Pergamon

Tetrahedron 57 (2001) 9137–9147

TETRAHEDRON

Synthesis of new pentacarbon chain streptocyanines (pentamethinium salts)

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Received 30 April 2001; revised 24 July 2001; accepted 12 September 2001

Abstract—Pentacarbon chain streptocyanines, symmetrical and dissymmetrical, mono- and dicationic are obtained by action of aliphatic mono- and diamines on pentacarbon carboxonium salts.

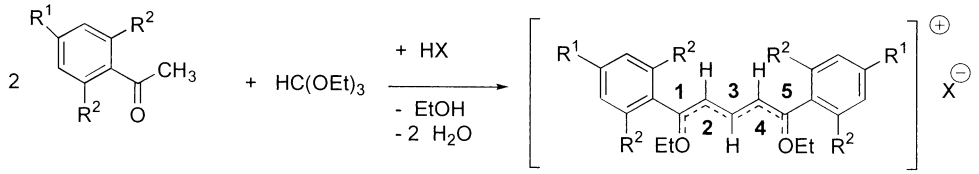
1. Introduction

Cyanines, carbocationic conjugated organic compounds, possess an odd carbon chain with terminal nitrogen groups. Their industrial interest is underlined by the number of patents, predominantly for their suitability as materials with novel electrical, optical, and mesogenic properties (optical devices, non-linear optic, erasable laser disks etc.). Their applications in chemistry are also important (dyes, sensitizing dyes in photographic emulsions, synthesis intermediates etc.). These important applications[1] justify the search for new synthetic methods allowing their structure to be modulated.

We first implemented a synthetic method for pentacarbon streptocyanines (or pentamethinium salts) by action of tris-(dialkylamino)arsanes and stibanes on 2,6-diarylpyrylium salts.[2] Owing to the great variety of synthetic ways to pyrylium salts,[3] this method allows a great variability of substitution on the chain, but has three limitations: (i) pyrylium salts must be 2,6-arylated; (ii) tris(dialkylamino)arsanes and stibanes can only lead to symmetrical (two identical dialkylamino groups) and acyclic pentamethinium salts and (iii) only a few tris(dialkylamino)-arsanes and stibanes are available.

We then attempted to overcome these obstacles. It appears that ethylorthoformate (triethoxymethane) is a good reagent for the synthesis of cyanines dyes. For instance, cyanines are obtained by action of indoles,[4] carbazoles, and pyrroles[5] on triethoxymethane in an acidic medium. They can also be obtained in basic medium by action of activated indole derivatives on triethoxymethane.[6]

A classical method for the synthesis of 2,6-diarylpyrylium salts is the action of arylethanones on triethoxymethane in acidic medium. Mezheritskii et al.[7] put in evidence, in this synthesis, a carboxonium intermediate as precursor of the



carboxonium salts 1-8

	1	2	2'	3	3'	4	5	6'	7	8
R^1	H	Me	Me	OMe	OMe	NHAc	Me	I	F	CN
R^2	H	H	H	H	H	H	Me	H	H	H
X	ClO_4	ClO_4	BF_4	ClO_4	BF_4	ClO_4	ClO_4	BF_4	ClO_4	ClO_4

Scheme 1.

Keywords: cyanines; pentamethinium salts.

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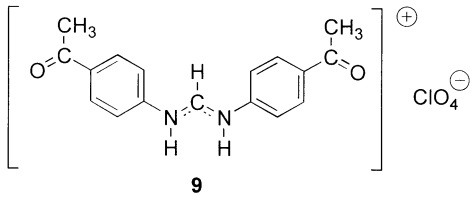
PII: S0040-4020(01)00919-X



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Scheme 2.

pyrylium salt. In order to identify this precursor, they added an aromatic amine in situ. They obtained and characterized the corresponding pentamethinium salt. Their objective was the synthesis of polycyclic pyridinium salts, which is not yet the ultimate.

Our aim was the generalization of this method to primary and secondary alkylamines. Preliminary results have already been published.[8] We report here the whole results obtained with aliphatic amines.

2. Results and discussion

All products described below were identified by ^{1}H and ^{13}C NMR, as well as MS (DCI for monocations, FAB>0 and electrospray for dications). These results and experimental data are gathered in Section 4. All NMR spectra data are given only for some representative examples because the NMR spectra of the streptocyanines are very similar.

2.1. Synthesis of carboxonium precursors 1–8

We synthesized the carboxonium salts **1**–**8** from various substituted arylethanones and triethoxymethane with $HClO_4$ or HBF_4 as acid, according to the reaction in Scheme 1.

Whereas (4-acetaminophenyl)ethanone with a protected amino group gave the expected carboxonium salt **4**, the same reaction with (4-aminophenyl)ethanone led to the formamidinium salt **9** only Scheme 2.

We attempted to synthesize analogous carboxonium salts from various other enolizable ketones i.e. 3,3-dimethylbutanone, 1-phenylpropan-1-one, 1-phenyl-2-chloroethanone, and 1,2-diphenylethanone. We obtained no reaction or, when there was one, the corresponding pyrylium salt was formed.

Carboxonium **1**–**4**, **6**–**8** are unstable and transform quickly into pyrylium salts in contact with water of undried organic solvents or with atmospheric moisture. Carboxonium salt **5** is stable. According to Lüning,[9] this stability is due to the steric repulsions of the *ortho*-methyl groups which prevent planarity between the pyrylium ring and the phenyl groups.

2.2. Synthesis of hemicarboxonium salts 10–11

We previously proved that action of amines on carboxonium salts with 1/1 stoichiometry leads to a stable hemicarboxonium salt[8] (Scheme 3). This result opens the way to unsymmetrical salts: the second –OEt group, still reactive, can be subsequently substituted by another amine. This dissymmetry induces a perturbation in the electronic delocalization, the positive charge being located preferentially on the carbon substituted by the stronger donor amino group, and can lead to compounds likely to exhibit nonlinear optic properties.[10] The hemicarboxonium salts, **10**,[8] **10′**, and **11**, synthesized by action of one equivalent of Et_2NH on **2**, **2′**, and **3**, respectively are more stable than the corresponding carboxonium salts.

2.3. Synthesis of monocationic pentamethinium salts

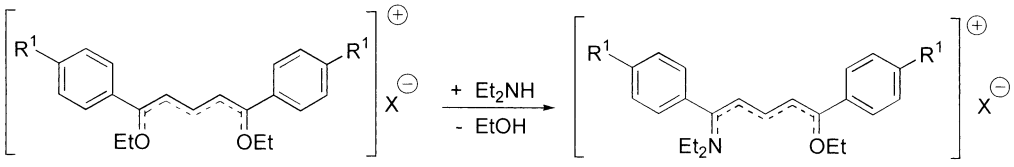
As positively charged odd carbons are electrophilic sites, specially C_1 and C_5, OEt group are substitutable by various amines on carboxonium salts (except **5**, unreactive in all cases), or on hemicarboxonium salts.

2.3.1. Symmetrical pentacarbon streptocyanines. They are obtained by action of nucleophilic amines using stoichiometry amine/carboxonium salt 2:1 (Scheme 4). Yields run between 60 and 87% whatever the anion (ClO_4^- or BF_4^-) may be.

With primary alkylamines R′=H, R=Et **a**, *i*Pr **b**, *n*Bu **c**, *i*Bu **d**, *t*Bu **e**, nC_6H_{13} **f**, nC_8H_{17} **g**, $nC_{10}H_{21}$ **h**, $CH_3O(CH_2)_2$ **i**, furfuryl **j** and carboxonium salts **1**, **2**, **2′**, **3** and **3′**, the following pentamethinium salts are obtained: **1a**, **1g–i**, **2a–b**, **2i**, **2′c**; **3a–j**, **3′c**, **3′h–j**.

With secondary alkylamines:

diethylamine **k** on carboxonium salts **1**–**4**, **2′**, **3′**, **6**, **7′**, **8**, leads to pentamethinium salts: **1k–4k**, **6k**, **8k**, **2′k**, **3′k**, **7′k**.

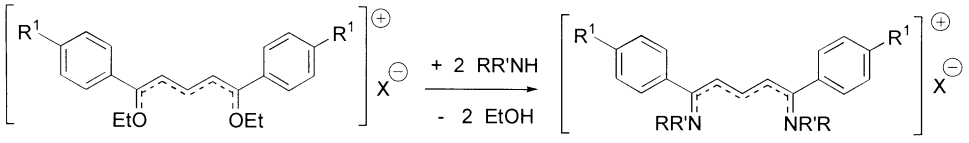


carboxonium salts 2, 2', 3

hemicarboxonium salts 10, 10', 11

	10	10'	11
R^1	Me	Me	OMe
X	ClO_4	BF_4	ClO_4

Scheme 3.



1-4, 7, 8, 2', 3', 6' — **1a-3a, 2b, 3b,2'c, 3c, 3'c, 3d, 3e, 3f,1g, 3g, 1h, 3h,3'h, 1i- 3i, 3'i, 3j, 3'j, 1k, 2k, 2'k, 3k, 4k, 6'k, 7k, 8k, 2'l, 3'l**

	1a	**2a**	**3a**	**2b**	**3b**	**2'c**	**3c**	**3'c**
R^1	H	Me	OMe	Me	OMe	Me	OMe	OMe
R	Et	Et	Et	iPr	iPr	nBu	nBu	nBu
R'	H	H	H	H	H	H	H	H
X	ClO_4	ClO_4	ClO_4	ClO_4	ClO_4	BF_4	ClO_4	BF_4

	3d	**3e**	**3f**	**1g**	**3g**	**1h**	**3h**	**3'h**
R^1	OMe	OMe	OMe	H	OMe	H	OMe	OMe
R	iBu	tBu	nC_6H_{13}	nC_8H_{17}	nC_8H_{17}	$nC_{10}H_{21}$	$nC_{10}H_{21}$	$nC_{10}H_{21}$
R'	H	H	H	H	H	H	H	H
X	ClO_4	ClO_4	ClO_4	ClO_4	ClO_4	ClO_4	ClO_4	BF_4

	1i	**2i**	**3i**	**3'i**	**3j**	**3'j**	**1k**	**2k**
R^1	H	Me	OMe	OMe	OMe	OMe	H	Me
R	$MeO(CH_2)_2$	$MeO(CH_2)_2$	$MeO(CH_2)_2$	$MeO(CH_2)_2$	furfuryl	furfuryl	Et	Et
R'	H	H	H	H	H	H	Et	Et
X	ClO_4	ClO_4	ClO_4	BF_4	ClO_4	BF_4	ClO_4	ClO_4

	2'k	**3k**	**4k**	**6'k**	**7k**	**8k**	**2'l**	**3'l**
R^1	Me	OMe	NHAc	I	F	CN	Me	OMe
R	Et	Et	Et	Et	Et	Et	nBu	nBu
R'	Et	Et	Et	Et	Et	Et	Me	Me
X	BF_4	ClO_4	ClO_4	BF_4	ClO_4	ClO_4	BF_4	BF_4

Scheme 4.

