The First Synthesis and Electronic Properties of Tetrakis[(hetero)phenanthrenyl]methanes

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Dedicated to Prof. Dr. Wolfgang Beck on the occasion of his 70th birthday

Keywords: Cyclic voltammetry / Cyclization / Heck reaction / Heterocycles / Photolysis / Redox chemistry

The tetrakis[(hetero)phenanthryl]methanes **9** have been synthesized from tetrakis(*p*-iodophenyl)methane (**1**) in a two-step sequence consisting of a Heck aryl vinylation to give the tetrakis[β-(aryl)-*p*-styryl]methanes **3** and subsequent oxidative photocyclization. The absorption and emission spectra of the stilbene derivatives **3** showed significant electronic coupling of the four branches both in the ground and in the excited states. According to cyclic voltammetry, the electron-rich dimethylamino (**3c**) and the electroneutral thienyl systems (**3d**) displayed a rapid, cooperative oxidative fragmentation that could be partially suppressed at high scan rates. In the ferrocenyl systems (**3g**), the organometallic fragments were oxidized simultaneously without notable mutual electronic communication. For the tetrakis[(hetero)phenanthryl]methanes **9**, both UV/Vis and fluorescence spectroscopy showed significant bathochromic shifts as a consequence of pronounced intramolecular coupling between the four chromophores. In a multicycle cyclic voltammetry experiment, the naphthothienyl derivative **9c** was electropolymerized to give a thin, multicolored, transparent film on the anode.

Introduction

A tetrahedral core with suitable functionality at its vertices is an attractive starting point for the construction of nanometer-sized molecular materials:[1] in particular, diamond-like rigid-rod molecular architectures and dendrimers with spherical topologies.[2] As well as the numerous opportunities offered by the tetrahedral geometry, the fabrication of organic crystals with tailor-made crystallinity and improved solid-state properties, such as organic glasses, has also become an important issue.[3] Among 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 homoconjugation, simultaneous mutual orthogonality, and high degeneracy of the molecular orbitals of the conjugated chains.[5] Although quite a number of functionalized tetrakis(arylene)methane tetrahedra with organometallic,[6] porphyrin,[4d,7] pyrimidyl,[8] and oxadiazole[9] substitution at their peripheries have been prepared in recent years, the class of condensed and annealed (hetero)aromatic systems directly linked to the sp^3-hybridized center has so far remained unknown. In particular, four phenanthrenyl or naphthoheteroaryl substituents brought together in close proximity might display interesting emission and/or electrochemical behavior. As part of our program directed towards exploration of the synthesis and electronic properties of novel tetraarylmethanes with electro- and fluorophores,[8,10] we have also focussed on sterically loaded systems. Here we wish to report the first synthesis of tetrakis[(hetero)phenanthryl]methanes and the first investigations of their electronic properties (absorption and emission spectra, cyclic voltammetry).

Results and Discussion

Phenanthrenes are highly fluorescent compounds with enormous Stokes shifts (the wavenumber difference between the longest wavelength absorption band and the emission maximum). Retrosynthetically, oxidative photocyclization of stilbenes represents the most promising access to phenanthrenes (Scheme 1).[11] Stilbenes can, in turn, readily be prepared by Heck reactions, starting from aryl halides and vinyl arenes. In particular, the fourfold Heck coupling of tetrakis(*p*-halophenyl)methane with styrenes has recently been reported.[4b,4c,4g,12]

Our synthesis of tetrakis[(hetero)phenanthryl]methanes therefore began with the fourfold Heck vinylation of tetra-

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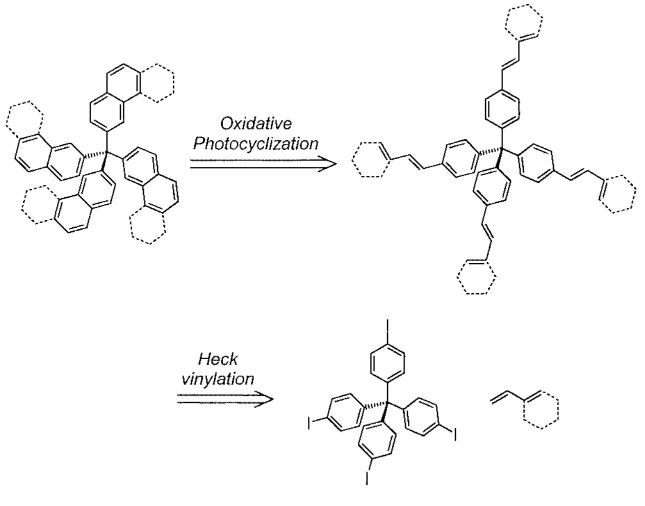
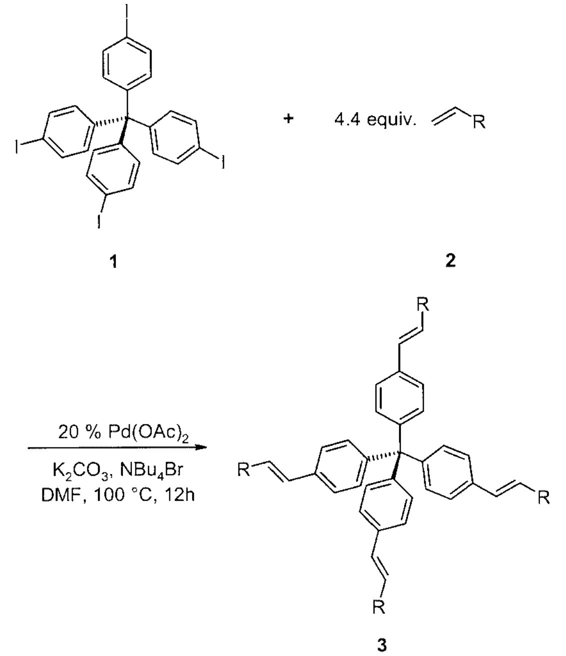


Scheme 1. Retrosynthetic analysis of tetrakis(phenanthrenyl)methanes



3a R = Ph[12b]

3b R = p-C$_6$H$_4$CH$_3$ (40 %)

