Synthesis and Electronic Properties of Tetrakis[4-(pyrimidyl)phenyl]methanes – A Novel Class of Electronically Active Nanometer-Sized Scaffolds

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Tetrakis[4-(arylpyrimidyl)phenyl]methanes **4** can be readily synthesized by using a highly convergent vinamidinium salt cyclocondensation strategy. The conjugated side-chains of these novel nanostructures display interesting cooperative electronic features such as intramolecular exciplex coupling and ECEC redox processes in the cathodic region.

Introduction

Three-dimensional highly symmetrical building blocks with flexible substitution patterns have aroused a considerable interest for the design of nanometer-sized molecular materials.[1] Therefore, a tetrahedral core unit with suitable functionality at the vertices is an attractive starting point for the construction of diamond-like rigid-rod molecular architectures, as well as dendrimers with spherical topologies.[2] Additionally, the tetrahedral geometry opens numerous opportunities for the fabrication of organic crystals and materials such as organic glasses, with tailor-made crystallinity and thus improved solid-state properties.[3] Among the structural motifs with tetrahedral symmetry, tetraarylmethanes are of particular interest.[4] The sp^3-hybridized center links four substituents with extended π-systems in the sense of a homoconjugation, simultaneous mutual orthogonality, and high degeneracy of the molecular orbitals of the conjugated chains.[5] Although in the past, quite a number of tetrakis(oligophenylene)methane tetrahedra have been synthesized,[4a] electron-deficient heteroaromatic branches on the tetrahedral scaffold have not been known so far. In particular, substituents incorporating pyrimidine units could display interesting electronic and electrochemical behavior. As part of our program initiated to develop straightforward synthetic approaches to novel oligo(diazaphenylene) nanostructures[6] for application as NLO (*n*on-*l*inear *o*ptical) materials and organic LEDs (*l*ight-*e*mitting *d*iode) we have now focused on tetrahedral structural motifs with pyrimidyl substituents, based upon the tetraphenylmethane core. Here we wish to communicate the synthesis and first investigations of the electronic properties (absorption and emission spectra, cyclic voltammetry) of tetrakis[4-(pyrimidyl)phenyl]methanes.

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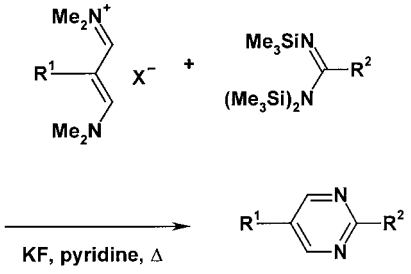
Results and Discussion

Recently, we reported on a general approach to homologous series of diazaphenylene oligomers applying a repetitive sequence of pyrimidine syntheses.[6b] The key step in this convergent strategy to diaza-analogous oligophenylenes is the cyclocondensation of vinamidinium salts with persilylated amidines in the presence of potassium fluoride (Scheme 1).



Scheme 1

Following this synthetic concept, quite a number of pyrimidine-based donor-acceptor substituted NLO chromophores, intensively blue light emitting fluorophores, and electroluminophores with a higher electron affinity than the corresponding oligophenylenes and PPV [poly(*p*-phenylenevinylene)] are now readily available.[6b] Thus, for the construction of three-dimensional tetrahedral architectures such as tetrakis[4-(pyrimidyl)phenyl]methanes, tetrakis(4-cyanophenyl)methane (**1**) appears to be a suitable starting material. Therefore, our synthesis commences with the addition of an excess of lithium hexamethyldisilazane (LiHMDS) to the tetranitrile **1** in THF (Scheme 2). After a reaction time of seven days and a change of solvents, the tetraamidine anions are trapped with trimethylsilyl chloride, and after filtration of the lithium salts and removal of the solvent, the persilylated tetraamidine **2** is isolated. Now the stage is set for the fourfold pyrimidine cyclocondensation. A solution of **2** in pyridine is treated at 90 °C with various 2-substituted vinamidinium salts **3** in the presence of potas-

