.8, 129.2, 130.2, 130.7, 130.8, 131.7, 134.4, 134.6, 137.5, 140.8, 141.5, 145.4, 148.5, 157.5, 168.5, 169.2 (two carbons overlapping); ν_{max} ($CHCl_3$)/cm^{-1} 1734, 1685, 1654, 1261; *m*/*z* (FAB) 1285 (M^+ + 1) (Found: C, 75.1; H, 4.2; N, 3.8. $C_{87}H_{56}N_4O_8\cdot3/2CH_2Cl_2$ requires C, 75.24; H, 4.21; N, 3.97%).

Preparation of 10f,g

A solution of **11a** or **12a** (1 mmol) and **8c** (2 or 4 mmol) in a mixture of CH_2Cl_2 (20 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on SiO_2 by using hexane–AcOEt (1 : 1) as the eluent to give the product **10f** or **10g** (Table 1, Runs 8 and 9)

For 10f. Orange powder; mp 225–226 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 3.39 (6H, s, Me), 5.50 (2H, s, Fn_2CH), 6.00 (1H, s, MPn_2CH), 6.70–6.78 (6H, m, Fn-6, MPn-6), 6.73 (2H, d, *J* 9.3, MPn-8), 6.82–6.97 (16H, m, Fn-5, 7, 8, MPn-5, 7), 6.92 (1H, s, Ph-4), 6.97 (2H, s, Ph-2, 6), 7.34 (4H, d, *J* 11.4, Fn-4), 7.70 (2H, d, *J* 11.3, MPn-4); δ_C (150MHz) 26.4, 35.4, 35.8, 108.8, 111.1, 113.7, 113.9, 125.1, 126.4, 128.3, 128.5, 128.7, 130.0, 130.6, 130.8, 131.9, 134.7, 137.9, 141.0, 141.3, 144.7, 148.6, 157.5, 168.4, 169.1; ν_{max} (KBr)/cm^{-1} 1734, 1653, 1269; *m*/*z* (FAB) 1011 (M^++1) (Found: C, 70.5; H, 3.6; N, 2.4. $C_{65}H_{42}N_2O_{10}\cdot3/2CH_2Cl_2$ requires C, 70.16; H, 3.98; N, 2.46%).

For 10g. Orange powder; mp 248–249 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 3.37 (12H, s, Me), 5.45 (1H, s, Fn_2CH), 5.96 (2H, s, MPn_2CH), 6.68–6.88 (16H, m, Fn-5, 6, 7, 8, MPn-5, 6), 6.70 (4H, d, *J* 8.8, MPn-8), 6.91 (1H, s, Ph-2), 6.92 (2H, s, Ph-4, 6), 7.30 (2H, d, *J* 11.6, Fn-4), 7.68 (4H, d, *J* 10.9, MPn-4); δ_C (150MHz, DMSO-d_6) 26.4, 35.5, 35.9, 109.0, 110.9, 113.4, 114.1, 125.6, 126.9, 128.5, 128.6, 128.6, 129.7, 130.3, 130.7, 131.7, 134.3, 137.4, 140.7, 140.9, 144.7, 148.4, 157.5, 168.5, 169.2; ν_{max} (KBr)/cm^{-1} 1734, 1653, 1261; *m*/*z* (FAB) 1037 (M^+ + 1) (Found: C, 72.1; H, 5.1; N, 4.5. $C_{67}H_{48}N_4O_8\cdot CH_2Cl_2$ requires C, 72.79; H, 4.49; N, 4.99%).

Preparation of 10h

A solution of **12c** (1 mmol) and **8b** (2 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on SiO_2 by using hexane–AcOEt (1 : 1) as the eluent to give the product **10h** (Table 1, Run 10).

For 10h. Orange powder; mp 256–258 °C (from CH_2Cl_2–EtOH); δ_H (400 MHz) 3.32 (12H, s, Me), 5.94 (2H, s, MPn_2CH), 6.02 (1H, s, PPn_2CH), 6.55–6.80 (20H, m, PPn-5, 6, 7, 8, MPn-5, 6, 8), 6.80–6.97 (5H, m, Ph-2, MPn-7), 7.00–7.23 (6H, m, Ph-4, 6, NPh), 7.36–7.44 (6H, m, NPh), 7.67–7.85 (6H, m, PPn-4, MPn-4); δ_C (150MHz) 26.3, 36.0, 36.1, 110.6, 112.3, 113.5, 114.3, 126.2, 126.3, 128.1, 128.5, 128.9, 129.1, 129.5, 129.9, 130.0, 130.1, 130.6, 134.6, 134.7, 140.2, 140.3, 140.8, 141.2, 141.4, 144.7, 145.4, 168.6, 168.6; ν_{max} ($CHCl_3$)/cm^{-1} 1676; *m*/*z* (FAB) 1187 (M^+ + 1) (Found: C, 78.4; H, 4.4; N, 6.5. $C_{79}H_{58}N_6O_6$ requires C, 78.38; H, 4.86; N, 6.91%).