3c R = p-C$_6$H$_4$N(CH$_3$)$_2$ (47 %)

3d R = 2-thienyl (27 %)

3e R = 1-naphthyl (75 %)

3f R = 2-naphthyl (38 %)

3g R = ferrocenyl (73 %)

Scheme 2. Synthesis of tetrakis[β-(aryl)-*p*-styryl]methanes **3**

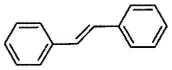
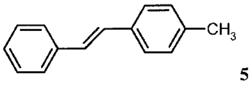
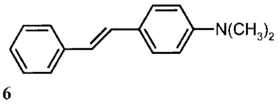
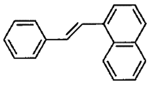
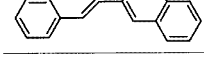
kis(*p*-iodophenyl)methane[12c] (**1**) with styrene (**2a**),[12b] *p*-methylstyrene (**2b**), *p*-dimethylaminostyrene (**2c**), 2-vinylthiophene (**2d**), 1-vinylnaphthalene (**2e**), 2-vinylnaphthalene (**2f**), and vinylferrocene (**2g**) to give (after recrystallization of the crude products) the analytically pure tetrakis[β-(aryl)-*p*-styryl]methanes **3** in moderate to good yields as colorless to yellow needles (**3a−d**, **3f**), as a colorless resin (**3e**), or as an orange powder (**3g**) (Scheme 2). Although the yields of the crude tetravinylated products **3** were relatively high, recrystallization of some of the less soluble tetrahedral molecules substantially reduced the yields of the analytically pure materials.

With the exceptions of those of the naphthyl derivatives **3e** and **3f**, the ^{1}H and ^{13}C NMR spectra of the stilbenoid derivatives **3** were reasonably well resolved, with the appearance of single sets of resonances for the magnetically and chemically equivalent stilbenoid branches strongly supporting their tetrahedral structures. The diagnostic *trans* couplings of the vicinal protons on the double bonds (^{3}J = 16−16.5 Hz) in the ^{1}H NMR spectra unambiguously attested to the *all-E* configurations of the stilbene substituents. As a consequence of the close proximity of the four conjugated branches, the inner *p*-phenylene protons (AA′BB′ splitting pattern) were shielded, their resonances appearing at δ = 7.2−7.4 and δ = 7.4−7.6 ppm, largely independently of the solvent used for recording the spectra. According to the ^{13}C NMR spectra, the outer-sphere 2-styryl substitution pattern had only a small electronic influence on the inner carbon resonances [i.e., the central quaternary carbon atom (δ = 64.8−64.9 ppm) and the adjacent *ipso*-position (δ = 145.3−145.6 ppm)] in the ground state. The molecular structures were also strongly supported by correct combustion analyses and the significant presence of the molecular peaks in the EI mass spectra. With the exceptions of the donor-substituted compounds **3c** and **3g**, in which the molecular peaks were more intense, the basis peaks of the tetrakis[β-(aryl)-*p*-styryl]methanes were [(hetero)arylstyryl]C^{+} ions, due to the pronounced stability of tri(aryl)carbenium ions.

Closer inspection of the electronic spectra (absorption and emission) revealed some peculiar properties of the tetrakis[β-(aryl)-*p*-styryl]methanes **3** (Table 1). (The ferrocenyl system did not show any significant fluorescence and is omitted in the discussion.) In comparison to those of models taken for a single branch, such as stilbene (**4**),[13,14] 4-methylstilbene (**5**),[15,16] 4-dimethylaminostilbene (**6**),[16,17] 1-styrylnaphthalene (**7**),[18,19] and 2-styrylnaphthalene (**8**),[19,20] the absorption maxima of the longest-wavelength transitions of **3** were red-shifted by $\Delta\tilde{\nu}$ = 700−1400 cm^{-1}. However, the naphthyl-substituted systems ($\Delta\tilde{\nu}$ = 700−800 cm^{-1}) showed distinctly smaller bathochromic shifts than the stilbene analogues ($\Delta\tilde{\nu}$ = 1300−1400 cm^{-1}). This behavior can be interpreted in terms of significant electronic interaction between the branches in the ground state. The fluorescence behavior attributable to the structural properties of the excited electronic states, though, clearly showed a strong dependence on the substitution pattern. Although the Stokes shifts of tetrakis(stilbenoid)methanes **3** were relatively large, encompassing $\Delta\tilde{\nu}$ = 3900−4700 cm^{-1}, they were clearly larger than those of the branch models **4** and

5 only for the tetrakis(stilbenyl)- (**3a**) and tetrakis(4-methylstilbenyl)methanes (**3b**). For the dimethylamino-substituted tetrahedral system **3c**, the Stokes shift was identical to that of the stilbene **6**, whereas the Stokes shifts for the two naphthyl compounds **3e** and **3f** were considerably smaller than those of the models **7** and **8**. In addition, the emission spectra of the thienyl (**3d**) and the naphthyl derivatives (**3e**, **3f**) displayed longer-wavelength bands that could not be detected for the branch models **7** or **8**, indicating a substantial and more complex fluorophore interaction, presumably as a consequence of intramolecular exciplex formation. Interestingly, a change in the Stokes shift upon permanent arrangement of four stilbenoid chromophores in close tetrahedral proximity can be regarded as a probe of enhanced or diminished electronic coupling of the branches in the excited state. This suggested the conclusion that the less extended the π-electron system in the stilbenoid unit, the more pronounced the positive electronic coupling and intramolecular chromophore-chromophore interaction in the excited state.