N-methylbutylamine **l** on carboxonium salts 2′ and 3′ gives pentamethinium salts **2′l** and **3′l**.
in all cases, diisopropylamine leads to a mixture that could not be identified. This is certainly due to the instability of the products related to the steric hindrance of the diisopropyl group.

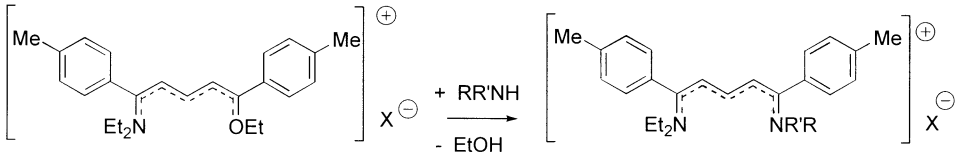
2.3.2. Dissymmetrical pentacarbon streptocyanines. They are synthesized by using the stoichiometry amine/ hemicarboxonium salt 1:1 (Scheme 5).

Unsymmetrical salts **10b**, **10′c** and **10′l** were obtained in good yields.

2.4. Synthesis of dicationic pentamethinium salts

This method was then extended to aliphatic diamines (H_2N–$(CH_2)_n$–NH_2 (n=3 **m**, 6 **n**, 8 **o**, 9 **p**), NH_2–$((CH_2)_2O)_2(CH_2)_2$–NH_2 **q**). Under analogous identical experimental conditions, two kinds of dicationic systems are obtained.

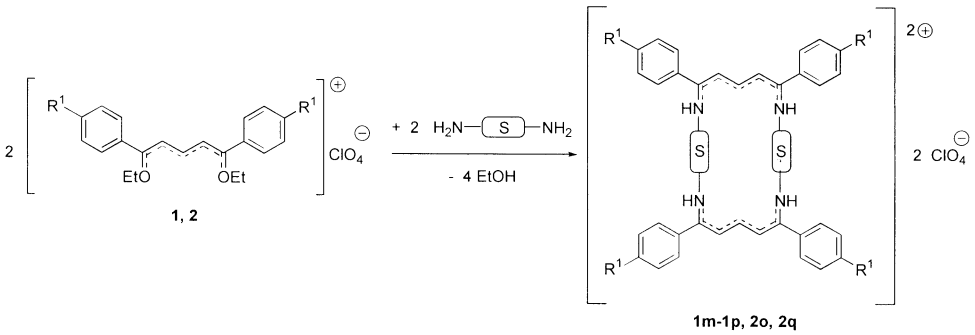
2.4.1. Macrocyclic dicationic streptocyanines. 1m–p, 2o, 2q, are obtained by action of carboxonium salts **1–2** on diamine in 1:1 stoichiometry (Scheme 6). The reaction can lead to a mixture of monomer, dimer, and other oligomers, whose proportions depend on the shape of cycle, nature of activating group, and experimental



10, 10' — **10b, 10'c, 10'l**

	10b	**10'c**	**10'l**
R	iPr	nBu	nBu
R'	H	H	Me
X	ClO_4	BF_4	BF_4

Scheme 5.



	1m	1n	1o	1p	2o	2q
R^1	H	H	H	H	Me	Me
S	$-(CH_2)_3-$	$-(CH_2)_6-$	$-(CH_2)_8-$	$-(CH_2)_9-$	$-(CH_2)_8-$	$-((CH_2)_2O)_2(CH_2)_2-$

Scheme 6.

conditions (temperature, solvent, reaction time, reagents, concentration).

As the pentacarbon chain of the carboxonium cation is plane, it was determined by modeling that its insertion in a monomer cyclic structure is only possible with diamines $H_2N-(CH_2)_n-NH_2$ which possess a long carbon chain ($n > 9$) to avoid Pitzer strains and *trans*-annular interactions.

With diamines **m**–**p**, the synthesis conditions are the same as those for monocationic compounds. With 2,2′-(ethylendioxy)-bis(ethylamine) **q**, ^{13}C NMR shows the splitting of the only signals of carbons of the (ethylendioxy)-bis(ethylamine) moiety, revealing the formation of an unorganized system of conformers in 1/3–2/3 ration. This phenomenon is due to the chain flexibility of the diamine. To avoid it, we used a complex of diamine with Ca^{2+}. The dicationic compound is obtained with a perfect organization of the ethylendioxy chain, witnessed by the uniqueness of the signals of ethylenedioxy carbons in ^{13}C NMR.

2.4.2. Acyclic dicationic streptocyanines. They are obtained by action of hemicarboxonium salts **10** and **11** on diamine in 2/1 stoichiometry (Scheme 7). Yields run between 35 and 47%. With 2,2′(ethylendioxy)-bis(ethylamine), the best results were obtained after complexion of the reactant with calcium perchlorate.

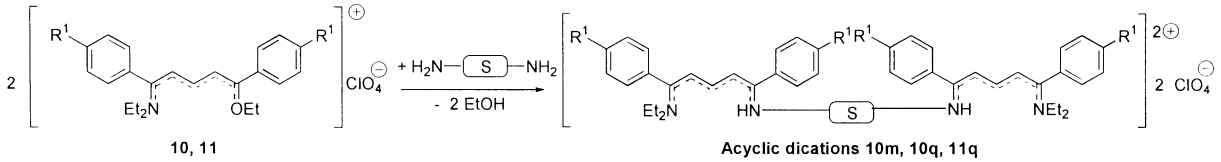
For all dicationic systems, mass spectroscopy (FAB>0 and electrospray) confirms the formation of the dicationic pentamethinium salts (two characteristic peaks m/z (M^{2+}, ClO_4^-) and ($M^{2+}-H^+$)).

3. Conclusion

Carboxonium salts and their hemicarboxonium derivatives are good precursors for a versatile synthesis of pentamethinium monocationic and dicationic, symmetric and dissymmetric from a great variety of primary and secondary alkylamines and diamines (except diisopropylamine). This method was further extended to other nitrogen derivatives: guanidines and phosphaimines,[11] amidines,[12] hydrazines and derivatives.[13]

4. Experimental

^1H NMR spectra were recorded on Bruker AC250 spectrometer (250.30 MHz) or AC200 (200.13 MHz) or AC80, (80.13 MHz) ^{13}C NMR spectra were recorded on Bruker AC200 (62.89 MHz) or AC200 (50.32 MHz). Perkin–Elmer model 1600 spectrometer was used for infrared spectrometry. No influence of the nature of the anion (perchlorate or tetrafluoroborate) was detected for NMR



	10m	10q	11q
R^1	Me	Me	OMe
S	$-(CH_2)_3-$	$-((CH_2)_2O)_2(CH_2)_2-$	$-((CH_2)_2O)_2(CH_2)_2-$

Scheme 7.

spectra. Mass spectra were recorded on NERMAG R10-10H spectrometer by direct chemical ionization (DCI/NH_3) for monocationic compounds and FAB with matrix Gly (glycerol) or MNBA (3-nitrobenzylalcohol) for dicationic compounds. M^+or M^{2+} means the peak of the cation. UV/visible spectra were recorded on Perkin–Elmer Lambda 17 spectrometer. Melting points were measured with a Büchi melting points apparatus.

All syntheses of carboxonium, hemicarboxonium and pentaethinium salts were carried out under inert atmosphere (argon) with a vacuum line. Ethanol, dichloromethane, benzene and pentane were distilled; diethylether was distilled and dried on sodium. Acetonitrile was distilled and dried on 3 Å sieves. Diethylamine was distilled and dried on potassium hydroxyde. Other commercial reactives were used as purchased.

4.1. Synthesis of carboxonium salts 1–8

25 mL (150 mmol) of triethoxymethane are added to 5 mL (37 mmol) of 4-methylphenylethanone under argon atmosphere at room temperature. 18.5 mmol of the acid (1.6 mL of 70% perchloric acid dissolved in 5 mL of triethoxymethane, or 2.4 mL of 54% tetrafluoroboric acid in diethylether) are added dropwise. The solution becomes deep brown. The mixture is left under magnetic stirring for 40–50 min. 200 mL of anhydrous diethylether are added. The carboxonium salt precipitates. After 4 h of magnetic stirring, carboxonium salt is filtered off under argon atmosphere, washed with anhydrous diethylether, dried under vacuum, and preserved under argon.

4.1.1. 1: 1,5-Diethoxy-1,5-diphenylpenta-2,4-dienylium perchlorate. See Refs. 7,8.

4.1.2. 2 (X=ClO_4); 2′(X=BF_4): 1,5-Diethoxy-1,5-bis-(4-methylphenyl)penta-2,4-dienylium perchlorate[8] or tetrafluoroborate. Yield=65%; yellow powder; ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1,49 (t, 6H, CH_3CH$_2$, J=7.0 Hz); 2,38 (2s, 6H, CH_3C$_6$H$_4$); 2.38 (q, 4H, CH$_3$CH_2, J=7.0 Hz); 6.86 (d, 2H, H$_2$–H$_4$, syst. A$_2$X, J_{AX}=13.0 Hz); 7.11–7.64 (8H, C$_6$H$_4$, syst. AA′BB′, J_{AB}=$JA'B'$=8.0 Hz); 8.03 (t, 1H, H$_3$, syst. A$_2$X, J_{AX}=13.0 Hz); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 14.5 (CH_3CH$_2$)); 71.5 (CH$_3$CH_2); 21.8 (CH_3C$_6$H$_4$); 112.1 (C$_2$–C$_4$); 130.6–146.8 (C$_6$H$_4$); 175.5 (C$_3$); 190.4 (C$_1$–C$_5$).