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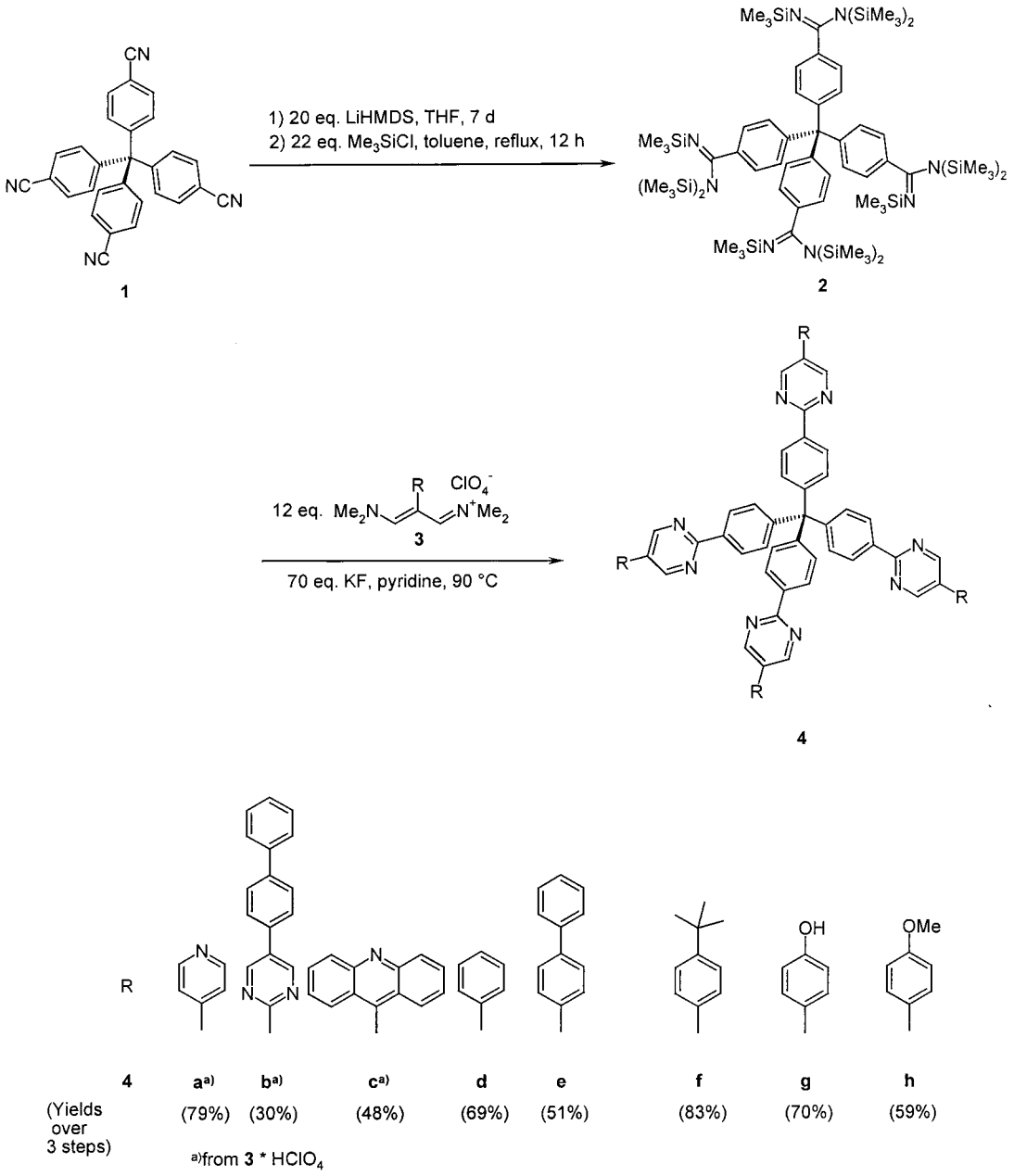
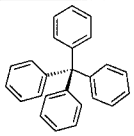
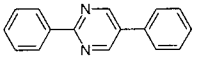
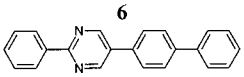


Scheme 2

sium fluoride, to furnish the tetrakis[4-(2-pyrimidyl)phenyl]-methanes **4** in moderate to good yields as beige to yellow microcrystals or powders.

The molecular structure of the tetrahedral frameworks **4** is strongly supported by the appearance of the significant molecular peak in the EI or FAB mass spectra of **4**, and the correct elemental analyses. Expectedly, and in accordance with the tetrahedral symmetry in the proton and carbon NMR spectra, only one set of signals was found for the four magnetically and chemically equivalent oligo(diazaphenylene) branches. According to MM2 calculations[7] the distances of the vertices range from 2.1 (**4a**) to 3.4 nm (**4b**), and classify these novel tetrahedral molecules as nanometer-sized entities. In the UV/Vis spectra (Table 1) these novel tetraheteroarylmethanes display interesting features. In comparison to the single-branch models **6** and **7**, most systems displayed a modest red-shift of the longest wavelength absorption band, with only a small observed substituent effect. However, in the case of the donor-substituted frameworks **4g** and **4h**, the bathochromic shift is almost 20 nm. There are two further exceptions, the spectrum of the tetraacridyl compound **4c**, which is strongly dominated by the lowest energy absorption of the acridyl substituent at 362 nm (acridine absorbs at 357 nm in acetonitrile),[8] and the longest wavelength band of the biphenyl-substituted compound **4e**, which is shifted hypsochromically by

Table 1. Absorption and emission maxima in solution (recorded in DMSO at 20 °C) and in solid state (emission maxima), Stokes shifts, and reduction potentials (cyclic voltammetry, DMSO) of **4**, **5**, **6**, **7** and **15**

	λ_{max} [nm] Absorption in solution	λ_{max} [nm] Emission in solution	λ_{max} [nm] Emission in solid state	Stokes shift[a] $\Delta\tilde{\nu}$ [cm^{-1}]	Reduction potentials [V]
 **5**	272	332	335	6700	–
 **6**	290	392	–	9000	–
 **7**	308	431	–	9300	–1.94[b] –2.33[c]
4a	304	373	414 (sh) 451 479	6100	–
4b	–	–	–	–	–
4c[d]	254 295 362	435	513	4600	–1.134[e] –0.718[f] –1.497[g]
4d	307	374	416 445 476	5900	–
4e	276	385 406 (sh)	389 405	10200	–
4f	308	373	413 477	5700	–1.245[e] –0.594[f]
4g	319	415	417 451 480 510	7200	–
4h	322	394	396 445	5700	–
15	301	422	457 479	9500	–

[a] Difference of the longest wavelength maxima [cm^{-1}] in solution. – [b] Reversible one-electron reduction. – [c] Irreversible one-electron oxidation. – [d] Recorded in $CHCl_3$. – [e] E_p^{red}, quasi-reversible two-electron reduction. – [f] E_p^{ox}, quasi-reversible two-electron oxidation. – [g] Reversible one-electron reduction of an acridine.

almost 30 nm. Presumably, this peculiar behavior can be attributed to the extremely low solubility of **4e** in common organic solvents, and therefore π-stacking effects seem to cause the formation of *H*-aggregates.[22] Regarding the solvent, fluorescence spectra of all compounds show significant Stokes shifts between 4600 and 10200 cm^{-1}. With the exception of compound **4e**, the magnitudes of the Stokes shifts are more similar to that of tetraphenylmethane (**5**) than to the reference compounds **6** and **7**. Expectedly, the structures **4a**, **4d**, and **4f** do not show any substituent effect for the emission maxima, and appear at about 374 nm. A hypsochromic shift of the emission maximum relative to the reference compound **6**, can be interpreted as a cooperative effect of the adjacent chromophore branches, i.e. an intramolecular exciplex.[9] By comparison, the emission maxima of the two donor-substituted systems **4g** and **4h** are shifted bathochromically with respect to the model chromophore **6**. However, for the solid-state emission spectra in all cases, besides the maxima already observable in solution spectra, several red-shifted bands appear, indicating a strong contribution of excimer fluorescence as a consequence of intermolecular electronic interactions in the crystal lattice.[10]