Table 1. Absorption and emission maxima and Stokes shifts in solution (recorded in $CHCl_3$ at 20 °C) of **3**

	λ_{max} [nm] Absorption	λ_{max} [nm] Emission	Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}]
3a	322[12b]	379[12b]	4700
3b		366sh	
	325	382	4600
	338sh		
3c	364	431	4300
3d		387sh	
	338	398	4500
	353sh	425	
3e	334	389	4200
		407	
3f	333	383	3900
		398	
 **4**	309[13]	349[14]	3700
 **5**	311 (MeOH)[15]	349 (MeOH)[16]	3500
 **6**	346[17]	407 (Et_2O)[16]	4300
 **7**	325 (AcCN)[18]	390 (AcCN)[19]	5100
 **8**	325 (AcCN)[20]	380 (AcCN)[19]	4500

Electrochemical data for the oxidation of compounds **3** by cyclic voltammetry were only obtained for the compounds **3c**, **3d**, and **3g**, in the anodic region up to 1.5 V. At low scan rates ($v = 100$ mVs^{-1}), the tetrakis(*p*-dimethylaminostilbenyl)methane (**3c**) showed an irreversible oxidation at a potential of $E_p^{ox} = 0.6$ V (see a in Figure 1) to give a radical cation species that was consumed by an irreversible intramolecular bispirocyclization with a subsequent fragmentation of the tetraarylmethane framework. This behavior was similar to that seen in the case of tetrakis(dimethylaminophenyl)methane,[10] in which dicationic specimens with significantly anodically shifted oxidation potentials were formed, adsorbing or reacting at the electrode. At higher scan rates ($v = 1000$ mVs^{-1}, see b in Figure 1), however, this consumption of the radical cation intermediates was partially suppressed, and the evolution of a quasireversible redox process indicated a cooperative intramolecular electronic interaction between the electrophore branches. Although the oxidation was accomplished at a relatively low oxidation potential, this radical cation system was only persistent for reversible ECEC processes at fairly fast electron transfer rates from and to the anode. The highly delocalized radical ion, with a significant spin density at the inner *ipso* carbon atom of the *para*-phenylene substituent, has a pronounced propensity to cyclize, with concomitant fragmentation of the tetraarylmethane framework. Assuming a product development control of the subsequent chemical reactions the dimethylaminophenyl substituents are potent donors to stabilize triaryl or diaryl methylium cations, both constituents of important classes of colorants.

An analogous irreversible oxidative process at a potential of $E_p^{ox} = 1.2$ V could be observed in the case of the thienyl derivative **3d** (Figure 2). Here, oxidative thienyl coupling at the 2-positions could be ruled out, since the peak currents of the oxidation decreased with every cycle and there was no indication of a new cathodically shifted reversible oxidation event as a consequence of bithienyl formation. Therefore, as in the case of **3c**, oxidative fragmentation of the tetrahedral framework was also favored. If a significant spin density at the inner *para*-phenyl carbon atom is again taken into account, as exemplified for the SOMO of the styryl thiophene radical cation as a model,[21] this rapid intramolecular process can also be interpreted (Figure 3). Because of the diminished stability of the radical cationic specimen, this oxidative degradation could not be suppressed even at higher scan rates.

Finally, our interest focussed on an easily oxidizable electrophore that would also guarantee pronounced charge and spin localization. The vinyl ferrocenyl-substituted tetraphenylmethane **3g** showed only one fully reversible multielectron oxidation at a potential $E_{rev}^{0/+4} = 0.43$ V, slightly shifted cathodically with respect to ferrocene ($E_{rev}^{0/+1} = 0.45$ V),[22] as a consequence of the +M effect of the stilbenyl substitution (Figure 4). Since there were no further oxidation waves up to a potential of 1.5 V, the current ratio (i_p^c/i_p^a) was almost unity, and the anodic and cathodic peak potential separation $\Delta(E_p^{ox} - E_p^{red})$ was significantly below 60 mV upon extrapolation to a scan rate of 0 mV/s, it can be assumed that all ferrocenyl fragments were oxidized simultaneously to the corresponding ferrocenium species. The spin density at the inner *para*-phenylene *ipso* carbon atoms

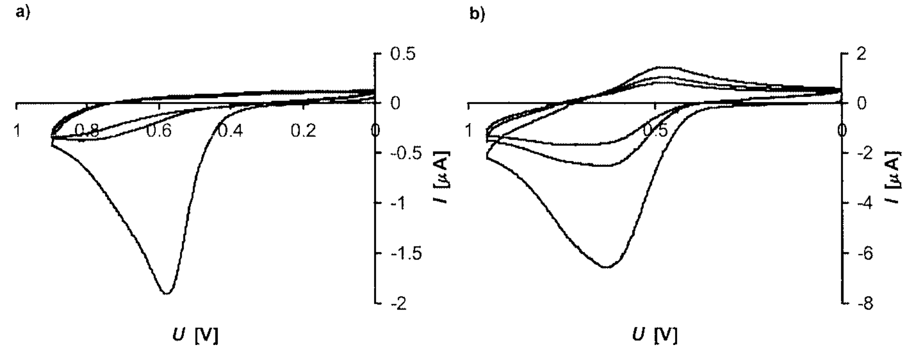


Figure 1. Cyclic voltammograms of **3c** in the anodic region at scan rates of a) 100 mV/s and b) 1000 mV/s (CH_2Cl_2, 20 °C, Pt disk electrode, reference electrode Ag/AgCl, supporting electrolyte: $NnBu_4^+PF_6^-$)

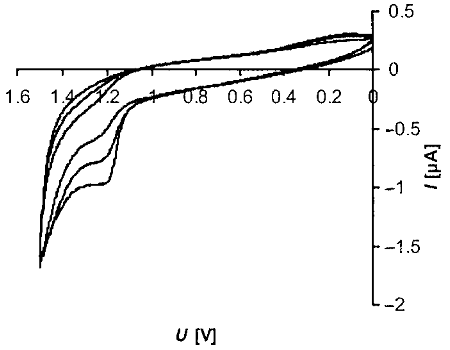


Figure 2. Cyclic voltammogram of **3d** in the anodic region (CH_2Cl_2, 20 °C, Pt disk electrode, reference electrode Ag/AgCl, scan rate = 100 mV/s, supporting electrolyte: $NnBu_4^+PF_6^-$)

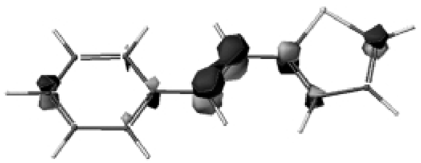


Figure 3. SOMO of the styrylthiophene radical cation

therefore had to be negligently small, and so the intramolecular electronic communication of the styryl ferrocenyl electrophore branches was not detectable.