4.1.3. 3 (X=ClO_4); 3′ (X=BF_4): 1,5-Diethoxy-1,5-bis-(4-methoxyphenyl)penta-2,4-dienylium perchlorate or tetrafluoroborate. Yield=80%; orange powder; ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.53 (t, 6H, CH_3CH$_2$, J=7.0 Hz); 3.88 (2s, 6H, CH_3OC$_6$H$_4$); 4.55 (q, 4H, CH$_3$CH_2, J=7.0 Hz); 6.79 (d, 2H, H$_2$–H$_4$, syst. A$_2$X, J_{AX}=13.0 Hz); 7.05–7.68 (8H, C$_6$H$_4$, syst. AA′BB′, J_{AB}=$J_{A'B'}$=8.9 Hz); 7.97 (t, 1H, H$_3$, syst. A$_2$X, J_{AX}=13.0 Hz); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 14.5 (CH_3CH$_2$); 21.8 (CH_3OC$_6$H$_4$); 71.1 (CH$_3$CH_2); 111.5 (C$_2$–C$_4$); 130.6–146.8 (C$_6$H$_4$); 173.8 (C$_3$); 188.6 (C$_1$–C$_5$).

4.1.4. 4: 1,5-Diethoxy-1,5-bis(4-acetaminophenyl) penta-2,4-dienylium perchlorate. Yield=55%; red powder; IR (KBr pellet) ν cm^{-1}: 3345 (N–H), 1114 (ClO); ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.50 (t, 6H, CH_3CH$_2$, J=7.0 Hz); 2.20 (s, 6H, CH_3CONHC$_6$H$_4$); 4.57 (q, 4H, CH$_3$CH_2, J=7.0 Hz); 6.87 (d, 2H, H$_2$–H$_4$, syst. A$_2$X, J=14.4 Hz); 7.61 and 7.71 (8H, C$_6$H$_4$, syst. AA′BB′, J_{AB}=$J_{A'B'}$=8.7 Hz); 7.94 (t, 1H, H$_3$, syst. A$_2$X, J=14.4 Hz); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 14.5 (CH_3CH$_2$); 24.4 (CH_3CO–), 71.3 (CH$_3$CH_2); 111.9 (C$_2$–C$_4$); 120–145 (C$_6$H$_4$); 171.6 (CO), 174.4 (C$_3$); 188.8 (C$_1$–C$_5$).

4.1.5. 5: 1,5-Diethoxy-1,5-bis(2,4,6-trimethylphenyl)-penta-2,4-dienylium perchlorate. Yield=80%; yellow crystals; IR (KBr pellet) ν cm^{-1}: 1090 (Cl–O); ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.50 (t, 6H, CH_3CH$_2$, J=7.0 Hz); 1.97 (s, 12H, 2,6-CH$_3$); 2.24 (s, 6H, 4-CH$_3$); 4.56 (q, 4H, CH$_3$–CH_2, J=7.0 Hz); 6.79 (s, 4H, C$_6$H$_2$); 6.90–7.11 (m, 3H, H$_2$, H$_3$, H$_4$, syst. A$_2$X; J_{AX}=14.0 Hz; RMN ^{13}C (50.32 MHz, CD_3CN) δ ppm: 14.4 (CH_3–CH$_2$); 19.5 (CH_3 *ortho*); 21.3 (CH_3, *para*); 72.2 (CH$_3$–CH_2–); 114.3 (C$_2$–C$_4$); 129.1–142.3 (Ph); 176.5 (C$_3$); 195.4 (C$_1$–C$_5$).

4.1.6. 6′: 1,5-Diethoxy-1,5-bis(4-iodophenyl)penta-2,4-dienylium tetrafluoroborate. ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.52 (t, 6H, J=7.0 Hz, CH$_3$); 4.15 (q, 4H, J=7.0 Hz, CH$_3$–CH_2); 6.85 (d, 2H, H$_2$–H$_4$, J=11.2 Hz); 7.34 and 7.93 (m, 8H, C$_6$H$_4$, J=8.5 Hz); 7.9 (t, 1H, H$_3$, J=11.2 Hz).

4.1.7. 7: 1,5-Diethoxy-1,5-bis(4-fluorophenyl)penta-2,4-dienylium perchlorate and 8: 1,5-diethoxy-1,5-bis-(4-cyanophenyl)penta-2,4-dienylium perchlorate. The titled compounds were prepared in situ and not isolated.

4.1.8. 9: Di(4-acetylphenylamino)methinium perchlorate. Yield=80%; orange crystals; mp=129°C; IR (KBr pellet): ν cm^{-1}: 3018 (N–H); 1676 (C=O); 1598 (C=C arom.); 1105 (ClO). ^{1}H NMR (80 MHz, CD_3CN) δ ppm, J Hz: 2.5 (s, 6H, CH$_3$); 7.7 and 8.1 (8H, C$_6$H$_4$, syst. AA′BB′, J_{AB}=$J_{A'B'}$=9.5 Hz); 8.8 (s, 1H, CH); 10.6 (s,2H, NH); RMN ^{13}C (50.32 MHz, CD_3CN) δ ppm: 27.2 (CH$_3$); 120.7–175.0 (C$_6$H$_4$); 153.1 (–N–C=N–); 197.8 (>C=O); MS (DCI NH_3): m/z=281 (100%) [M$^{\oplus}$].

4.2. Synthesis of monocationic symmetrical penta-methinium salts

Under argon, a solution of 2.64 mmol of alkylamine in 50 mL of dry acetonitrile is added to 1.32 mmol of carboxonium salt. The mixture is stirred during 4 h. After evaporation of the solvent, the crude product is washed with pentane, recrystallized in 100% ethanol and dried under vacuum at 40°C.

4.2.1. 1a: 1,5-Bis(ethylamino)-1,5-diphenylpenta-2,4-dienylium perchlorate. Yield=60%; yellow powder; mp=144°C; IR (KBr pellet) ν cm^{-1}: 3315 (N–H); 1100 (Cl–O); UV (CH_2Cl_2): λ_{max}=435 nm, ϵ=66 000 mol^{-1} L cm^{-1}; ^{1}H NMR (250 MHz, CD_3CN) δ ppm, J Hz: 1.32 (t, 6H, CH_3–CH$_2$, J=7.2 Hz); 3.49 (q, 4H, CH$_3$–CH_2; J=7.2 Hz); 6.18 (d, 2H, H$_2$–H$_4$, syst. A$_2$X, J_{AX}=13.0 Hz); 7.07 (t, 1H, H$_3$, syst. A$_2$X; J_{AX}=13.0 Hz); 7.22–7.53 (m, 10H, C$_6$H$_5$); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 13.7 (CH_3–CH$_2$); 40.8 (CH$_3$–CH_2); 103.8 (C$_2$–C$_4$); 129.6–134.8 (C$_6$H$_5$);

162.9 (C_3); 170.2 (C_1–C_5); MS (DCI, NH_3): m/z=305 (100%) [$M^{\oplus}$].

4.2.2. 1g: 1,5-Bis(*n*-octylamino)-1,5-diphenylpenta-2,4-dienylium perchlorate. Yield=60%; yellow crystals; mp=80°C; IR (KBr pellet) ν cm^{-1}: 3291 (N–H); 1112 (Cl–O); UV (CH_2Cl_2) λ_{max}=437 nm; ϵ=81 225 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 0.88 (t, 6H, CH_3–$(CH_2)_7$, J=6.8 Hz); 1.30–1.71 (m, 24H, $(CH_2)_6$–CH_2); 3.44 (broad t, 4H, CH_2–N, J=6.8 Hz); 6.23 (d, 2H, H_2–H_4, syst. A_2X; J_{AX}=13.8 Hz); 7.33–7.40 (m, 9H, C_6H_4+H_3); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 14.5 (CH_3–$(CH_2)_7$); 23.4–32.6 ($(CH_2)_6$); 45.6 (CH_2–N); 103.8 (C_2–C_4); 129.6–134.6 (C_6H_4); 162.8 (C_3); 170.4 (C_1–C_5); Anal. calcd for $C_{33}H_{49}N_2ClO_4$: C, 69.15; H, 8.62; N, 4.89. Found: C, 69.24; H, 8.71; N, 4.81; MS (DCI, NH_3): m/z=473 (30%) [$M^{\oplus}$].

4.2.3. 1h: 1,5-Bis(*n*-decylamino)-1,5-diphenylpenta-2,4-dienylium perchlorate. Yield=60%; yellow crystals; mp=98°C; IR (KBr pellet) ν cm^{-1}: 3291 (N–H); 1117 (Cl–O); UV (CH_2Cl_2): λ_{max}=437 nm; ϵ=80 781 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 0.88 (t, 6H, CH_3–$(CH_2)_9$, J=6.8 Hz); 1.29–1.69 (m, 32H, $(CH_2)_8$); 3.45 (t, 4H, CH_2–N, J=6.8 Hz); 6.21 (d, 2H, H_2–H_4, syst. A_2X; J_{AX}=13.8 Hz); 7.29–7.45 (m, 11H, C_6H_4+H_3); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 14.5 (CH_3–$(CH_2)_9$–); 23.4–32.7 ($(CH_2)_8$); 45.6 (–CH_2–N); 103.7 (C_2–C_4); 129.6–134.8 (C_6H_4); 162.8 (C_3); 170.4 (C_1–C_5); Anal. calcd for $C_{37}H_{57}N_2ClO_4$: C, 70.62; H, 9.13; N, 4,45. Found: C, 70.82; H, 9.40; N, 4.37; MS (DCI, NH_{33}): m/z= 529 (78%) [$M^{\oplus}$].

4.2.4. 1i: 1,5-Bis(2-methoxylethylamino)-1,5-diphenylpenta-2,4-dienylium perchlorate. See Ref. 8.

4.2.5. 1k: 1,5-Bis(diethylamino)-1,5-diphenylpenta-2,4-dienylium perchlorate. See Ref. 8.