Interestingly, the reduction potentials in the cyclic voltammograms (Table 1, Figure 1) of the sufficiently soluble structures **4c** and **4f** also support a strong intramolecular electronic coupling of the conjugated branches. In comparison to the reference compound **7** ($E_0^{0/-1} = -1.94$ V; $E_0^{-1/-2} = -2.33$ V) the tetrakis[4-(4-aryl-2-pyrimidyl)phenyl]methanes **4c** and **4f** are reduced at considerably lower potentials (**4c**: $E_0^{0/-2} = -1.134$ V; **4f**: $E_0^{0/-2} = -1.245$V). Although the current ratio i_p^c/i_p^a is almost unity for both compounds, the anodic and cathodic peak separations rather large for a scan rate of 100 mV/s [**4c**: $\Delta(E_p^{ox} - E_p^{red}) = 0.416$ V; **4f**: $\Delta(E_p^{ox} - E_p^{red}) = 0.651$ V]. This electrochemical cycle can therefore be considered as a quasi-reversible two-electron reduction (**4c**: $i_p^c = -1.134$ V; **4f**: $i_p^c = -1.245$V) followed by chemical reaction that can be reversed after a two-electron oxidation (**4c**: $E_p^{ox} = -0.718$ V;

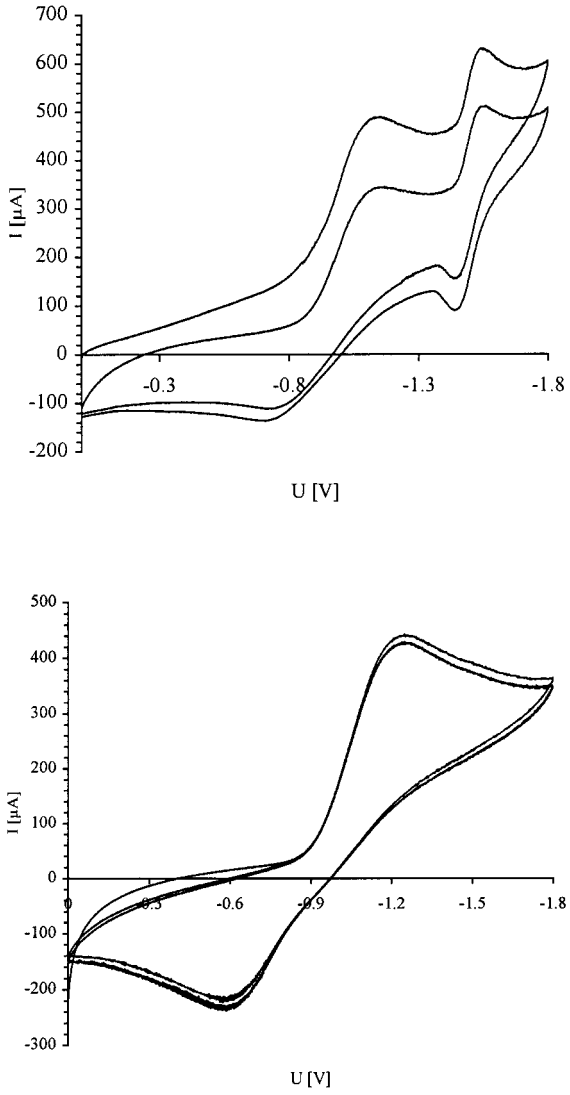


Figure 1. Cyclic voltammograms of **4c** (top) and **4f** (bottom) in the cathodic region (DMSO, 20 °C, scan rate 100 mV/s, supporting electrolyte nBu$_4$N$^+$PF$_6^-$)

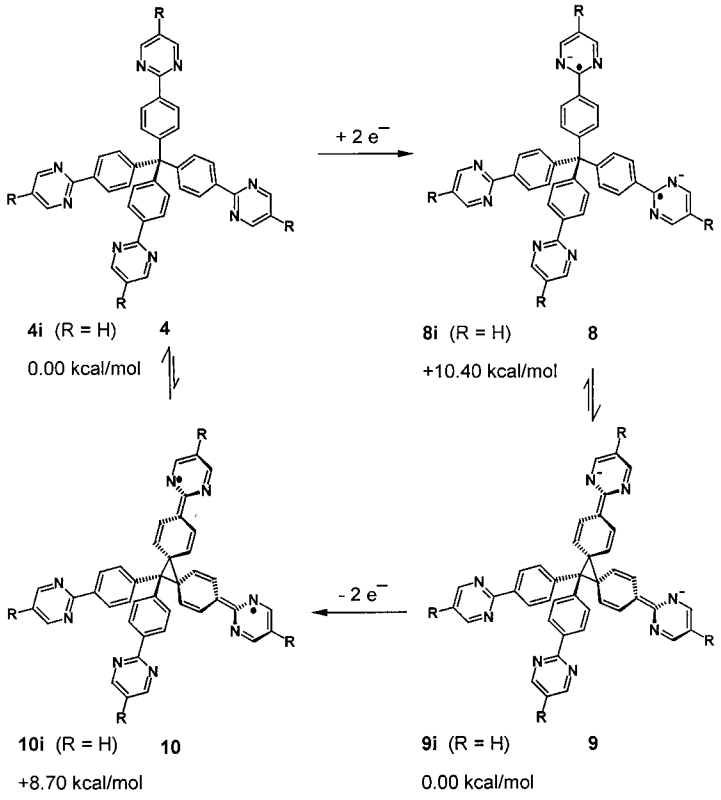
4f: $E_p^{ox} = -0.594$ V), i.e., an ECEC process.[11] Additionally, for **4c** a reversible one-electron reduction of one acridyl fragment can be found at a potential of $E_0^{-2/-3} = -1.497$ V. Since the quasi-reversible appearance of the cyclic voltammograms does not change at higher scan rates (v = 250, 500, and 1000 mV/s) a fast chemical reaction with a large equilibrium constant, e.g., an intramolecular cyclization is very likely. Diarylmethanes have been known to display a significant anchimeric stabilization of radical anions,[12] and oxidative cyclizations have also been promoted electrochemically.[13] However, in the case of spiro-annellated methanofullerenes, electrochemically induced cyclopropane ring opening reactions have been observed.[14] According to semiempirical calculations on the PM3 level of theory[7] performed for the tetrakis[4-(2-pyrimidyl)phenyl]methane (**4i**; R = H) and several reduced and isomeric species (**8i**, **9i**, and **10i**), the spin density in the *ortho* and *para* positions with respect to the pyrimidyl substituents are significantly higher, and a diradical ring closure to give a cyclopropane is very likely. The redox cycle can be thus be rationalized as follows (Scheme 3). A diradical cyclization of the diradical dianion **8i**, arising from two independent one-electron reductions, gives the bispirocyclic dianion **9i** (favored by $\Delta G = -10.4$ kcal/mol). Likewise, after the two independent one-electron oxidations, the bispirocyclic diradical **10i** is disfavored in comparison to isomer **4i** by $\Delta G = +8.7$ kcal/mol, and hence, to complete the redox cycle, **10** ring-opens the cyclopropane to give the tetraheteroarylmethane **4**.