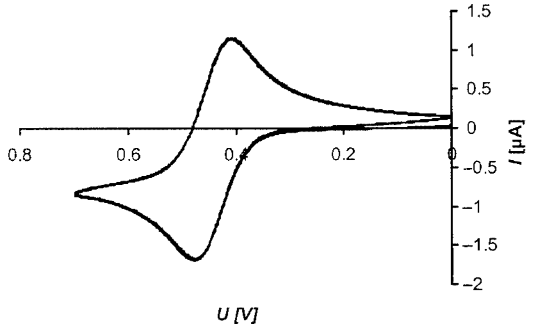
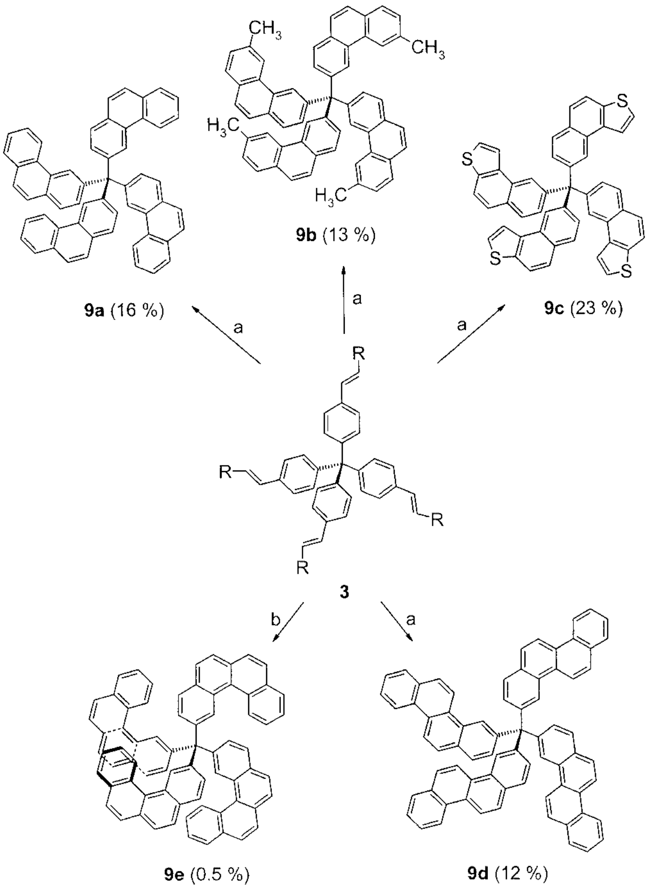


Figure 4. Cyclic voltammogram of **3g** in the anodic region (CH_2Cl_2, 20 °C, Pt disk electrode, reference electrode Ag/AgCl, scan rate = 100 mV/s, supporting electrolyte: $NnBu_4^+PF_6^-$)

From these cyclic voltammetric studies with these three electron-rich tetrakis(arylstyryl)methanes, electronic communication, either in the sense of a fragmentation or of quasireversible behavior, depended not only on the spatial separation of the oxidizable substituent, but also to a large extent on delocalization as a consequence of the spin density at the inner *para*-phenylene *ipso* carbon centers. In the case of **3g**, the spin density was largely localized on the stable ferrocenium substituents, whereas in the cases of **3c** and **3d** the oxidation of one (or multiple) branch(es) furnished a fully delocalized radical ion that was able to participate in intramolecular communication processes and ultimately in subsequent chemical reactions, such as degradation.

With the tetrastilbenoid systems **3** in hand, the stage was now set for a fourfold oxidative photocyclization. Thus, hot toluene solutions of compounds **3a**, **3b**, **3d**, **3e**, and **3f** were rapidly cooled to room temperature and subsequently irradiated in the presence of catalytic amounts of iodine and with constant saturation of the solutions with air. After chromatography, this furnished the photodehydrocyclization products 9 in 0.5 to 23% yields, as colorless to beige powders (Scheme 3). The choice of toluene as solvent for these oxidative photocyclization proved to be favorable, since the large excess of toluene resulted in the formation of considerable amounts of benzyl alcohol, benzaldehyde, benzoic acid, diphenylethane, and diphenylethanol, all of these being toluene photooxidation products. As a consequence, possible photooxidations and -degradations of the just formed tetrakis[(hetero)phenanthryl]methanes **9** were at least to some extent suppressed. The highest yield in these experiments (23%) was achieved on irradiation of the thienyl derivative **3d** to furnish the tetrakis(naphthothien-8-yl)methane (**9c**), which is also the first reported compound with four identical heterocycles linked by one carbon atom.

Attempted oxidative photocyclizations of the dimethylamino derivative **3c** and the ferrocenyl compound **3g** failed and resulted only in intractable and unidentified products. For **3c**, the $n-\pi^*$ transition was lower in energy than the desired π-π^*-excitation, causing a high quantum yield for intersystem crossing in the excited state from S_1 to T_1.



Scheme 3. Synthesis of tetrakis[(hetero)phenanthryl]methanes **9** [a] hν, I_2/O_2, toluene, room temp., 12 h. [b] hν, O_2, toluene, room temp., 12 h.

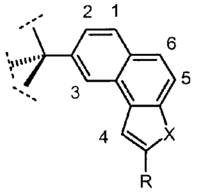
Photocyclizations, however, occur only from the first excited singlet state and not from the triplet state.[11c,11f] Similarly, for **3g**, metal-to-ligand charge-transfer transitions and an enhanced spin-orbit coupling due to iron as a heavy element both also resulted in increased intersystem crossing and, thus, in no population of the required S_1 state.