4.2.6. 2a: 1,5-Bis(ethylamino)-1,5-bis(4-methylphenyl) penta-2,4-dienylium perchlorate. Yield=70%; orange crystals; mp=180°C; IR (KBr pellet) ν cm^{-1}: 3287 (N–H); 1066 (Cl–O); UV (CH_2Cl_2): λ_{max}=437 nm; ϵ=66 500 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.63 (t, 6H, CH_3–CH_2, J=7.2 Hz); 2.71 (s, 6H, CH_3–C_6H_4); 3.87 (q, 4H, CH_3–CH_2–, J=7.2 Hz); 6.50 (d, 2H, H_2–H_4, syst. A_2X; J_{AX}=13.0 Hz); 7.30 (t, 1H, H_3, syst. A_2X; J_{AX}=13.0 Hz); 6.90 and 7.10, (m, 8H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 13.8 (CH_3–CH_2); 21.4 (CH_3–C_6H_4); 40.5 (CH_3–CH_2); 103.4 (C_2–C_4); 130.2–142.8 (C_6H_4); 163.1 (C_3); 170.3 (C_1–C_5); MS (DCI, NH_3): m/z=333 (100%) [$M^{\oplus}$].

4.2.7. 2b: 1,5-Bis(isopropylamino)-1,5-bis(4-methylphenyl)penta-2,4-dienylium perchlorate. Yield=70%; yellow crystals; mp=166°C; IR (KBr pellet) ν cm^{-1}: 3273 (N–H); 1067 (Cl–O); UV (CH_2Cl_2): λ_{max}=438 nm; ϵ= 73 100 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.32 (d, 12H, $(CH_3)_2CH$, J=6.4 Hz); 2.35 (s, 6H, CH_3–C_6H_4); 4.04 (hept, 2H, $(CH_3)_2CH$, J=6.4 Hz); 6.17 (d, 2H, H_2–H_4, syst. A_2X; J_{AX}=13.1 Hz); 6.96 (t, 1H, H_3, syst. A_2X; J_{AX}=13.1 Hz); 7.03–7.26 (m, 8H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 21.4 (CH_3–C_6H_4); 22.0 ($(CH_3)_2CH$); 47.8 $(CH_3)_2CH$); 103.6 (C_2–C_4); 130.1–142.6 (C_6H_4); 163.3 (C_3); 169.4 (C_1–C_5); Anal. calcd for $C_{25}H_{33}N_2ClO_4$: C, 65.14; H, 7.22; N, 6.08. Found: C, 65.61; H, 7.48; N, 6.05; MS (DCI, NH_3): m/z=361 (100%) [$M^{\oplus}$].

4.2.8. 2′c: 1,5-Bis(*n*-butylamino)-1,5-bis(4-methylphenyl)-penta-2,4 dienylium tetrafluoroborate. Yield=70%; yellow crystals; mp=154°C; IR (KBr pellet) ν cm^{-1}: 3273 (N–H), 1053 (B–F); UV (CH_2Cl_2): λ_{max}=439 nm; ϵ= 76 500 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 0.96 (t, 6H, CH_3–$(CH_2)_3$, J=7.2 Hz); 1.41–1.65 (m, 8H, $(CH_2)_2$); 2.35 (s, 6H, CH_3–C_6H_4); 3.44 (t, 4H, CH_2–N, J=7.2 Hz); 6.14 (d, 2H, H_2–H_4, syst. A_2X; J_{AX}=13.1 Hz); 6.98 (t, 1H, H_3, syst. A_2X; J_{AX}=13.1 Hz); 7.08–7.22 (m, 8H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 14.0 (CH_3–$(CH_2)_3$); 20.8 (CH_3–CH_2–); 21.4 (CH_3–C_6H_4); 31.0 (CH_2–CH_2N); 45.3 (CH_2N); 103.5 (C_2–C_4); 130.2–142.8 (C_6H_4); 162.9 (C_3); 170.4 (C_1–C_5); MS (DCI, NH_3): m/z=389 (100%) [$M^{\oplus}$].

4.2.9. 2i: 1,5-Bis(methoxyethylamino)-1,5-bis(4-methylphenyl)penta-2,4-dienylium perchlorate. See Ref. 8.

4.2.10. 2k: 1,5-Bis(diethylamino)-1,5-bis(4-methylphenyl)-penta-2,4-dienylium perchlorate. See Ref. 8.

4.2.11. 2′k: 1,5-Bis(diethylamino)-1,5-bis(4-methylphenyl)-penta-2,4-dienylium tetrafluoroborate. Yield=60%; orange crystals; mp=262°C; IR (KBr pellet) ν cm^{-1}: 1021 (B–F); UV (CH_2Cl_2): λ_{max}=444 nm, ϵ=107 000 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN): δ ppm, J Hz: 1.01 and 1.32 (2t, 12H, J=7.0 Hz, C$H_3$$CH_2$); 2.34 (s, 6H, C$H_3$$C_6H_4$); 3.15 and 3.63 (2q, 8H, J=7.0 Hz, CH_3CH_2); 5.98–6.12 (3H, H_2, H_3, H_4, syst. A_2B, J=13.0 Hz); 6.85 and 7.11 (8H, C_6H_4 syst. AA′BB′, J_{AB}=$J_{A'B'}$=8.0 Hz); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 12.7 and 14.3 (CH_3CH_2); 45.7 and 48.9 (CH_2CH_3); 21.5 ($CH_3C_6H_4$); 106.1 (C_2–C_4); 129.1–147.0 (C_6H_4); 162.9 (C_3); 170.4 (C_1–C_5); MS (DCI, NH_3): m/z=389, (100%) [$M^{\oplus}$].

4.2.12. 2′l: 1,5-Bis(*N*-methyl-*N*-*n*-butylamino)-1,5-bis-(4-methylphenyl)penta-2,4-dienylium tetrafluoroborate. Yield=75%; orange crystals; mp=140°C; IR (KBr pellet) ν cm^{-1}: 1064 (B–F); UV (CH_2Cl_2): λ_{max}=446 nm; ϵ= 107 700 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 0.71 (t, 3H, CH_3–$(CH_2)_3$, J=7.1 Hz); 1.03 (m, 2H+3H, CH_3–C$H_2$$(CH_2)_2$); 1.45 and 1.85 (m, 6H, CH_2–CH_2–CH_2); 2.33 (6H, CH_3–C_6H_4); 2.85 and 3.20 (2s, 6H, CH_3N) 3.12 and 3.56 (2t, 4H, CH_2–N, J=7.0 Hz); 6.06–6.10 (3H, H_2, H_3, H_4, syst. A_2B); 6.85–7.13 (8H, C_6H_4, syst. AA′BB′, J_{AB}=$J_{A'B'}$=8.3 Hz); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 13.8 and 14.2 (CH_3–$(CH_2)_3$–N); 20.3 and 20.8 (CH_2)–$(CH_2)_2$–N); 21.4 (CH_3–C_6H_4); 29.4 and 30.5 (–CH_2–CH_2–N); 39.1 and 42.5 (CH_3–N); 53.8 and 55.8 (CH_2–N); 106.0 and 106.5 (C_2–C_4); 129.3–140.9 (C_6H_4); 162.5 and 162.8 (C_3); 170.4 (C_1–C_5); Anal. calcd for $C_{29}H_{41}N_2BF_4$: C, 69.05; H, 8.19; N, 5.55. Found: C, 68.99; H, 8.33; N, 5.48; MS (DCI, NH_3): m/z=417 (100%) [$M^{\oplus}$].

4.2.13. 3a: 1,5-Bis(ethylamino)-1,5-bis(4-methoxyphenyl)-penta-2,4-dienylium perchlorate. Yield=80%; yellow crystals; mp=226°C; IR (KBr pellet) ν cm^{-1}: 3308

(N–H); 1077 (Cl–O); UV (CH_2Cl_2): λ_{max}=445 nm; ϵ=73 100 mol^{-1} L cm^{-1}; Anal. calcd for $C_{23}H_{29}N_2ClO_6$: C, 59.42; H, 6.29; N, 6.03. Found: C, 59.01; H, 6.26; N, 6.08; MS (DCI, NH_3): *m/z*=365 (100%) [$M^{\oplus}$].

4.2.14. 3b: 1,5-Bis(isopropylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate. Yield=70%; orange crystals; mp=246°C; IR (KBr pellet) ν cm^{-1}: 3290 (N–H); 1079 (Cl–O); UV (CH_2Cl_2): λ_{max}=445 nm; ϵ=72 900 mol^{-1} L cm^{-1}; Anal. calcd for $C_{25}H_{33}N_2ClO_6$: C, 60.91; H, 6.75; N, 5.68. Found: C, 60.92; H, 6.83; N, 5.46; MS (DCI, NH_3): *m/z*=393 (100%) [$M^{\oplus}$].

4.2.15. 3c (X=ClO_4); 3′c (X=BF_4): 1,5-Bis(*n*-butylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate or tetrafluoroborate. Yield=75%; yellow crystals; mp=154°C (X=ClO_4); yield=70%; yellow crystals; mp=136°C (X=BF_4); IR (KBr pellet) ν cm^{-1}: 3311 (N–H); 1108 (Cl–O), 1053 (B–F); UV (CH_2Cl_2): λ_{max}=446 nm, ϵ=74 200 mol^{-1} L cm^{-1} (X=ClO_4); λ_{max}=446 nm, ϵ=73 400 mol^{-1} L cm^{-1} (X=BF_4); Anal. calcd for $C_{27}H_{37}N_2ClO_6$: C, 62.24; H, 7.16; N, 5.38. Found: C, 62.17; H, 7.21; N, 5.32 Anal. calcd for $C_{27}H_{37}N_2BF_4O_2$; C, 63.79; H, 7.34; N, 5.51. Found: C, 63.54; H, 7.35; N, 5.37; MS (DCI, NH_3): *m/z*=421 (100%) [$M^{\oplus}$].