Furthermore, the pyrimidine synthesis strategy also allows an access to the regioisomeric tetrakis[4-(2-aryl-5-pyrimidyl)phenyl]methane series. Friedel–Crafts acylation (Scheme 4) of tetraphenylmethane (**5**) gives, almost quantitatively, the tetraacetylated compound **11**. This tetrakis(acetophenone) is treated with sulfur and morpholine under the conditions of a Willgerodt–Kindler reaction[15] to furnish the tetrakis(thioamide) **12** in good yield. After an alkaline thioamide hydrolysis, the tetrakis(phenylacetic acid) **13** is obtained as a colorless powder. Under the conditions of a Vilsmeier–Haack–Arnold reaction,[16] and after an anion metathesis, the tetrakis(vinamidinium salt) **14** is isolated in good yields as beige crystals. Finally, **14** is cyclo-condensed with benzamidinium hydrochloride in pyridine at 90 °C to give tetrakis[4-(2-phenyl-4-pyrimidyl)phenyl]methane (**15**), the regioisomer of **4d**, in 80% yield as a gray powder.

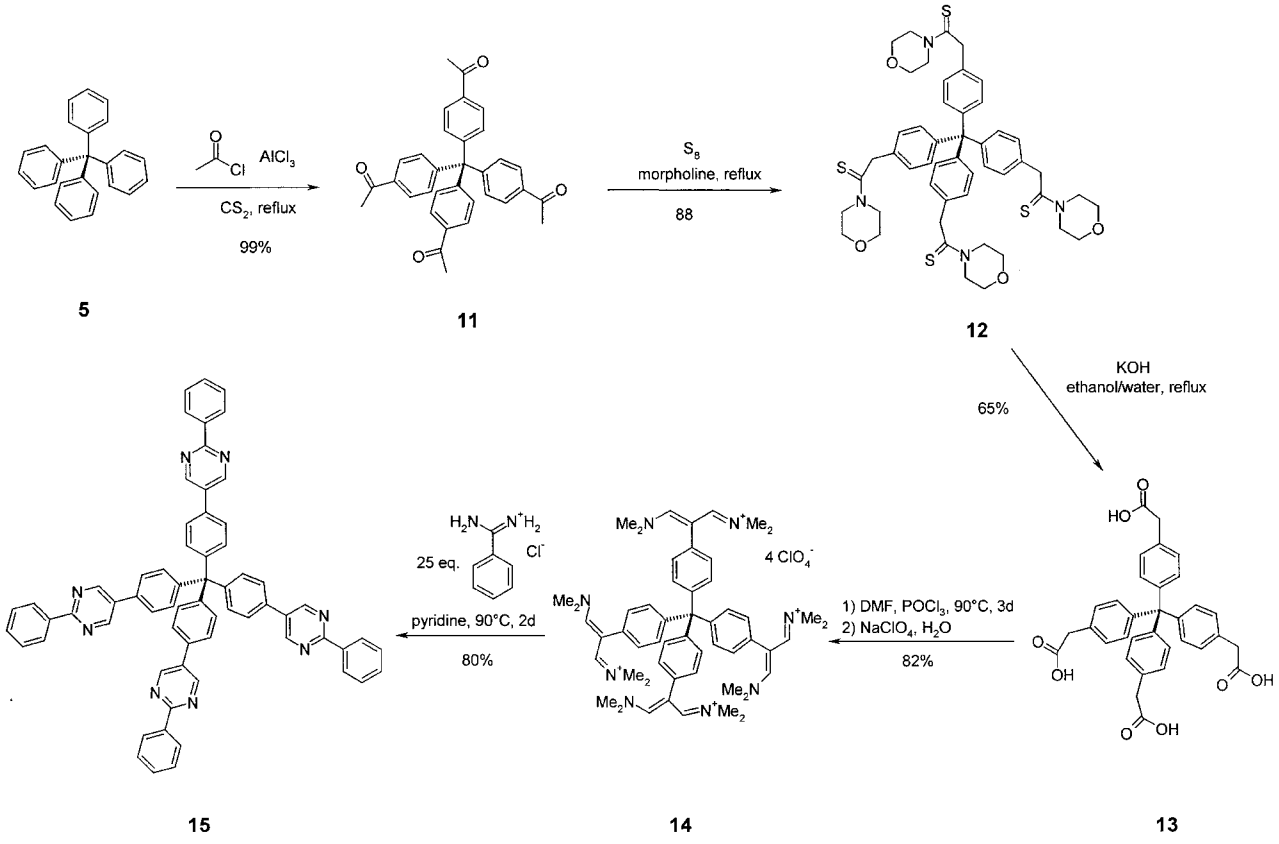
Although, the compound **15** displays almost the same electronic absorption behavior as the regioisomer **4d** it significantly deviates with respect to the emission properties (Table 1). The Stokes shift for **15** ($\Delta\tilde{\nu} = 9500$ cm^{-1}) is almost twice as large as for most systems of **4**. Again, the emission in the solid state shows a significant bathochromic shift and can be attributed to strong excimer coupling among individual tetrahedra in the crystal lattice.[10]