All the photodehydrocyclization products **9** were soluble in chloroform, and the tetrahedral symmetries of the tetrakis(phenanthrenyl)methane derivatives **9a−d** could readily be deduced from the appearance of single sets of resonances for the magnetically and chemically equivalent tri- and tetracyclic branches in their well resolved ^{1}H and ^{13}C NMR spectra. The derivative **9e** was obtained only in a small quantity, and was therefore characterized only by mass spectrometry (vide infra). With the aid of H,H-COSY and C,H-COSY experiments, the structures and connectivities were unambiguously assigned, establishing the phenanthrenyl framework. Most characteristically, as a consequence of anisotropic deshielding and van der Waals radii compression,[23] the inner protons in the ^{1}H NMR spectra at position 3 in the "bay region"[24] appeared at low field, between $\delta = 8.53$ and 9.15 ppm (Table 2). Protons of this type, experiencing a deshielding ring current, were also found in the chrysenyl derivative **9d**, as a consequence of the S-shaped π-perimeter. In the ^{13}C NMR spectra the resonances for the central quaternary aliphatic cores could be found between $\delta = 64.4$ and 66.7 ppm, indicating transposition of substituent effects from the various outer shells through the conjugated π-systems to the centers of the molecules.

In addition, the molecular structures of compounds **9** were strongly supported by correct combustion analyses and characteristic fragmentation patterns in their EI mass spectra (Table 3). The molecular peaks were followed by the basis peaks representing $[(\text{hetero})\text{phenanthrenyl}]_3C^+$ ions, less intensive signals from the di(hetero)aryl carbenium radical cations, and finally the cyclized fluorenylium-type ions. Comparisons of the found and calculated isotope distributions for the molecular peaks (Table 4) revealed the efficiency of the oxidative photocyclization event. There was no indication that the products **9** contained any contamination by partially hydrogenated compounds, which should cause significant increases in the $M^+ + 2$ and $M^+ + 4$ signal intensities.

For the photodehydrocyclization of **3f**, the constitution was deduced through comparison with the photochemical behavior of the single branch model, 2-styryl naphthalene (**10**).[11c] Starting from the *E*-configured compound **10-*E***, irradiation caused a *trans-cis* isomerization of the double bond to give the *Z*-configured isomer **11-*Z***. In principle, there were two possible transition state conformations (derived from *s-trans* **11-*Z*** and *s-cis* **11-*Z***), affording either the *syn* (**12**) or the *anti* (**13**) photocyclization products (Scheme 4). The reaction was finally concluded by oxidation of the cyclization products **12** and **13**, which should have furnished the helical benzo[c]phenanthrene (**14**) and the J-shaped benzo[a]anthracene (**15**). In fact, only **14** was formed under the conditions of the oxidative photocyclization with only oxygen as oxidant.[11c] This peculiar selectivity, furnishing the strained and thermodynamic less stable product **14** [$\Delta\Delta H_f$ (MM2) = +11.9 kcal/mol; $\Delta\Delta H_f$ (PM3) = +3.2 kcal/mol], was interpretable with the aid of semiempirical calculations,[25] considering steric (MM2) and electronic (PM3) influences on the structures **10−15** (Scheme 4). Neither the **10-*E*** nor the *trans-cis*-isomerized **10-*Z*** conformers showed significant steric or electronic energy differences. However, the PM3 energies of the products of the photochemically allowed conrotatory 6π-electron cyclization − **12** and **13** − showed remarkable differences. The structure **12** was 11.8 kcal/mol lower in PM3 energy than the constitutional isomer **13**, although **13** was less strained (according to MM2) than **12** by 3.6 kcal/mol. This apparent discrepancy was already explicable by the VB-representation of the drawn molecular structures. For the formation of **13**, the complete aromatic resonance stabilization would have to be sacrificed to achieve the cyclization, whereas after the formation of **12** one aromatic sextet would still be preserved. This simple picture was also supported by inspection of the calculated bond orders: whereas for **12** one six-membered ring was completely delocalized, the typical polyene bond alternation could be found for **13**. The activation energies for the photocyclization are known to be very small (0−3 kcal/mol), from experimental and theor-

Table 2. ^{1}H NMR shifts and coupling constants (multiplicity, [Hz]) of **9** (recorded in $CDCl_3$ at 20 °C)



9

	1-H	2-H	3-H	4-H	5-H	6-H	Additional signals
9a (X = CH=CH; R = H)	7.87 (d, ^3J = 8.7)	7.68 (dd, ^3J = 8.7, ^4J = 1.8)	8.99 (d, ^4J = 1.8)	8.28 (d, ^3J = 8.0)	7.79 (s)	7.79 (s)	7.45 (ddd, ^3J = 8.0, ^4J = 1.5); 7.53 (ddd, ^3J = 8.0, ^4J = 1.5; R = H); 7.89 (dd, ^3J = 8.0, ^4J = 1.5)
9b (X = CH=CH; R = CH_3)	7.85 (dd, ^3J = 8.5, ^4J = 1.5)	7.64 (dd, ^3J = 8.5, ^4J = 1.5)	8.98 (d, ^4J = 1.5)	8.06 (s)	7.71 (d, ^3J = 8.8)	7.74 (d, ^3J = 8.8)	2.30 (s, R = CH_3); 7.36 (d, ^3J = 8.0); 7.77 (d, ^3J = 8.0)
9c (X = S; R = H)	7.87 (d, ^3J = 8.8)	7.54 (dd, ^3J = 8.8, ^4J = 1.8)	8.53 (d, ^4J = 1.8)	7.60 (d, ^3J = 5.5)	7.92 (d, ^3J = 8.4)	7.76 (d, ^3J = 8.4)	7.45 (d, ^3J = 5.5, R = H)
9d (X = C_6H_4; R = H)	8.00 (d, ^3J = 8.9)	7.79 (d, ^3J = 8.9)	9.15 (s)	8.33 (d, ^3J = 9.3)	8.79 (d, ^3J = 9.3)	8.06 (d, ^3J = 9.3)	7.59 (dd, ^3J = 8.0); 7.68 (dd, ^3J = 8.0); 7.80 (d, ^3J = 9.3); 7.89 (d, ^3J = 8.0); 8.77 (d, ^3J = 8.0)

Table 3. Selected EI-MS data (70 eV) of the molecule fragments *m*/*z* of **9** (relative intensity in%)