Preparation of 13

A solution of **11c** (1 mmol) and **8b** (1 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on SiO_2 by using hexane–AcOEt (1 : 1) as the eluent to give the products **13** and recovery of **11c** (Table 1, Run 11).

For 13. Orange powder; mp 234–235 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 3.44 (6H, s, Me), 6.16 (1H, s, PPn_2CH), 6.19 (1H, s, MPn_2CH), 6.69 (2H, d, *J* 8.9, PPn-8), 6.74–6.79 (4H, m, PPn-6, MPn-6), 6.78 (2H, d, *J* 9.8, MPn-8), 6.83–6.91 (6H, m, PPn-5, 7, MPn-5), 6.98 (2H, dd, *J* 10.1, 9.8, MPn-7), 7.23–7.48 (10H, m, NPh), 7.49 (1H, s, Ph-4), 7.60 (1H, s, Ph-2 or 6), 7.73 (1H, s, Ph-2 or 6), 7.83 (2H, d, *J* 11.3, PPn-4 or MPn-4), 7.85 (2H, d, *J* 11.3, PPn-4 or MPn-4), 9.88 (1H, s, CHO); δ_C (150MHz) 26.5, 35.5, 35.7, 111.3, 112.7, 113.0, 113.5, 127.6, 127.7, 128.4, 128.6, 128.7, 128.9, 129.1, 129.2, 129.3, 129.5, 130.0, 130.5, 130.7, 131.1, 134.4, 134.5, 136.8, 141.1, 141.3, 141.6, 144.7, 145.4, 168.47, 168.49, 192.8; ν_{max} (KBr)/cm^{-1} 1676; *m*/*z* (FAB) 887 (M^+ + 1) (Found: C, 77.6; H, 4.1; N, 5.8. $C_{59}H_{42}N_4O_5$ requires C, 77.86; H, 4.70; N, 6.12%).

Preparation of 10i

A solution of **8a** (2 mmol) and **13** (1 mmol) in a mixture of CH_2Cl_2 (20 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on SiO_2 by using hexane–AcOEt (1 : 1) as the eluent to give the product **10i** (Table 1, Run 12)

For 10i. Yellow powder; mp 242–243 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 3.36 (6H, s, Me), 5.50 (1H, s, Fn_2CH), 6.02 (1H, s, MPn_2CH), 6.18 (1H, s, PPn_2CH), 6.60 (2H, d, *J* 9.0, PPn-8), 6.67–6.96 (22H, m, Fn-5, 6, 7, 8, PPn-5, 6, 7, MPn-5, 6, 7, 8), 6.95 (1H, s, Ph-6), 7.08 (1H, s, Ph-2), 7.10 (1H, s, Ph-4), 7.18–7.19 (4H, m, NPh), 7.34 (2H, d, *J* 11.3, Fn-4), 7.38–7.50 (6H, m, NPh), 7.74 (2H, d, *J* 11.2, PPn-4 or MPn-4), 7.79 (2H, d, *J* 11.3, PPn-4 or MPn-4); δ_C (150 MHz) 26.4, 29.0, 30.0, 30.4, 35.6, 36.0, 108.9, 110.9, 112.5, 113.0, 113.4, 113.5, 114.2, 125.8, 128.3, 128.5, 128.6, 128.8, 129.0, 129.2, 129.6, 129.7, 130.3, 130.7, 130.9, 131.1, 131.7, 131.8, 132.5, 134.4, 134.6, 137.6, 140.9, 141.5, 144.7, 145.4, 148.5, 157.6, 167.8, 168.5, 169.2; ν_{max} (KBr)/cm^{-1} 1734, 1669, 1269; *m*/*z* (FAB) 1161 (M^+ + 1) (Found: C, 72.5; H, 4.0; N, 4.2. $C_{77}H_{52}N_4O_8\cdot5/3CH_2Cl_2$ requires C, 72.52; H, 4.28; N, 4.30%).