Conclusion

With an efficient pyrimidine synthesis in hand we have been able to construct nanometer-sized molecules with tetrahedral symmetry in a rapid, straightforward, and highly convergent fashion. First investigations of the absorption and emission behavior reveal a strong intra- and intermolecular (in the solid state) coupling between the individual branches of the tetrahedra. Most peculiar, however, is the cooperative reduction behavior according to cyclic voltammetry, where a quasi-reversible redox cycle indicates an electrochemically mediated bispirocyclization that can be performed repeatedly in several cycles. These interesting cooperative electronic effects make tetrakis[4-(arylheteroaryl)phenyl]methanes very promising candidates for electronic manipulations of nanometer-sized molecules both in bulk and as individual entities by scanning probe microscopy. Syntheses and investigations of other tetraarylmethanes with further chromo- and electrophores are currently under way.



Scheme 3



Scheme 4

Experimental Section

Reagents and solvents were purchased reagent-grade and used without further purification. Toluene and THF were dried and distilled according to standard procedures.[17] Tetrakis(4-cyanophenyl)-methane (**1**)[18] and the vinamidinium salts **3a**,[19] **3b**−**f**,[20] **3g**,[21] and **3h**[20] were prepared according to literature procedures. − Column chromatography: Silica gel 60 (Merck, Darmstadt), mesh 70−230. TLC: Silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Reichert-Jung Thermovar. − ^{1}H and ^{13}C NMR spectra: Bruker ARX 300, Varian VXR 400S [D_6]DMSO. The assignments of quaternary C, CH, CH_2, and CH_3 have been made by using DEPT spectra. − IR: Perkin−Elmer Lambda 3. − UV/Vis: Beckman DK-2-A, Beckman UV 5240 and Perkin−Elmer Models Lambda 16. − Fluorescence spectra: Perkin−Elmer LS 50 B (irradiation at approximately 20 nm less in energy than the longest wavelength absorption maximum). − MS: Finnigan MAT 90 and MAT 95 Q. − Elemental analysis were carried out in the Microanalytical Laboratory of the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

Electrochemistry: Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed DMSO at room temperature and at scan rates of 100, 250, 500, and 1000 mV·s^{-1}. The electrolyte was 0.10 M Bu_4NPF_6. The working electrode was a 1-mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. The potential of Fc/Fc$^+$ was determined in DMSO ($E_{1/2}$ = 320 mV).

Synthesis of the Tetrakis[4-(4-aryl-2-pyrimidyl)phenyl]methanes 4. − General Procedure: A mixture of tetrakis(4-cyanophenyl)methane[18] (**1**) (1 equiv.) and lithium hexamethyldisilazane (LiHMDS) (20 equiv.) in 50 mL of dry THF was stirred for 7 d at room temperature under nitrogen. The solvent was then removed in vacuum and replaced by 50 mL of dry toluene. After chlorotrimethylsilane (22 equiv.) was added, the mixture was heated to reflux temperature for 12 h under nitrogen. After cooling under a continuous stream of nitrogen, the formed precipitate was filtered by suction. From the filtrate the solvent was removed in vacuo and the residue was dissolved in 50 mL of pyridine. To that solution the vinamidinium salt **3** (24 equiv.) and potassium fluoride (68 equiv.) were added subsequently, and the mixture was stirred at 90 °C for 18 h. After cooling to room temperature, the reaction mixture was poured into 600 mL of 2 N hydrochloric acid. The precipitate was filtered by suction and was washed successively with water and methanol. Finally, this residue was recrystallized from a suitable solvent to give the pure compound **4**. The experimental details are summarized in Table 2.

Tetrakis(2′,6′,4′′-triaza-1,1′:4′,1′′-terphenyl-4-yl)methane (4a): Beige needles, m.p. > 250 °C (DMSO). − ^{1}H NMR (300 MHz, [D]TFA): δ = 7.91 (d, ^3J = 9 Hz, 8 H), 8.63 (d, ^3J = 9 Hz, 8 H), 8.71 (d, ^3J = 7 Hz, 8 H), 9.14 (d, ^3J = 7 Hz, 8 H), 9.92 (s, 8 H). − ^{13}C NMR (75 MHz, [D]TFA): δ = 69.1 ($C_{quat.}$), 128.2 (CH), 129.8 ($C_{quat.}$), 130.5 ($C_{quat.}$), 132.5 (CH), 134.4 (CH), 144.9 (CH), 151.8 ($C_{quat.}$), 154.5 ($C_{quat.}$), 159.1 (CH), 162.7 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 940 (27) [M$^+$], 810 (13) [$(C_{15}H_{10}N_3)_3CC_6H_4CN^+$], 708 (100) [$(C_{15}H_{10}N_3)_3C^+$], 578 (35) [$(C_{15}H_{10}N_3)_2CC_6H_4CN^+$], 475 (60) [$C_{31}H_{19}N_6^+$]. − IR (KBr): $\tilde{\nu}$ = 3032 cm^{-1}, 1597, 1582, 1432, 820, 791. − UV/Vis (DMSO): λ_{max} = 304 nm. − $C_{61}H_{40}N_{12}$ (941.1): calcd. C 77.85, H 4.28, N 17.86; found C 77.69, H 4.24, N 17.89.