4.2.16. 3d: 1,5-Bis(isobutylamino) 1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate. Yield=70%; orange crystals; mp=156°C; IR (KBr pellet) ν cm^{-1}: 3302 (N–H); 1098 (Cl–O); UV (CH_2Cl_2): λ_{max}=448 nm; ϵ=71 100 mol^{-1} L cm^{-1}; ^{1}H NMR (200 MHz, CD_3CN) δ ppm, *J* Hz: 1.08 (d, 12H, $(CH_3)_2CH–CH_2$); 2.07 (m, 4H, $(CH_3)_2CH–CH_2$); 3.27 (d, 4H, $(CH_3)_2CH–CH_2$); 3.82 (s, 6H, OCH_3); 6.15 (d, 2H, $H_2–H_4$, syst. A_2X; J_{AX}=13.0 Hz); 7.13 (t, 1H, H_3, syst. A_2X; J_{AX}=13.0 Hz); 6.94–7.34 (8H, C_6H_4, syst. AA′BB′, $J_{AB}=J_{A'B'}$=8.7 Hz); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 20.4 ($(CH_3)_2CH–CH_2$); 28.7 $(CH_3)_2CH–CH_2$); 52.8 ($(CH_3)_3CH–CH_2$); 56.3 (OCH_3); 103.6 ($C_2–C_4$); 115.0–163.0 (C_6H_4); 162.8 (C_3); 170.2 ($C_1–C_5$); Anal. calcd for $C_{27}H_{37}N_2ClO_6$: C, 62.24; H, 7.16; N, 5.38. Found: C, 62.43; H, 7.27; N, 5.33; MS (DCI, NH_3): *m/z*=421 (100%) [$M^{\oplus}$].

4.2.17. 3e: 1,5-Bis(*t*-butylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate. Yield=75%; orange crystals; mp=226°C; IR (KBr pellet) ν cm^{-1}: 3295 (N–H); 1066 (Cl–O); UV (CH_2Cl_2): λ_{max}=443 nm; ϵ=69 800 mol^{-1} L cm^{-1}; ^{1}H NMR (200 MHz, CD_3CN) δ ppm, *J* Hz: 1.51 (s, 18H, $(CH_3)_3C$), 3.80 (s, 6H, OCH_3); 6.36 (d, 2H, $H_2–H_4$, syst. A_2X; J_{AX}=13 Hz); 7.00 (t, 1H, H_3, syst. A_2X; J_{AX}=13.0 Hz); 6.88–7.25 (8H, C_6H_4, syst. AA′BB′, $J_{AB}=J_{A'B'}$=7.0 Hz); ^{13}C NMR (50.52 MHz, CD_3CN) δ ppm: 29.2 ($(CH_3)_3C$); 56.1 ($(CH_3)_3C$); 56.3 (OCH_3); 105.8 ($C_2–C_4$); 114.8–162.8 (C_6H_4); 163.5 (C_3); 169.2 ($C_1–C_5$); Anal. calcd for $C_{27}H_{37}N_2ClO_6$: C, 62.24; H, 7.16; N, 5.38. Found: C, 62.09; H, 7.26; N, 5.05; MS (DCI, NH_3): *m/z*=421 [M^+].

4.2.18. 3f: 1,5-Bis(*n*-hexylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate. Yield=87%; yellow crystals; mp=122°C; IR (KBr pellet) ν cm^{-1}: 3287 (N–H); 1108 (Cl–O); UV (CH_2Cl_2): λ_{max}=446 nm, ϵ=73 800 mol^{-1} L cm^{-1}; ^{1}H NMR (200 MHz, CD_3CN) δ ppm, *J* Hz: 0.94 (t, 6H, $CH_3–(CH_2)_5$, *J*=6.5 Hz); 1.30–1.96 (m, 16H, $(CH_2)_4$); 3.43 (t, 4H, $CH_2–N$, *J*=6.9 Hz); 3.80 (s, 6H, OCH_3); 6.15 (d, 2H, $H_2–H_4$, syst. A_2X; J_{AX}=13.0 Hz); 7.00 (t, 1H, H_3, syst. A_2X; J_{AX}=13.0 Hz), 6394–7.33 (8H, C_6H_4, syst. AA′BB′, $J_{AB}=J_{A'B'}$=8.7 Hz); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 14.4 ($CH_3–(CH_2)_5$); 23.3 ($CH_3–CH_2–(CH_2)_4$); 27.3 ($CH_3–CH_2–CH_2–(CH_2)_3$); 28.9 ($CH_3–(CH_2)_2–CH_2–(CH_2)_2$); 32.2 ($CH_3–(CH_2)_3–CH_2–(CH_2)$); 45.6 ($CH_2–N$); 56.3 ($OCH_3$); 103.4 ($C_2–C_4$); 115.0–163.0 ($C_6H_4$); 162.6 ($C_3$); 169.8 ($C_1–C_5$); Anal. calcd for $C_{31}H_{45}N_2ClO_6$: C, 64.51; H, 7.86; N, 4.85. Found: C, 64.54; H, 7.93; N, 4.79; MS (DCI, NH_3): *m/z*=477 (80%) [$M^{\oplus}$].

4.2.19. 3g: 1,5-Bis(*n*-octylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate. Yield=75%; yellow crystals; mp=128°C; IR (KBr pellet) ν cm^{-1}: 3289 (N–H); 1114 (ClO); UV (CH_2Cl_2): λ_{max}=447 nm; ϵ=75 200 mol^{-1} L cm^{-1}; Anal. calcd for $C_{35}H_{53}N_2ClO_6$: C, 66.38; H, 8.44; N, 4.42. Found: C, 66.19; H, 8.45; N, 4.29; MS (DCI, NH_3): *m/z*=533 (100%) [$M^{\oplus}$].

4.2.20. 3h (X=ClO_4); 3′h (X=BF_4): 1,5-Bis(*n*-decylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate or tetrafluoroborate. Yield=80%; yellow crystals; mp=134°C (X=ClO_4); yield=75%; yellow crystals; mp=136°C (X=BF_4); IR (KBr pellet) ν cm^{-1}: 3289 (N–H); 1105 (ClO); 3328 (N–H); 1076 (B–H); UV (CH_2Cl_2): λ_{max}=448 nm; ϵ=74 000 mol^{-1} L cm^{-1} (X=ClO_4); λ_{max}=446 nm; ϵ=73 800 mol^{-1} L cm^{-1} (X=BF_4); Anal. calcd for $C_{39}H_{61}N_2ClO_6$: C, 67.95; H, 8.92; N, 4.06. Found: C, 67.83; H, 8.96; N, 3.89; Anal. calcd for $C_{39}H_{61}N_2BF_4O_2$: C, 69.22; H, 9.09; N, 4.14. Found: C, 69.28; H, 9.25; N, 4.12; MS (DCI, NH_3): *m/z*=589 (100%) [$M^{\oplus}$].

4.2.21. 3i (X=ClO_4); 3′i (X=BF_4): 1,5-Bis(methoxyethylamino)-1,5-bis(4-methoxyphenyl)-penta-2,4-dienylium perchlorate or tetrafluoroborate. Yield=70%; yellow crystals; mp=188°C (X=ClO_4); yield=70%; yellow crystals; mp=186°C (X=BF_4); IR (KBr pellet) ν cm^{-1}: 3299 (N–H); 1064 (Cl–O); 3301 (N–H); 1066 (B–F); UV (CH_2Cl_2): λ_{max}=447 nm, ϵ=72 000 mol^{-1} L cm^{-1} (ClO_4); λ_{max}=446 nm, ϵ=74 000 mol^{-1} L cm^{-1} (BF_4); ^{1}H NMR (200 MHz, CD_3CN) δ ppm, *J* Hz: 3.34 (s, 6H, $CH_3–O(CH_2)_2$); 3.62 (s, 8H, $CH_3O(CH_2)_2N$); 3.82 (s, 6H, $CH_3O–C_6H_4$); 6.19 (d, 2H, $H_2–H_4$, syst. A_2X; J_{AX}=13.0 Hz); 6.94–7.32 (m, 9H, 8H C_6H_4+H_3); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 45.5 (CH_2N); 56.4 ($CH_3O–C_6H_4$); 59.1 ($CH_3O–CH_2–$); 70.3 ($O–CH_2$); 103.8 ($C_2–C_4$); 115.1–163.1 (C_6H_4); 163.0 (C_3); 170.4 ($C_1–C_5$); Anal. calcd for $C_{25}H_{33}N_2ClO_8$: C 57.20; H 6.34; N 5.34. Found: C, 57.18; H, 6.34; N, 5.28; Anal. calcd for $C_{25}H_{33}N_2BF_4O_4$: C, 58.61; H, 6.49; N, 5.47. Found: C, 58.49; H, 6.53; N, 5.37; MS (DCI, NH_3): *m/z*=425 (100%) [$M^{\oplus}$].

4.2.22. 3j (X=ClO_4); 3′j (X=BF_4): 1,5-Bis(1-furfurylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate or tetrafluoroborate. Yield=87%; yellow crystals; mp=174°C (X=ClO_4); yield=72%; yellow crystals; mp=184°C (X=BF_4); IR (KBr pellet) ν cm^{-1}: 3287 (N–H); 1065 (Cl–O) or 1021 (B–F); UV (CH_2Cl_2):

λ_{max}=453 nm; λ=71 800 mol^{-1} L cm^{-1} (X=ClO_4); λ_{max}= 451 nm; λ=71 700 mol^{-1} L cm^{-1} (X=BF_4); ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 3.80 (s, 6H, OCH_3); 4.65 (s, 4H, CH_2–N); 6.26 (d, 2H, H_2–H_4, syst. A_2X; J_{AX}=13.8 Hz); 6.45 (2H, CH_2 furfuryl); 6.94–7.35 (8H, C_6H_4, syst. AA′BB′, J_{AB}=$J_{A'B'}$=9.0 Hz); 7.00 (t, 1H, H_3, syst. A_2X; J_{AX}=13.8 Hz); 7.35–7.52 (m, 3H, furanyl); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 42.1 (*C*H_2–N); 56.4 (O*C*H_3); 100.9, 115.0, 144.1, 150.3 (furanyl); 104.4 (C_2–C_4); 110.0–163.3 (C_6H_4); 163.8 (C_3); 170.3 (C_1–C_5); Anal. calcd for $C_{29}H_{29}N_2ClO_8$: C, 61.22; H, 5.14; N, 4.92. Found: C, 61.23; H, 5.12; N, 4.84; Anal. calcd for $C_{29}H_{29}N_2BF_4O_4$: C, 62.61; H, 5.25; N, 5.04. Found: C, 62.24; H, 5.24; N, 4.64;

4.2.23. 3k (X=ClO_4); 3′k (X=BF_4): 1,5-Bis(diethylamino)-1,5-bis(4-methoxyphenyl) penta-2,4-dienylium perchlorate or tetrafluoroborate. Yield=70%; yellow crystals; mp=222°C (X=ClO_4); yield=70%; yellow crystals; mp=202°C (X=BF_4); IR (KBr pellet) ν cm^{-1}: 1096 (Cl–O) or 1058 (B–F); UV (CH_2Cl_2): λ_{max}=444 nm, ϵ=105 000 mol^{-1} L cm^{-1} (X=ClO_4) λ_{max}=444 nm, ϵ= 108 000 mol^{-1} L cm^{-1} (X=BF_4) Anal. calcd for $C_{27}H_{37}N_2ClO_6$: C, 62.24; H, 7.16; N, 5.38. Found: C, 62.24; H, 7.20; N, 5.33; Anal. calcd for $C_{27}H_{37}N_2BF_4O_2$: C, 63.79; H, 7.34; N, 5.47. Found: C, 63.64; H, 7.33; N, 5.46; MS (DCI, NH_3): m/z=421 (100%) [$M^{\oplus}$].