General synthetic procedure for the 1,3,5-tris[bis(heteroazulen-3-yl)methyliumyl]benzene tris(tetrafluoroborate) 14a–i·3BF$_4^-$

To a stirred solution of tris[bis(heteroazulen-3-yl)methyl]benzenes **10** (0.05 mmol) in CH_2Cl_2 (10 cm^3) was added DDQ (70 mg, 0.3 mmol) and the mixture was stirred at rt for 1 h until the reaction was complete. After evaporation of the CH_2Cl_2, the residue was dissolved in a mixture of acetic anhydride (5 cm^3) and 42% HBF_4 (1 cm^3) at 0 °C, and the mixture was stirred for 1 h. To the mixture was added Et_2O (100 cm^3), and the precipitates were collected by filtration to give **14a–i·3BF$_4^-$**. The results are summarized in Table 1.

For 14a. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 6.85–7.46 (6H, m), 7.71 (6H, d, *J* 10.0), 7.75 (3H, s, Ph), 7.91–8.46 (18H, m); ν_{max} (KBr)/cm^{-1} 1734, 1260, 1084; *m*/*z* (FAB) 983 [(M^+ + 2) − 3BF$_4$] (Found: M^+ + 2 − 3BF$_4$, 983.2161. $C_{63}H_{33}B_3F_{12}O_{12}$ requires M + 2 − 3BF$_4$, 983.2129) (Found: C, 61.1; H, 2.3. $C_{63}H_{33}B_3F_{12}O_{12}$ requires C, 60.91; H, 2.68%).

For 14b. Dark violet powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 7.30–8.40 (63H, m); ν_{max} (KBr)/cm^{-1} 1696, 1084; *m*/*z* (FAB) 1431 ($M^+ - 3BF_4$) (Found: $M^+ - 3BF_4$, 1431.4829. $C_{99}H_{63}B_3F_{12}N_6O_6$ requires $M - 3BF_4$, 1431.4813) (Found: C, 66.6; H, 3.2; N, 5.1. $C_{99}H_{63}B_3F_{12}N_6O_6 \cdot HBF_4$ requires C, 66.77; H, 3.62; N, 4.72%).

For 14c. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 3.50–3.56 (18H, m, Me), 7.21–7.25 (3H, m), 7.85–8.23 (30H, m); ν_{max} (KBr)/cm^{-1} 1685, 1084; *m*/*z* (FAB) 1059 ($M^+ - 3BF_4$) (Found: $M^+ - 3BF_4$, 1059.3879. $C_{69}H_{51}B_3F_{12}N_6O_6$ requires $M - 3BF_4$, 1059.3870) (Found: C, 56.4; H, 4.1; N, 5.4. $C_{69}H_{51}B_3F_{12}N_6O_6 \cdot 5/3HBF_4$ requires C, 56.50; H, 3.62; N, 5.73%).

For 14d. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 7.37–8.27 (43H, m); ν_{max} (KBr)/cm^{-1} 1684, 1653, 1261, 1084; *m*/*z* (FAB) 1132 ($M^+ + 1 - 3BF_4$) (Found: $M^+ + 1 - 3BF_4$, 1132.2976. $C_{75}H_{43}B_3F_{12}N_2O_{10}$ requires $M + 1 - 3BF_4$, 1132.2997) (Found: C, 51.3; H, 2.8; N, 1.9. $C_{75}H_{43}B_3F_{12}N_2O_{10} \cdot 4HBF_4$ requires C, 51.66; H, 2.72; N, 1.61%).

For 14e. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 7.37–8.37 (53H, m); ν_{max} (KBr)/cm^{-1} 1684, 1653, 1261, 1084; *m*/*z* (FAB) 1283 [($M^+ + 2) - 3BF_4$] (Found: $M^+ + 2 - 3BF_4$, 1283.4020. $C_{87}H_{53}B_3F_{12}N_4O_8$ requires $M + 2 - 3BF_4$, 1283.4023) (Found: C, 59.7; H, 3.4; N, 3.3. $C_{87}H_{53}B_3F_{12}N_4O_8 \cdot 5/2HBF_4$ requires C, 59.29; H, 3.17; N, 3.18%).

For 14f. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 3.42–3.58 (6H, m, Me), 6.72 (2H, s, Ph), 6.77 (1H, s, Ph), 7.40–7.45 (27H, m), 7.55–7.66 (4H, m), 7.70–8.45 (2H, m); ν_{max} (KBr)/cm^{-1} 1734, 1653, 1261, 1084; *m*/*z* (FAB) 1008 [($M^+ + 1) - 3BF_4$] (Found: $M^+ + 1 - 3BF_4$, 1008.2665. $C_{65}H_{39}B_3F_{12}N_2O_{10}$ requires $M + 1 - 3BF_4$, 1008.2684) (Found: C, 54.9; H, 3.0; N, 2.0. $C_{65}H_{39}B_3F_{12}N_2O_{10} \cdot 5/3HBF_4$ requires C, 55.18; H, 2.90; N, 1.98%).