Tetrakis(2′,6′,2′′,6′′-tetraaza-1,1′:4′,1′′:4′′,1′′′:4′′′, 1′′′′-quinquephenyl-4-yl)methane (4b): Beige powder, m.p. > 250 °C (nitrobenzene). − ^{1}H NMR (300 MHz, [D]TFA): δ = 7.42 (t, ^3J = 7 Hz, 4 H), 7.50 (t, ^3J = 7 Hz, 8 H), 7.71 (d, ^3J = 7 Hz,), 7.92−7.97 (m, 24 H), 8.68 (d, ^3J = 8 Hz, 8 H), 9.63 (s, 8 H), 10.31 (s, 8 H). − ^{13}C NMR (75 MHz, [D]TFA): δ = the quaternary aliphatic carbon resonance was not detected, 128.9 (CH), 129.3 ($C_{quat.}$), 129.5 (2 signals, CH, $C_{quat.}$), 130.5 (2 signals, CH, $C_{quat.}$), 130.7 (CH), 131.0 (CH), 132.4 (CH), 134.4 (CH), 139.3 ($C_{quat.}$), 141.4 ($C_{quat.}$), 147.3 ($C_{quat.}$), 154.4 ($C_{quat.}$), 154.5 ($C_{quat.}$), 157.7 (CH), 159.6 (CH), 162.6 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 1553 (25) [M$^+$], 1475 (5) [M$^+$ − Ph], 1270 (9) [$(C_{26}H_{17}N_4)_3CC_6H_4CN^+$], 1168 (78) [$(C_{26}H_{17}N_4)_3C^+$], 386 (90) [$C_{26}H_{18}N_4^+$], 178 (100) [$PhC_6H_4C{\equiv}CH^+$]. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 1574, 1411, 839, 805. − $C_{105}H_{68}N_{16}$ (1553.8): calcd. C 81.17, H 4.41, N 14.42; found C 80.89, H 4.34, N 14.29.

Tetrakis-[5′-(9-acridyl)-2′,6′-diaza-1,1′:4′-biphenyl-4-yl]-methane (4c): Yellow needles, m.p. > 250 °C (chloroform/diethyl ether). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (dd, ^3J = 9 Hz), 7.71 (d, ^3J = 9 Hz, 8 H), 7.78 (d, ^3J = 9 Hz, 8 H), 7.89 (dd, ^3J = 9 Hz, 8 H), 8.45 (d, ^3J = 9 Hz, 8 H), 8.65 (d, ^3J = 9 Hz, 8 H), 8.98 (s, 8 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = the quaternary aliphatic carbon resonance was not detected, 125.3 (CH), 125.5 (CH), 127.1 (CH), 127.3 ($C_{quat.}$), 128.2 (CH), 129.2 ($C_{quat.}$), 131.1 (2 signals, CH, $C_{quat.}$), 131.7 (CH), 135.3 ($C_{quat.}$), 147.6 ($C_{quat.}$), 149.4 ($C_{quat.}$), 158.2 (CH), 164.6 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 1341 (33) [M$^+$], 1110 (3) [$(C_{23}H_{14}N_3)_3CC_6H_4CN^+$], 1008 (100) [$(C_{23}H_{14}N_3)_3C^+$], 778 (11) [$(C_{23}H_{14}N_3)_2CC_6H_4CN^+$], 675 (25) [$C_{45}H_{27}N_6^+$], 670 (25) [M^{2+}], 504 (15) [$(C_{23}H_{14}N_3)_3C^{2+}$, $C_{23}H_{14}N_3^+$]. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 254 nm (370700), 295 (83800), 362 (48300). − $C_{93}H_{56}N_{12}$ (1341.6): calcd. C 83.26, H 4.21, N 12.53; found C 83.02, H 4.11, N 12.40.

Table 2. Experimental details for the synthesis of the compounds **4**

Tetranitrile **1**[18] g (mmol)	LiHMDS g (mmol)	TMSCl mL (mmol)	Vinamidinium salt **3** g (mmol)	KF g (mmol)	Yield of **4** g (%)
0.42 (1.0)	3.4 (20)	2.8 (22)	6.0 (22) of **3a**[19]	4.0 (70)	0.74 (79) of **4a**
0.42 (1.0)	3.4 (20)	2.8 (22)	7.3 (12) of **3b**[20]	4.0 (70)	0.47 (30) of **4b**[a]
0.42 (1.00)	3.4 (20)	2.8 (22)	6.5 (12) of **3c**[20]	4.0 (70)	0.64 (48) of **4c**
0.35 (0.83)	2.79 (16.7)	2.31 (18.3)	4.54 (15.0) of **3d**[20]	2.83 (48.8)	0.55 (69) of **4d**
0.30 (0.71)	2.39 (14.3)	1.98 (15.6)	5.68 (15.0) of **3e**[20]	2.82 (48.6)	0.45 (51) of **4e**
0.35 (0.83)	2.79 (16.7)	2.31 (18.3)	5.38 (15.0) of **3f**[20]	2.83 (48.8)	0.80 (83) of **4f**
1.00 (2.38)	8.00 (47.81)	6.70 (52.96)	17.50 (55.96) of **3g**[21]	9.40 (162)	1.67 (70) of **4g**[b]
0.35 (0.83)	2.79 (16.7)	2.31 (18.3)	4.99 (15.0) of **3h**[20]	2.83 (48.8)	0.54 (59) of **4h**

[a] After several extractions with boiling acetonitrile. − [b] The crude mixture was dissolved in 2 N sodium hydroxide and reprecipitated with 2 N hydrochloric acid before recrystallization.