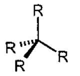
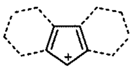
 **9**	$M^{\bullet+}$ (= $R_4C^{\bullet+}$)	R_3C^+	$R_2C^{\bullet+}$	 fluorenylium type ion
9a	720 (48)	543 (100)	366 (19)	365 (19)
9b	776 (49)	585 (100)	394 (17)	393 (16)
9c	744 (47)	561 (100)	-	377 (52)
9d	920 (20)	693 (100)	466 (21)	465 (23
9e	920 (38)	693 (100)	-	465 (20)

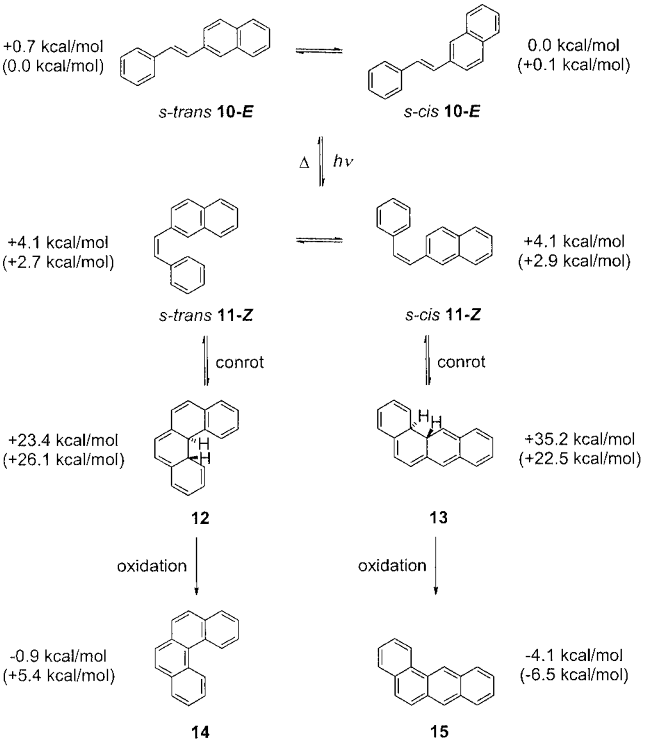
Table 4. Found and calculated (in parentheses) isotope distributions of the molecule peaks of **9** (scaled to the intensity of $M^{\cdot+}$)

	[M^+]	[M^+ + 1]	[M^+ + 2]	[M^+ + 3]	[M^+ + 4]
9a	47.75 (47.75)	28.07 (30.53)	9.77 (9.59)	2.58 (1.97)	0.80 (0.30)
9b	49.06 (49.06)	31.74 (33.61)	11.37 (11.33)	2.30 (2.50)	0.57 (0.41)
9c	47.06 (47.06)	27.77 (27.33)	15.21 (16.13)	6.04 (6.23)	-
9d	20.53 (20.53)	16.49 (16.80)	6.67 (6.78)	1.85 (1.80)	0.36 (0.35)
9e	38.55 (38.55)	31.11 (31.55)	12.57 (12.74)	3.42 (3.38)	0.70 (0.66)

etical studies on the photochemistry of stilbenes, whereas the activation barrier for thermal ring-opening once the dihydrophenanthrene had formed was found be fairly high (23 kcal/mol).[26] In our case, the photochemical equilibria result solely in population of structure **12**, as a consequence of the large energy difference. Given a rapid oxidative rearomatization, **12** would be continuously removed from this equilibrium, to furnish **14** as the only reaction product under kinetic control.

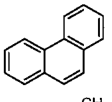
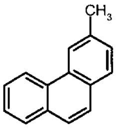
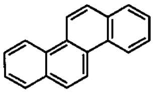
The electronic spectra (absorption and emission) of the tetrakis(phenanthrenyl)methanes **9** were rich in structure and revealed interesting properties of this novel class of tetraarylmethanes (Table 5). In the absorption spectra of compounds **9a**−**c**, very similar structures were apparent, indicating that substituent effects in these comparable π-perimeters were rather small. As would be expected, the absorption maxima of **9d** were shifted bathochromically due to the more extended π-system. In comparison with models taken for a single branch, such as phenanthrene (**16**),[27−29] 3-methylphenanthrene (**17**),[30,31] and chrysene (**18**)[28,32,33] the absorption maxima of the longest-wavelength transitions of **9** were red-shifted by $\Delta\tilde{\nu} = 1600-2300\ \mathrm{cm}^{-1}$, but showed similar structures (Figure 5). These bathochromic shifts were attributable to significant intramolecular electronic communication in the ground state.

Interestingly, the fluorescence behavior, relating to the structure properties of the excited electronic states, clearly showed a strong dependence on the substitution pattern.



Scheme 4. Relative energies according to PM3 and MM2 (in parentheses) calculations of the oxidative photocyclization of **10**

Table 5. Absorption and emission maxima (extinction maxima are indicated in bold face) and Stokes shifts of **9** in solution (recorded in $CHCl_3$ at 20 °C) and in the solid state

	λ_{max} [nm] Absorption in solution	λ_{max} [nm] Emission In solution ($CHCl_3$)	λ_{max} [nm] Emission In the solid state	Stokes shift $\Delta\tilde{\nu}$ [cm^{-1}]
9a	**265** 284 304	364 **384**	416 **443**	11700
9b	**266** 286 306	365sh **376** 392sh	–	11000
9c	**265** 297 308	356 **431**	–	14500
9d	**282** 299sh 310 326	372sh **388** 408sh	–	9700
 **16**	250 (cyclohexane)[27]	346 (cyclohexane)[28]	437[29]	11100
 **17**	255 (CH_2Cl_2)[30]	355 (acetonitrile)[31]	–	11000
 **18**	259 (cyclohexane)[32] **269** 320	361[28]	**388**[33] 408 432	9500

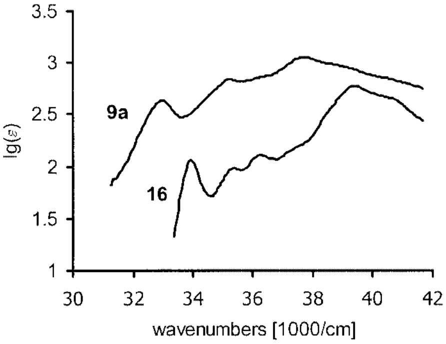


Figure 5. UV/Vis spectra of **9a** and **16** (recorded in $CHCl_3$, 20 °C)

The emission maxima of the tetrakis(phenanthrenyl)methanes **9** were considerably red-shifted in comparison to those of the single branch models (Table 5) and the Stokes shifts are enormous and encompass $\Delta\tilde{\nu}$ = 9700−14500 cm^{-1} (Figure 6), with a comparable magnitude.