4.2.24. 3′l: 1,5-Bis(*N*-methyl-*N*-*n*-butylamino)-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium tetrafluoroborate. Yield=75%; yellow crystals; mp=186°C; IR (KBr pellet) ν cm^{-1}: 1055 (B–F); UV (CH_2Cl_2): λ_{max}=446 nm; ϵ= 100 000 mol^{-1} L cm^{-1}; Anal. calcd for $C_{29}H_{41}N_2BF_4O_2$: C, 64.93; H, 7.70; N, 5.17. Found: C, 65.07; H, 7.80; N, 5.13; MS (DCI, NH_3): m/z=449 (100%) [$M^{\oplus}$].

4.2.25. 4k: 1,5-Bis(diethylamino)-1,5-bis(4-acetaminophenyl)penta-2,4-dienylium perchlorate. Yield=67%; ocher crystals; mp=253°C; IR (KBr pellet) ν cm^{-1}: 3363 (N–H), 1074 (Cl–O); 1696 (C=O); UV (CH_2Cl_2): λ_{max}= 447 nm, ϵ_{max}=93 460 mol^{-1} L cm^{-1}; ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.02 and 1.31 (2t, 12H, CH_3CH$_2$, J=7.1 Hz); 2.10 (s, 6H, CH_3CONH); 3.19–3.60 (2q, 8H, CH_3CH_2, J=7.1 Hz); 6.09–6.12 (m, 3H, H_2, H_3, H_4, syst. A_2B; J_{AB}=13.0 Hz); 6.92 and 7.48 (8H, C_6H_4, syst. AA′BB′; J_{AB}=$J_{A'B'}$=8.4 Hz); 8.56 (s, 2H, NH); ^{13}C NMR(50.32 MHz, CD_3CN) δ ppm: 12.6 and 14.3 (*C*H_3–CH_2); 24.6 (*C*H_3–CO); 45.7 and 49.0 (CH_3–*C*H_2); 106.0 (C_2–C_4); 120.0–130.0 (C_6H_4); 141.0 (NH–C–); 163.0 (C_3); 170.1 and 170.0 (C_1–C_5 and C=O); Anal. calcd for $C_{29}H_{39}N_4ClO_6$: C, 60.57; H, 6.84; N, 9.74. Found: C, 60.16; H, 6.81; N, 9.67; MS (DCI, NH_3): m/z=475 (30%) [$M^{\oplus}$].

4.2.26. 6′k: 1,5-Bis(diethylamino)-1,5-bis(4-iodophenyl)-penta-2,4-dienylium tetrafluoroborate. Yield=66%; yellow crystals; mp=222°C; IR (KBr pellet) ν cm^{-1}: 1096 (Cl–O); UV (CH_2Cl_2): λ_{max}=448 nm, ϵ_{max}=107 000 mol^{-1} L cm^{-1}; MS (DCI, NH_3): m/z=613 (100%) [$M^{\oplus}$].

4.2.27. 7k: 1,5-Bis(diethylamino)-1,5-bis(4-fluorophenyl)-penta-2,4-dienylium perchlorate. Yield=65%; yellow crystals; mp>280°C; IR (KBr pellet) ν cm^{-1}: 1096 (Cl–O); UV (CH_2Cl_2): λ_{max}=444 nm, ϵ=120 000 mol^{-1} L cm^{-1}; Anal. calcd for $C_{25}H_{31}N_2BF_6$: C, 60.42; H, 6.29 N, 5.64. Found: C, 60.54; H, 6.32; N, 5.73; MS (DCI, NH_3): m/z=397 (100%) [$M^{\oplus}$].

4.2.28. 8k: 1,5-Bis(diethylamino)-1,5-bis(4-cyanophenyl)-penta-2,4-dienylium perchlorate. Yield=68%; yellow crystals; mp>280°C; IR (KBr pellet) ν cm^{-1}: 1096 (Cl–O); UV (CH_2Cl_2): λ_{max}=448 nm, ϵ=109 000 mol^{-1} L cm^{-1}; Anal. calcd for $C_{27}H_{31}N_4BF_4$: C, 63.42; H, 6.11; N, 10.96. Found: C, 63.34; H, 6.04; N, 10.81; MS (DCI, NH_3): m/z=411 (100%) [$M^{\oplus}$].

4.3. Synthesis of monocationic dissymmetrical pentamethinium salts

First step: hemicarboxonium salt. 4.3 mmol (42 μL) of diethylamine are added to a solution of 4.3 mmol of carboxonium salt in acetonitrile (40 mL). The compound is recrystallized in ethanol.

4.3.1. 10: 1-Ethoxy-5-diethylamino-1,5-bis(4-methylphenyl)-penta-2,4-dienylium perchlorate. See Ref. 8.

4.3.2. 10′: 1-Ethoxy-5-diethylamino-1,5-bis(4-methylphenyl)penta-2,4-dienylium tetra-fluoroborate. Yield= 80%; yellow crystals; IR (KBr pellet) ν cm^{-1} 1055 (B–F); ^{1}H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.17 and 1.42 (2t, 6H, CH_3CH$_2$N, J=7.2 Hz); 1.53 (t, 3H, CH_3CH$_2$O, J=7.0 Hz); 2.33 and 2.37 (2s, 6H, CH_3C$_6$H$_4$); 3.51 and 3.91 (2q, 4H, NCH_2CH$_3$, J=7.2 Hz);); 4.20 (q, 2H, OCH_2CH$_3$, J=7.0 Hz); 6.22–6.61 (3H, H_2, H_3, H_4, syst. AMX, J=11.4 and 12.0 Hz); 7.10–7.35 (m, 8H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 13.4 and 14.6 (*C*H_3CH$_2$N); 14.0 (*C*H_3CH$_2$O); 21.4 and 21.5 (*C*H_3C$_6$H$_4$); 48.1 and 51.6 (CH_3*C*H_2N); 67.3 (CH_3*C*H_2O) 104.2 (C_4); 117.0 (C_2); 127.5–129.7 (C_6H_4); 162.2 (C_3);175.3 (C_1); 176.8 (C_5); MS (DCI, NH_3): m/z=362 (100%) [$M^{\oplus}$].

4.3.3. 11: 1-Ethoxy-5-diethylamino-1,5-bis(4-methoxyphenyl)penta-2,4-dienylium perchlorate. Yield=70%; yellow crystals; IR (KBr pellet) ν cm^{-1}: 1094 (Cl–O); ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm, J Hz: 1.22 and 1.51 (2t, 6H, CH_3CH$_2$N, J=7.2 Hz); 1.45 (t, 3H, CH_3CH$_2$O, J= 7.0 Hz); 3.51 and 3.99 (2q, 4H, CH_3CH_2N, J=7.2 Hz); 3.82 and 3.84 (2s, 6H, CH_3O); 4.24 (t, 2H, CH_3CH_2O, J= 7.0 Hz); 6.25–6.92 (3H, H_2, H_3, H_4, syst. AMX, J=11.5 and 12 Hz); 6.72–7.26 (m, 8H, C_6H_4); ^{13}C NMR(50.32 MHz, $CDCl_3$) δ ppm: 13.3 and 14.4 (*C*H_3CH$_2$N); 14.0 (*C*H_3CH$_2$O); 47.4 and 50.3 (CH_3*C*H_2N); 55.5 and 55.6 (CH_3O); 66.7 (CH_3*C*H_2O); 104.3 (C_4); 113.6–161.9 (C_6H_4–OMe); 116.0 (C_2); 162.5 (C_3); 174.8 (C_1); 175.2 (C_5); Anal. calcd for $C_{25}H_{32}NClO_7$: C, 60.79; H, 6.53; N, 2.84. Found: C, 61.05; H, 6.58; N, 2.79; MS (DCI, NH_3): m/z=394 (100%) [$M^{\oplus}$].

Second step: synthesis of dissymmetrical pentamethinium salts. To one equivalent of hemicarboxonium salt is added, in the same experimental conditions, one equivalent of alkylamine during four hours. The compound is purified by recrystallization in 100% ethanol.

4.3.4. 10b: 1-Diethylamino-5-isopropylamino-1,5-bis-(4-methyphenyl)penta-2,4-dienylium perchlorate. Yield=

75%; yellow crystals; mp=204°C; IR (KBr pellet) ν cm^{-1}: 3270 (N–H); 1105 (Cl–O); UV (CH_2Cl_2): λ_{max}= 440,7 nm; ϵ_{max}=73 400 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.05 (t, 3H, CH_3–CH_2–N, J=7.1 Hz); 1.27 (t, 9H, CH_3–CH_2, J=7.1 Hz+d, 6H, (CH_3)$_2$CH, J=6.5 Hz); 2.33 (s, 6H, CH_3–C_6H_4); 3.21 (q, 2H, CH_3–CH_2–N, J=7.1 Hz); 3.66 (q, 2H, CH_3–CH_2–N, J=7.1 Hz); 3.95 (hept, 1H, (CH_3)$_3$CH, J=6.5 Hz); 6.00–6.50 (3H, H_2, H_3, H_4, syst. AMX, J_{AM}=13.0 Hz; J_{MX}= 12.9 Hz); 6.92–7.22 (8H, m, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 12.7 (CH_3–CH_2); 14.3 (CH_3–CH_2); 21.4 (CH_3–C_6H_4); 21.9 (CH_3)$_3$CH); 45.9 (CH_3CH_2N); 47.5 (N–CH(CH_3)$_2$); 49.2 (–CH_2N); 102.4 (C_4); 107.1 (C_4); 129.1–142.2 (C_6H_4); 163.1 (C_3); 168.4 (C_5); 171.2 (C_1); Anal. calcd for $C_{26}H_{35}N_2ClO_4$: C, 65.74; H, 7.43; N, 5.90. Found: C, 65.58; H, 7.54; N, 5.94; MS (DCI, NH_3): m/z=375 (100%) [$M^{\oplus}$].