Tetrakis(2′,6′-diaza-1,1′:4′,1′′-terphenyl-4-yl)methane (4d): Beige needles, m.p. > 300 °C (1,2,4-trichloro benzene). − ^{1}H NMR (300 MHz, [D]TFA): δ = 7.6−8.5 (m, br, 36 H), 9.6 (s, 8 H). − MS (FAB); *m/z*: 937 [M$^+$]. − IR (KBr): ṽ = 1581 cm^{-1}, 1428, 792. − UV/Vis (DMSO): λ_{max} = 315 nm. − $C_{65}H_{44}N_8$·1/6$C_6H_3Cl_3$ (967.4): calcd. C 81.95, H 4.64, N 11.58; found C 81.97, H 4.50, N 11.88.

Tetrakis(2′,6′-diaza-1,1′:4′,1′′:4′′,1′′′-quaterphenyl-4-yl)-methane (4e): Colorless needles, m.p. > 350 °C (1,2,4-trichlorobenzene). − ^{1}H NMR (300 MHz, [D]TFA/D_2SO_4): δ = 7.5−8.0 (m, br, 52 H), 9.6 (s, 8 H). − IR (KBr): ṽ = 1582 cm^{-1}, 1431, 835, 794, 792. − UV/Vis (DMSO): λ_{max} = 276 nm. − $C_{89}H_{60}N_8$ (1241.5): calcd. C 86.10, H 4.87, N 9.03; found C 86.05, H 4.76, N 9.11.

Tetrakis(4′′-*tert*-butyl-2′,6′-diaza-1,1′:4′,1′′-terphenyl-4-yl)-methane (4f): Beige needles, m.p. > 300 °C (toluene/methyl cyclohexane). − ^{1}H NMR (300 MHz, [D]TFA): δ = 1.44 (s, 36 H), 7.7−8.5 (m, br, 32 H), 9.6 (s, 8 H). − MS (FAB); *m/z*: 1161 [M$^+$], 873 [M$^+$ − $C_{20}H_{19}N_2$]. − IR (KBr): ṽ = 1583 cm^{-1}, 1431, 831, 791. − UV/Vis (DMSO): λ_{max} (ε) = 308 nm (87800). − $C_{81}H_{76}N_8$ (1161.6): calcd. C 83.76, H 6.60, N 9.65; found C 84.12, H 6.61, N 9.56.

Tetrakis(4′′-hydroxy-2′,6′-diaza-1,1′:4′,1′′-terphenyl-4-yl)-methane (4g): Beige powder, m.p. > 300 °C. − ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 6.94 (d, ^3J = 8.4 Hz, 8 H), 7.51 (d, ^3J = 8.4 Hz, 8 H), 7.69 (d, ^3J = 8.3 Hz, 8 H), 8.60 (d, ^3J = 8.3 Hz, 8 H), 9.16 (s, 8 H), 9.88 (s, 4 H, OH). − ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 69.1 ($C_{quat.}$), 116.1 (CH), 124.1 ($C_{quat.}$), 127.2 (CH), 127.8 (CH), 130.7 (2 signals, CH, $C_{quat.}$), 134.9 ($C_{quat.}$), 148.2 ($C_{quat.}$), 154.1 (CH), 158.3 ($C_{quat.}$), 160.7 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 1000 (29) [M$^+$], 753 (100) [($C_{16}H_{11}N_2O$)$_3C^+$], 505 (22) [$C_{33}H_{21}N_4O_2^+$]. − IR (KBr): ṽ = 3430 cm^{-1}, 1610, 1431, 832. − UV/Vis (DMSO): λ_{max} (ε) = 319 nm (96500). − $C_{65}H_{44}N_8O_4$ (1001.1): calcd. C 77.99, H 4.43, N 11.19; found C 80.13, H 4.38, N 10.99.

Tetrakis(4′′-methoxy-2′,6′-diaza-1,1′:4′,1′′-terphenyl-4-yl)-methane (4h): Beige needles, m.p. > 300 °C (toluene/methylcyclohexane). − ^{1}H NMR (300 MHz, [D]TFA): δ = 4.07 (s, 12 H), 7.30 (d, ^3J = 8.8 Hz, 8 H), 7.81 (d, ^3J = 8.8 Hz, 8 H), 7.83 (d, ^3J = 8.8 Hz, 8 H), 8.47 (d, ^3J = 8.8 Hz, 8 H), 9.53 (s, 8 H). − MS (FAB); *m/z*: 1057 [M$^+$]. − IR (KBr): ṽ = 1609 cm^{-1}, 1431, 1252, 1181, 829, 794. − UV/Vis (DMSO): λ_{max} = 326 nm. − $C_{69}H_{52}N_8O_4$·1/2C_2H_6SO (1096.3): calcd. C 76.69, H 5.06, N 10.22; found C 76.61, H 4.87, N 10.24.

Tetrakis(4-acetylphenyl)methane (11): To a mixture of 3.20 g (10.0 mmol) of tetraphenylmethane (**5**), 4.00 g (51.0 mmol) of acetyl chloride and 50 mL of carbon disulfide was added 6.70 g (50.3 mmol) of aluminium chloride, and the mixture heated to reflux temperature for 18 h. After cooling, the carbon disulfide was decanted and ice, concentrated hydrochloric acid, and dichloromethane were added subsequently to the precipitate. The mixture was stirred until the precipitate completely dissolved. Then the organic layer was dried with sodium sulfate and the solvents were removed in vacuo. The residue was purified by chromatography on silica gel (acetone/petroleum ether) to give 4.82 g (99%) of **11** as a colorless powder. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.58 (s, 12 H), 7.34 (d, ^3J = 8.6 Hz, 8 H), 7.88 (d, ^3J = 8.6 Hz, 8 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.6 (CH_3), 65.6 ($C_{quat.}$), 128.2 (CH), 130.9 (CH), 135.5 ($C_{quat.}$), 150.1 ($C_{quat.}$), 197.4 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 488 (62) [M$^+$], 446 (14) [M$^+$ − C_2H_2O], 369 (100) [M$^+$ − $C_6H_4COCH_3$]. − IR (KBr): ṽ = 2922 cm^{-1}, 1684, 1601, 1270, 824. −$C_{33}H_{28}O_4$ (488.6): calcd. C 81.13, H 5.78; found C 81.20, H 5.81.