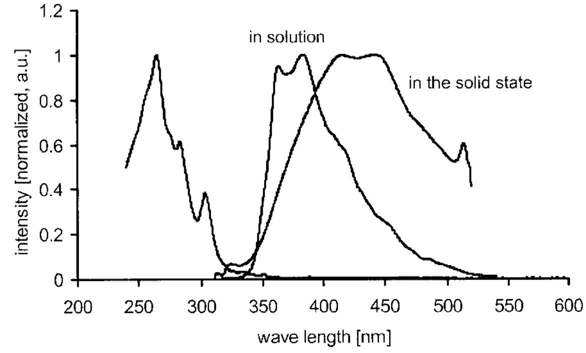


Figure 6. Solution UV/Vis and fluorescence spectra (both recorded in $CHCl_3$, 20 °C) and solid-state fluorescence of **9a**

Electrochemical data for the oxidation of compounds **9** by cyclic voltammetry were only obtained for tetrakis(naphtho[2,1-*b*]thien-8-yl)methane (**9c**), in the anodic region up to 1.5 V. In a 10-cycle experiment, **9c** showed a steadily increasing reversible oxidation at a potential of E_p^{ox} = 1.1 V (Figure 7), together with the formation of a thin, transparent, and multicolored film on the platinum working electrode, indicating electropolymerization of **9c**.

Anodic electropolymerization of thiophene and related derivatives is a common method for the preparation of highly conducting polythiophenes.[34,35] The electropolymerization of **9c** can be explained as follows (Scheme 5). Anodic oxidation of **9c** furnishes the oligo-radical cation species (electron transfer process E) $\mathbf{9c}^{n(\cdot+)}$, which can undergo dimerization or oligomerization (chemical process C) to give the oligo-cation **19**. The oligomer **19** aromatizes upon proton abstraction (chemical process C) and generates the pristine oligomer **20**, which is in turn oxidized on the anode (electron transfer process E) to give the oligo-radical cation species $\mathbf{20}^{n(\cdot+)}$, which now enhances the current flow on the working electrode. In the case of pyrroles in particular, mechanisms of electropolymerization to the corresponding polypyrroles have been investigated in detail, al-

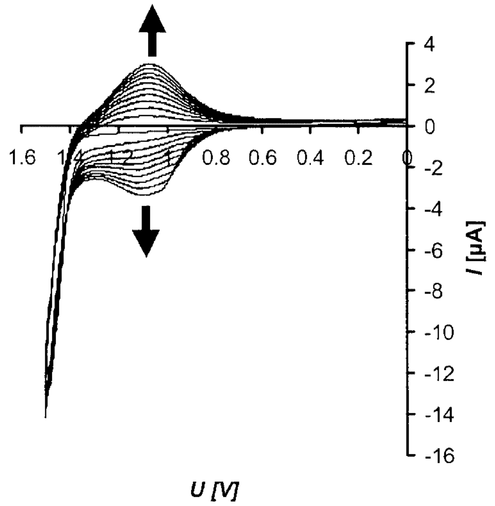


Figure 7. Cyclic voltammogram of **9c** in the anodic region (CH_2Cl_2, 20 °C, Pt disk electrode, reference electrode Ag/AgCl, scan rate = 100 mV/s, supporting electrolyte: $\mathrm{N}n\mathrm{Bu}_4{}^+\mathrm{PF}_6{}^-$)

though they are still a controversial subject.[36] However, the large orbital coefficient at the 2-position in the SOMO of the model naphtho[2,1-*b*]thiophene (Figure 8) supports an electropolymerization according to the ECCE mechanism presented. The spin density (orbital coefficients) is also large at the 4- and 5-positions of the heterocyclic framework, but because of the sterically demanding nature of the tetra(heteroaryl)methane framework the fastest reaction is likely to occur as shown. Interestingly, the coefficient at the 7-position that could be responsible for an intramolecular chemical reaction in **9c** is fairly small. The elucidation of the radical cationic species involved in this electropolymerization, as well as scaling up, characterization, and investigation of the charge-carrier mobilities of this novel type of organic material, is in progress and will be reported later.

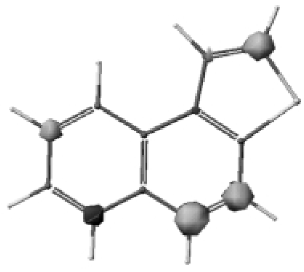
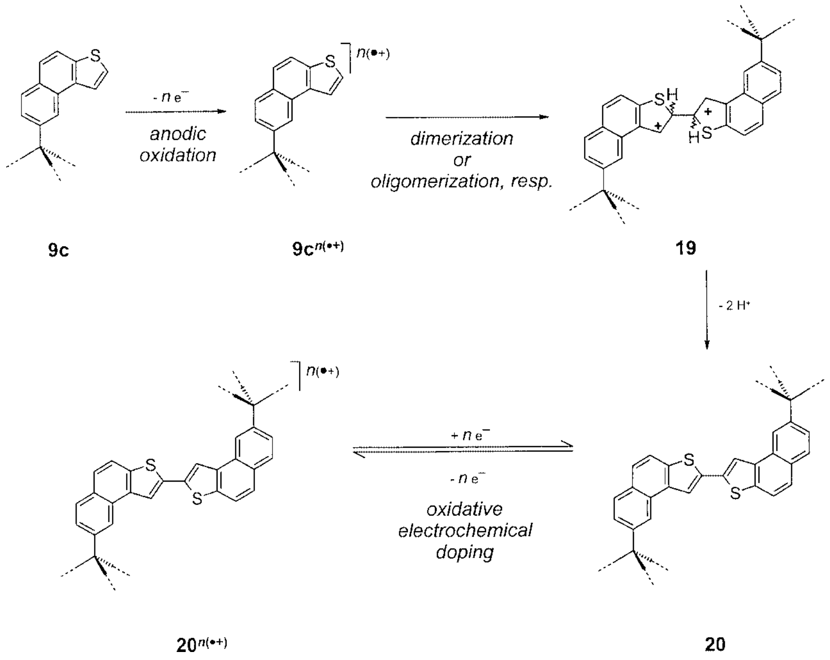