4.3.5. 10′c: 1-Diethylamino-5-*n*-butylamino-1,5-bis-(4-methylphenyl)penta-2,4-dienylium tetra-fluoroborate. Yield=70%; yellow crystals; mp=172°C; IR (KBr pellet) ν cm^{-1}: 1054 (B–F); UV (CH_2Cl_2): λ_{max}=440 nm; ϵ_{max}=70 000 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 0.99 (m, 6H, CH_3–CH_2–N+CH_3(CH_2)$_3$); 1.40 (m, 5H, CH_3–CH_2–N+CH_3–CH_2–(CH_2)$_2$); 1.85 (m, 2H, CH_2–CH_2–CH_2–N); 2.34 (s, 6H, CH_3–C_6H_4); 3.25 (q, 2H, CH_3–CH_2–N); 3.39 (t, 2H, CH_2–CH_2–N); 3.68 (q, 2H, CH_3–CH_2–N); 5.98–6.59 (3H, syst. AMX J_{AX}= 13.0 Hz; J_{MX}=12.9 Hz, H_2, H_3, H_4); 7.00–7.23 (m, 8H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 12.3 (CH_3–CH_2); 14.0 (CH_3–CH_2)$_3$); 14.3 (CH_3–CH_2–N); 20.8 (CH_3–CH_2–(CH_2)$_2$); 21.3 (CH_3–C_6H_4); 40.0 (CH_3–CH_2–CH_2–); 45.1 (–CH_2–N); 46.0 (CH_3–CH_2–N); 49.3 (CH_3–CH_2–N); 102.2 (C_4); 107.2 (C_2); 129.1–142.3 (C_6H_4); 162.9 (C_3); 169.4 (C_5); 171.3 (C_1); Anal. calcd for $C_{27}H_{37}N_2BF_4$: C, 68.07; H, 7.83; N, 5.88. Found: C, 68.33; H, 7.90; N, 5.72; MS (DCI, NH_3): m/z=389 (100%) [$M^{\oplus}$].

4.3.6. 10′l: 1-Diethylamino-5-*N*-methyl-*N*-*n*-butylamino-1,5-bis(4-methylphenyl)penta-2,4-dienylium tetrafluoroborate. Yield=70%; orange crystals; mp=180°C; IR (KBr pellet) ν cm^{-1}: 1052 (B–F); UV (CH_2Cl_2): λ_{max}=444 nm; ϵ=89 800 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, DMSO) δ ppm, J Hz: 0.88 (t, 3H, CH_3–(CH_2)$_3$–N–CH_3); 1.00 (m, 5H, CH_3–CH_2–N+CH_2–(CH_2)$_2$N–CH_3); 1.16–1.44 (m, 7H, CH_3–CH_2–N+(CH_2)$_2$$CH_2$–N); 2.32 (s, 6H, C$H_3$–$C_6H_4$); 3.20 (m, 4H, CH_3–CH_2–N+C_3H_7–CH_2–N); 3.86 (CH_3–CH_2–N); 5.8–6.27 (m, 3H, H_2, H_3, H_4, syst. AMX); 6.87–7.15 (m, 8H, C_6H_4, syst. AA′BB′, J_{AB}=$J_{A'B'}$=8.7 Hz); ^{13}C NMR (50.32 MHz, DMSO) δ ppm: 12.1 and 13.7 (two t (CH_3–CH_2–N); 13.2 (CH_3–(CH_2)$_3$–N–CH_3); 18.9 and 19.4 (CH_3–CH_2–(CH_2)$_2$); 20.7 (CH_3–C_6H_4); 28.1 and 29.5 (CH_3–CH_2–CH_2–CH_2); 38.0 and 41.4(CH_3–N); 44.3 and 47.6 (CH_3–CH_2–N); 52.2 and 54.0 (C_3H_7–CH_2–N); 104.9–105.5 ((C_2–C_4); 127.7–139.0 (C_6H_4); 161.1 (C_3); 168.3–169.2 (C_1–C_5); Anal. calcd for $C_{28}H_{39}N_2BF_4$: C, 68.57; H, 8.02; N, 5.71. Found: C, 68.49; H, 8.11; N, 5.62; MS (DCI, NH_3): m/z=403 (100%) [$M^{\oplus}$].

4.4. Synthesis of dicationic pentamethinium salts

Linear dications are obtained by action of the hemicarboxonium salt on the diamine in 2:1 stoichiometry.

A solution of 0.24 mmol of free or complexed diamine in 50 mL of dry acetonitrile is added dropwise on 0.49 mmol of hemicarboxonium salt. The mixture is left 24 h. under magnetic stirring, and becomes yellow. After evaporation of the solvent, the product is washed with pentane, and purified by precipitation in a mixture EtOH/hexane (2:1), washed by Et_2O/hexane and dried under vacuum at 40°C.

4.4.1. 10m: 5-(1′,3′-Diaminopropane)-1-bisdiethylamino-1,5-bis(4-methylphenyl)penta-2,4-dienylium diperchlorate. Yield=35%; yellow powder; mp=134°C; IR (KBr pellet) ν cm^{-1}: 1085 (Cl–O); UV (CH_2Cl_2): λ_{max1}= 456 nm; ϵ_1=113 450 mol^{-1} L cm^{-1}, λ_{max2}=436 nm; ϵ_2= 89 000 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ ppm, J Hz: 1.05 and 1.40 (2t, 12H, CH_3–CH_2, J=6.7 Hz); 2.10 (m, 2H, CH_2–CH_2–CH_2); 2.31 and 2.34 (2s, 6H, C$H_3C_6H_4$); 3.20 (q, 4H, N–CH_2–CH_3); 3.66 (m, 8H, N–CH_2–CH_3 and N–CH_2–CH_2–; 6.00–6.53 (3H, H_2, H_3, H_4, syst. AMX, $J_{H_3H_4}$=12.8 Hz $J_{H_2H_3}$=13.0); 6.94–7.24 (m, 16H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 12.5 and 14.3 (CH_3–CH_2); 21.3 and 21.4 ($CH_3C_6H_4$); 27.2 (CH_2–CH_2–CH_2); 42.7 (N–CH_2–CH_2); 46.1 and 49.4 (CH_3–CH_2–N); 102.2 (C_4); 107.8 (C_2); 129.1–142.4 (C_6H_4); 163.0 (C_3); 168.9 (C_5); 171.7 (C_1); Anal. calcd for C_{49} H_{62} N_4 Cl_2O_8: C, 64.96; H, 6.90; N, 6.18. Found: C, 63.90; H, 7.02; N, 6.67; MS (FAB>O, MNBA): m/z=805 (22%) [$M^{2\oplus}$+ClO_4^-]$^{\oplus}$; m/z=705 (100%) [$M^{2\oplus}$−$H^{\oplus}$]$^{\oplus}$.

4.4.2. 10q: Bis(ethylamino)-2,2′-(ethylendioxy)bis-(1-diethylamino)-1,5-bis(4-methylphenyl) penta-2,4-dienylium diperchlorate. Yield=40%; yellow powder; mp= 158°C; IR (KBr pellet) ν cm^{-1}: 1091 and 624 (Cl–O); 3308 (N–H); UV (CH_2Cl_2): λ_{max}=443 nm; ϵ_{max}=137 900 mol^{-1} L cm^{-1}; ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.07 and 1.35 (two t, 12H, CH_3–CH_2, J=6.9 Hz; 2.32 and 2.33 (2s, 12H, C$H_3C_6H_4$); 3.25 (q, 4H, CH_3–CH_2–N, J=6.9 Hz); 3.59 (s, O–CH_2–CH_2–O) 3.44–3.78 (m, 12H, CH_3–CH_2–N+N–CH_2–CH_2–O); 5.97–6.59 (3H, H_2, H_3, H_4, syst. AMX, $J_{H_2H_3}$=13.0 Hz, $J_{H_3H_4}$=12.8 Hz); 6.97–7.23 (m, 16H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 12.8 and 14.3 (CH_3–CH_2); 21.4 and 21.5 ($CH_3C_6H_5$); 45.2 (N–CH_2–CH_2–O); 46.1 (CH_3–CH_2–N); 49.4 (CH_3–CH_2–N); 68.7 (O–CH_2–CH_2–N); 71.0 (O(CH_2)$_2$O); 102.3 (C_4); 107.7 (C_2); 129.0–142.4 (C_6H_4); 163.0 (C_3); 169.1; (C_5); 171.7 (C_1); Anal. calcd for $C_{52}H_{68}N_4Cl_2O_{10}$: C, 63.73; H, 6.99; N, 5.72. Found: C, 62.77; H, 7.08; N, 5.76; MS (FAB>O, MNBA): m/z=879 (71%) [$M^{2\oplus}$+ClO_4^-]$^{\oplus}$; m/z=779 (100%) [$M^{2\oplus}$−$H^{\oplus}$]$^{\oplus}$.

4.4.3. 11q: Bis(ethylamino)-2,2′-(ethylenedioxy)bis(1-diethylamino)-1,5-bis(4-methoxy-phenyl)penta-2,4-dienylium perchlorate. Yield=38%; orange powder; mp=154°C; IR (KBr pellet) ν cm^{-1}: 1091 and 624 (Cl–O); 3308 (N–H); UV (CH_2Cl_2): λ_{max}=447 nm; ϵ= 155 950 mol^{-1} L cm^{-1}; Anal. calcd for $C_{52}H_{68}N_4Cl_2O_{14}$: C, 59.82; H, 6.57; N, 5.37. Found: C, 58.88; H, 6.45; N, 5.33; MS (FAB>O, MNBA): m/z=943 (60%) [$M^{2\oplus}$+ ClO_4^-]$^{\oplus}$; m/z=843 (100%) [$M^{2\oplus}$−$H^{\oplus}$]$^{\oplus}$.