For 14g. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 3.45–3.60 (12H, m, Me), 6.73 (1H s, Ph), 6.77 (2H, s, Ph), 7.41–7.45 (18H, m), 7.55–7.65 (2H, m), 7.80–8.42 (4H, m); ν_{max} (KBr)/cm^{-1} 1734, 1653, 1261, 1084; *m*/*z* (FAB) 1034 [($M^+ + 1) - 3BF_4$] (Found: $M^+ + 1 - 3BF_4$, 1034.3230. $C_{67}H_{45}B_3F_{12}N_4O_8$ requires $M + 1 - 3BF_4$, 1034.3318) (Found: C, 55.5; H, 2.8; N, 3.8. $C_{65}H_{39}B_3F_{12}N_2O_{10} \cdot 5/3HBF_4$ requires C, 55.85; H, 3.26; N, 3.89%).

For 14h. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 3.46–3.62 (12H, m, Me), 7.28–8.35 (43H, m); ν_{max} (KBr)/cm^{-1} 1685, 1084; *m*/*z* (FAB) 1184 [($M^+ + 1) - 3BF_4$] (Found: $M^+ + 1 - 3BF_4$, 1184.4248. $C_{79}H_{55}B_3F_{12}N_6O_6$ requires $M + 1 - 3BF_4$, 1184.4261) (Found: C, 61.8; H, 3.8; N, 5.4. $C_{79}H_{55}B_3F_{12}N_6O_6 \cdot HBF_4$ requires C, 61.91; H, 3.68; N, 5.48%).

For 14i. Purple powder; mp >300 °C (from CH_3CN–Et_2O); δ_H (400 MHz, CD_3CN) 3.43–3.60 (6H, m, Me), 7.37–8.27 (43H, m); ν_{max} (KBr)/cm^{-1} 1685, 1654, 1261, 1084; *m*/*z* (FAB) 1158 [($M^+ + 1) - 3BF_4$] (Found: $M^+ + 1 - 3BF_4$, 1158.3658. $C_{77}H_{49}B_3F_{12}N_4O_8$ requires $M + 1 - 3BF_4$, 1158.3628) (Found: C, 60.8; H, 3.7; N, 3.5. $C_{77}H_{49}B_3F_{12}N_4O_8 \cdot HBF_4$ requires C, 61.39; H, 3.35; N, 3.72%).

Determination of [pK_{R+}] values of trications 14a–i

Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of potassium hydrogen phthalate (0.1M) and HCl (0.1 M) (for pH 2.2–4.0), potassium hydrogen phthalate (0.1M) and NaOH (0.1 M) (for pH 4.1–5.9), KH_2PO_4 (0.1M) and NaOH (0.1 M) (for pH 6.0–8.0), $Na_2B_4O_7$ (0.025M) and HCl (0.1 M) (for pH 8.2–9.0), $Na_2B_4O_7$ (0.025M) and NaOH (0.1 M) (for 9.2–10.8), Na_2HPO_4 (0.05 M) and NaOH (0.1 M) (for pH 11.0–12.0), and KCl (0.2M) and NaOH (0.1 M) (for pH 12.0–14.0) in various portions. For the preparation of sample solutions, 1 cm^3 portions of the stock solution, prepared by dissolving 3–5 mg of cation **14a–i·BF$_4$$^-$** in MeCN (20 cm^3), were diluted to 10 cm^3 with the buffer solution (5 cm^3) and MeCN (4 cm^3). The UV–vis spectrum was recorded for each cation **14a–i** in 30 different buffer solutions. Immediately after recording the spectrum, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelengths (613 nm for **14a**; 623 nm for **14b**; 623 nm for **14c**, 606 nm for **14d**, 614 nm for **14e**, 609 nm for **14f**, 618 nm for **14g**, 628 nm for **14h**, and 614 nm for **14i**) of each cations was plotted against pH to give two or three-step titration curves, and the midpoints of each were taken as the [pK_{R+}] value. The results are summarized in Table 2.

Cyclic voltammetry of trications 14a–i

The reduction potentials of **14a–i** were determined by means of CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference $Ag/AgNO_3$ electrode. Nitrogen was bubbled through an acetonitrile solution (4 cm^3) of each compound (0.5 mmol dm^{-3}) and Bu_4NClO_4 (0.1 mol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1} and the voltammograms were recorded on a WX-1000-UM-019 (Graphtec Co) X-Y recorder. Immediately after the measurements, ferrocene (0.1 mmol) ($E_{1/2} = +0.083$) was added as the internal standard, and the observed peak potentials were corrected with reference to this standard. The compounds exhibited no reversible reduction wave: each of the reduction potentials was measured through independent scan, and they are summarized in Table 2.

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