Tetrakis(4-{[(morpholino)thiocarbonyl]methyl}phenyl)-methane (12): A mixture of 4.88 g (10.0 mmol) of **11**, 2.57 g (80.0 mmol) of sulfur, and 6.97 g (80.0 mmol) of morpholine was heated to reflux temperature for 18 h (135 °C oil bath). After cooling, dioxane was added to the reaction mixture and the resulting solution was poured into water. The yellow precipitate was collected by suction and dried to give 7.85 g (88%) of **12** as a yellow powder that was used without further purification for the next step. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.24 (s, 8 H), 3.64−3.90 (m, 16 H), 4.32−4.36 (m, 16 H), 7.02−7.22 (m, 16 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.90 (CH_2), 50.13 (CH_2), 50.83 (CH_2), 63.87 ($C_{quat.}$), 66.06 (CH_2), 66.64 (CH_2), 127.01 (CH), 131.41 (CH), 133.71 ($C_{quat.}$), 145.20 ($C_{quat.}$), 199.72 ($C_{quat.}$).

Tetrakis[4-(carboxymethyl)phenyl]methane (13): A mixture crude **12** (7.85 g, 8.79 mmol), 32 g (57 mmol) of potassium hydroxide pellets, 32 mL of water, and 50 mL of ethanol was heated to reflux temperature for 16 h. Then the ethanol was removed by distillation. The resulting reaction mixture was filtered and 2 N hydrochloric acid was added to the filtrate. A precipitate was formed and collected by suction. This solid was twice reprecipitated by dissolving in 2 N aqueous sodium hydroxide solution and adding 2 N hydrochloric acid. Finally, the residue was extracted with water in a Soxhlet extractor. The extract was acidified with concentrated hydrochloric acid. The precipitate was collected by suction and dried under high vacuum for several days to give 3.60 g (65%) of **13** as a colorless powder, m.p. > 250 °C (dec.). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.51 (s, 8 H, CH_2), 7.11 (d, ^3J = 8.5 Hz, 8 H), 7.18 (d, ^3J = 8.5 Hz, 8 H). − ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 40.0 (CH_2), 63.4 ($C_{quat.}$), 128.7 (CH), 130.1 (CH), 132.4 ($C_{quat.}$), 144.8 ($C_{quat.}$), 172.5 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 552 (10) [M$^+$], 417 (100) [M$^+$ − $C_6H_4CH_2CO_2$ H]. − IR (KBr): ṽ = 3430 cm^{-1}, 3027, 1709, 1610, 1507, 1413, 1235, 801. − $C_{33}H_{28}O_8$ (552.6): calcd. C 71.73, H 5.11; found C 71.48, H 5.00.

Tetrakis(iminium) Salt 14: Phosphoryl chloride (1.53 g, 10.0 mmol) was added dropwise under external cooling (ice/water bath) to 0.88 g (12 mmol) of *N*,*N*-dimethylformamide under nitrogen. After stirring for 2 h at room temperature, 0.55 g (1.0 mmol) of **13** was added and the reaction mixture was stirred and heated to 90 °C for 3 d until the evolution of gas had ceased. After cooling to room temperature, ice/water was added and a saturated aqueous solution of sodium perchlorate was added to the reaction mixture. The precipitate was collected by suction and dried under high vacuum to give 1.0 g (82%) of **14** as a beige powder. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 24 H), 3.24 (s, 24 H), 7.23−7.32 (m, 16 H), 7.70 (s, 8 H). − ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 40.1 (CH_3), 49.4 (CH_3), 64.0 ($C_{quat.}$), 104.3 ($C_{quat.}$), 129.9 (CH), 130.4 ($C_{quat.}$), 131.8 (CH), 146.6 ($C_{quat.}$), 162.9 (CH).

Tetrakis(3′,5′-diaza-1,1′:4′,1′′-terphenyl-4-yl)methane (15): A mixture of 0.24 g (0.20 mmol) of **14**, 1.00 g (5.43 mmol) of benzamidine hydrochloride and 15 mL of pyridine were stirred at 90 °C for 2 d. After cooling, the mixture was poured into 2 N hydrochloric acid. The precipitate was collected by suction and recrystallized from methanol/dioxane to give 0.15 g (80%) of **15** as a gray powder, m.p. > 250 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49−7.66 (m, 28 H), 8.48 (d, ^3J = 7 Hz, 8 H), 9.06 (s, 8 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 64.4 ($C_{quat.}$), 126.29 (CH), 128.15 (CH), 128.70 (CH), 130.87 (2 signals, CH, $C_{quat.}$), 131.92 (CH), 132.65 ($C_{quat.}$), 137.14 ($C_{quat.}$), 146.61 ($C_{quat.}$), 155.11 (CH), 163.57 ($C_{quat.}$). − MS (70 eV); *m/z* (%): 936 (26) [M$^+$], 705 (1000) [(Ph−$C_4H_2N_2$−C_6H_4)$_3C^+$]. − IR (KBr): ṽ = 1583 cm^{-1}, 1432, 828, 748. − UV/Vis (DMSO): λ_{max} (ε) = 301 nm (112700). −

$C_{65}H_{44}N_8$ (937.1): calcd. C 83.31, H 4.73, N 11.96; found C 83.11, H 4.58, N 11.88.

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