4.4.4. Synthesis of the 2,2′-(ethylenedioxy)bis(ethylamine)/calcium perchlorate complex. Equimolar amounts (10 mmol) of 2,2′-(ethylenedioxy)-bis(ethylamine) and hexahydrated calcium perchlorate are dissolved in

methanol. The complex is filtered off, washed with benzene, and dried under vacuum.

Yellow powder; IR (KBr pellet) ν cm^{-1}: 1070 and 625 (Cl–O); ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 2.11 (s, 4H, NH_2); 2.89 (t, 4H, (O–CH_2–CH_2N)); 3.63 (t, 4H, (O–CH_2–CH_2N)); 3.71 (s, 4H, O–CH_2–CH_2O); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 41.5 (NCH_2); 70.2 (N–CH_2–CH_2–O); 72.3 (O–CH_2–CH_2O).

4.5. Macrocyclic dications

A solution of 0.98 mmol of diamine in 50 mL of dry acetonitrile is added dropwise to the same amount of carboxonium salt. The product is washed several times with pentane, purified by precipitation in a mixture EtOH/hexane, washed by a mixture Et_2O/hexane and dried under vacuum at 40°C.

4.5.1. 1m: Bis(1,5-diaminopropane-1,5-diphenyl)penta-2,4-dienylium diperchlorate. Yield=45%; orange crystals; mp=202°C; IR (KBr pellet) ν cm^{-1}: 1091 and 624 (Cl–O); 3288 (N–H); ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 2.18 (m, 4H, HN–CH_2–CH_2–CH_2–NH); 3.50 (m, 8H, CH_2–NH); 6.75 (d, 4H, H_2–H_4, syst. A_2X, J=14.0 Hz); 7.23 (t, 2H, H_3, syst. A_2X, J=14.0 Hz); 7.25–7.47 (m, 20H, C_6H_5); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 29.3 (–NH–CH_2–CH_2–CH_2–NH–); 42.2 (NH–CH_2–CH_2); 104.4 (C_2–C_4); 129.8–134.4 (C_6H_5); 162.8 (C_3); 170.2 (C_1–C_5); Anal. calcd for $C_{40}H_{42}N_4Cl_2O_8$: C, 61.78; H, 5.44; N, 7.20. Found: C, 62.16; H, 5.86; N, 7.16; MS (FAB>O, glycerol): m/z=677 (10%) $[M^{2\oplus}+ClO_4^-]^{\oplus}$; m/z=577 (100%) $[M^{2\oplus}-H^{\oplus}]^{\oplus}$.

4.5.2. 1n: Bis(1,5-diaminohexane-1,5-diphenyl)penta-2,4-dienylium diperchlorate. Yield=47%; orange crystals, mp=180°C; IR (KBr pellet) ν cm^{-1}: 1091 and 624 (Cl–O); 3288 (N–H); ^1H NMR (200 MHz, DMSO) δ ppm, J Hz: 1.49–1.72 (m, 16H, HN–CH_2–(CH_2)$_4$–CH_2–NH); 3.49 (m, 8H, CH_2–NH); 6.34 (d, 4H, H_2–H_4, syst. A_2X, J=13.0 Hz); 6.93 (t, 2H, H_3, syst. A_2X, J=13.0 Hz); 7.31–7.48 (m, 20H, C_6H_5); ^{13}C NMR (50.32 MHz, DMSO) δ ppm: 25.8 (NH–(CH_2)$_2$–CH_2); 27.9 (NH–CH_2–CH_2–CH_2); 44.1 (NH–CH_2–CH_2); 102.6 (C_2–C_4); 128.3–135.6 (C_6H_5); 159.6(C_3); 167.9 (C_1–C_5); Anal. calcd for $C_{46}H_{54}N_4Cl_2O_8$: C, 64.11; H, 6.32; N, 6.50. Found: C, 63.96; H, 6.32; N, 6.25; MS (FAB>O, glycerol): m/z=761 (100%) $[M^{2\oplus}+ClO_4^-]^{\oplus}$; m/z=661 (45%) $[M^{2\oplus}-H^{\oplus}]^{\oplus}$; m/z=331 (29%) $[M^{2\oplus}/2]^{\oplus}$.

4.5.3. 1o: Bis(1,5-diaminooctane-1,5-diphenyl)penta-2,4-dienylium diperchlorate. Yield=55%; orange crystals; mp=170°C; IR (KBr pellet) ν cm^{-1}: 3291 (N–H); 1093 (Cl–O); UV (CH_2Cl_2): λ_{max}=436 nm; ϵ=135 200 mol^{-1} L cm^{-1}; ^1H NMR(200 MHz, CD_3CN) δ ppm, J Hz: 1.39 (m, 16H, –(CH_2)$_4$–); 1.71 (m, 8H, CH_2–CH_2–NH); 3.48 (m, 8H, CH_2–NH); 6.25(d, 4H, H_2–H_4, syst. A_2X, J=13.0 Hz); 7.12 (t, 2H, H_3, syst. A_2X, J=13.0 Hz); 7.34–7.46 (m, 20H, C_6H_5); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 27.4–29.7 (CH_2)$_6$); 45.6 (CH_2–NH); 103.8 (C_2–C_4); 129.6–134.8 (C_6H_5); 162.7 (C_3); 170.3 (C_1–C_5); Anal. calcd for $C_{50}H_{62}N_4Cl_2O_8$: C, 65.42; H, 6.81; N, 6.10. Found: C, 64.87; H, 6.96; N, 5.83; MS (FAB>O, MNBA): m/z=817 (87%) $[M^{2\oplus}+ClO_4^-]^{\oplus}$; m=717 (100%) $[M^{2\oplus}-H^{\oplus}]^{\oplus}$; m=359 (13%) $[M^{2\oplus}/2]^{\oplus}$.

4.5.4. 2o: Bis(1,5-diaminooctane-1,5-di(4-methylphenyl)-penta-2,4-dienylium diperchlorate. Yield=47%; orange crystals; mp=191°C (decomposition); IR (KBr pellet) ν cm^{-1}: 3288 (N–H); 1097 (Cl–O); UV (CH_2Cl_2): λ_{max}=438 nm; ϵ=103 700 mol^{-1} L cm^{-1}. Anal. calcd for $C_{54}H_{70}N_4Cl_2O_8$: C, 66.59; H, 7.24; N, 5.75. Found: C, 65.88; H, 7.24; N, 5.25; MS (FAB>O, MNBA): m/z=873 (100%) $[M^{2\oplus}+ClO_4^-]^{\oplus}$; m/z=773 (95%) $[M^{2\oplus}-H^{\oplus}]^{\oplus}$; m/z=387 (72%) $[M^{2\oplus}/2]^{\oplus}$.

4.5.5. 1p: Bis(1,5-diaminononane-1,5-diphenyl)penta-2,4-dienylium diperchlorate. Yield=35%; orange crystals; mp=121°C; IR (KBr pellet) ν cm^{-1}: 3283 (N–H); 1100 (Cl–O); UV (CH_2Cl_2): λ_{max}=432 nm; ϵ=134 380 mol^{-1} L cm^{-1}); ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 1.41–1.74 (m, 28H, (CH_2)$_7$), 3.48 (m, 8H, CH_2–NH); 6.24 (d, 4H, H_2–H_4, syst. A_2X, J=13.0 Hz); 7.07 (t, 2H, H_3, syst. A_2X, J=13.0 Hz); 7.30–7.50 (m, 20H, C_6H_5); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 27.5–30.2 (CH_2)$_7$); 45.5 (CH_2–NH); 103.8 (C_2–C_4); 129.6–134.8 (C_6H_5); 162.7 (C_3); 170.3 (C_1–C_5); Anal. calcd for $C_{52}H_{66}N_4Cl_2O_8$: C, 66.02; H, 7.03; N, 5.92. Found: C, 65.19; H, 7.22; N, 6.00; MS (FAB>O, MNBA): m/z=845 (60%) $[M^{2\oplus}+ClO_4^-]^{\oplus}$; m/z=745 (100%) $[M^{2\oplus}-H^{\oplus}]^{\oplus}$; m/z=373 (35%) $[M^{2\oplus}/2]^{\oplus}$.

4.5.6. 2q: Bis-1,5-(bis(ethylamino)-2,2′-(ethylendioxy)-bis(1-diethylamino)(4-methylphenyl)-penta-2,4-dienylium diperchlorate. Yield=30%; orange crystals; mp=118°C (decomposition); IR (KBr pellet) ν cm^{-1}: 3288 (N–H); 1097 (Cl–O); ^1H NMR (200 MHz, CD_3CN) δ ppm, J Hz: 2.32 and 2.34 (2s, 6H, CH_3–C_6H_4); 3.43–3.69 (m, 24H, (CH_2)$_2$O(CH_2)$_2$O(CH_2)$_2$); 6.16 (d, 4H, H_2–H_4, syst. A_2X, J=13.0 Hz); 7.06 (t, 2H, H_3, syst. A_2X, J=13.0 Hz); 7.19–7.34 (m, 16H, C_6H_4); ^{13}C NMR (50.32 MHz, CD_3CN) δ ppm: 21.5 (CH_3–C_6H_4); 45.5 (CH_2–NH); 68.7 (HN–CH_2–CH_2–O); 71.1 (O–(CH2)$_2$–O); 104.0 (C_2–C_4); 130.3–142.9 (C_6H_4); 163.2 (C_3); 170.7 (C_1–C_5); Anal. calcd for $C_{50}H_{62}N_4Cl_2O_{12}$: C, 61.16; H, 6.36; N, 5.71. Found: C, 60.19; H, 6.29; N, 5.11; MS (FAB>O, MNBA): m/z=881 (27%) $[M^{2\oplus}+ClO_4^-]^{\oplus}$; m/z=781 (100%) $[M^{2\oplus}-H^{\oplus}]^{\oplus}$; m/z=391 (3%) $[M^{2\oplus}/2]^{\oplus}$.

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