Figure 8. SOMO of the naphtho[2,1-*b*]thiophene radical cation

Conclusion

Heck vinylation of tetrakis(*p*-iodophenyl)methane (**1**) allows straightforward and versatile access to the class of tetrakis[2-(hetero)aryl-*p*-styryl]methanes **3**, which can in turn be oxidatively photocyclized to the hitherto unknown class of tetrakis[phenanthrenyl]methanes **9**. Both systems display highly interesting cooperative intramolecular electronic coupling, as shown by absorption and emission spectroscopy and cyclic voltammetry. As a qualitative guideline for the design of reversible electrochemical switches on the basis of ECEC processes on a tetraarylmethane framework, a balanced ratio between oxidation potential (ease of oxidation), degree of delocalization, and radical cation stability as deduced from cyclic voltammetry of three representatives of tetrakis[2-(hetero)aryl-*p*-styryl]methanes **3** can be proposed. The tetrakis(naphtho[2,1-*b*]thien-8-yl)methane (**9c**) can be electropolymerized by a multiple-cycle cyclic voltam-



Scheme 5. Mechanistic rationale for the formation of the electropolymerization product $\mathbf{20}^{n(\cdot+)}$

metry experiment to furnish a conductive polymeric film on the working electrode. These interesting cooperative electronic effects make tetrakis[phenanthrenyl]methanes **9** very promising candidates for novel hole-conducting materials in OLEDs (organic light-emitting diodes) and OFETs (organic field effect transistors) as a contribution to small molecule-based molecular electronics. Electro- and chemical polymerizations and investigations of tetrakis[phenanthrenyl]methanes **9** are currently underway.

Experimental Section

General: Reagents and solvents were purchased as reagent grade and used without further purification. Toluene and THF were dried and distilled according to standard procedures.[37] Tetrakis(*p*-iodophenyl)methane (**1**),[12c] 4-dimethylamino-styrene (**2c**),[38] 2-vinylthiophene (**2d**),[39] 1-vinylnaphthalene (**2e**),[40] and tetrakis(*p*-stilbenyl)methane (**3a**)[12b] were prepared according to literature procedures. Column chromatography: 60 silica gel (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; $CDCl_3$ (locked to Me_4Si), F_3CCOOD [locked to δ_H = 11.50 (s), δ_C = 116.5 (q, $^1J_{C,F}$ = 337 Hz), 164.4 (q, $^2J_{C,F}$ = 44 Hz)],[41] [D$_6$]DMSO (locked to Me_4Si). The assignments of quaternary C, CH, CH_2, and CH_3 were made by use of DEPT spectra. IR: Perkin−Elmer Lambda 3. UV/Vis: Beckman DK-2-A, Beckman UV 5240 and Perkin−Elmer Models Lambda 16. Fluorescence spectra (FL): Perkin−Elmer LS 50 B (irradiation at approximately 10 nm lower 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 Department of Chemistry, Ludwig-Maximilians-Universität, München.

Electrochemical Experiments: Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed CH_2Cl_2 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 CH_2Cl_2 ($E_0^{0/+1}$ = 450 mV).[22] The ferrocenyl derivative **2g** was calibrated to 9,10-diphenyl-anthracene ($E_0^{0/+1}$ = 1210 mV).

Synthesis of Tetrakis[β-(aryl)-*p*-styryl]methanes 3 (General Procedure): A mixture of tetrakis(*p*-iodophenyl)methane (**1**, 0.82 g, 1.00 mmol), vinyl compound **2** (9−14 mmol), tetrabutylammonium bromide (1.4 g, 4.4 mmol), potassium carbonate (0.70 g, 5.00 mmol), palladium(II) acetate (20 mg, 90 μmol), and *N*,*N*-dimethylformamide (20 mL, 20 mL) was stirred at 110 °C (oil bath) for 15 h under an atmosphere of nitrogen. After the mixture had cooled, 150 mL of methanol were added, and the precipitate was filtered and washed with methanol. The residue was recrystallized from toluene after filtration of the hot solution with 1 g of added Celite to give the analytically pure product **3**.

Tetrakis[β-(*p*-methylphenyl)-*p*-styryl]methane (3b): This compound was prepared by the General Procedure; compound **1** (0.82 g, 1.00 mmol) and 4-methyl styrene (**2b**, 1.5 mL, 11 mmol) furnished 0.31 g (40%) of **3b** as colorless needles. M.p. > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 12 H), 7.02 (d, ^3J = 16.5 Hz, 4 H), 7.06 (d, ^3J = 16.5 Hz, 4 H), 7.15 (d, ^3J = 8.1 Hz, 8 H), 7.25 (d, ^3J = 8.5 Hz, 8 H), 7.40 (d, ^3J = 8.1 Hz, 8 H), 7.41 (d, ^3J = 8.5 Hz, 8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 64.4 ($C_{quat.}$), 125.7 (CH), 126.4 (CH), 127.2 (CH), 128.7 (CH), 129.4 (CH), 131.3 (CH), 134.6 ($C_{quat.}$), 135.2 ($C_{quat.}$), 137.5 ($C_{quat.}$), 145.9 ($C_{quat.}$) ppm. MS (70 eV, EI): *m*/*z* (%) = 784 (69) [$M^{\cdot+}$], 591 (100) [$(C_{15}H_{13})_3C^+$], 398 (12) [$(C_{15}H_{13})_2C^+$]. IR (KBr): $\tilde{\nu}$ = 3023, 1628, 1513, 963, 817 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 325 nm (131800), 338 (sh, 10000). FL ($CHCl_3$): λ_{max} = 366 nm (sh), 382. $C_{61}H_{52}$ (785.1): calcd.: C 93.32, H 6.68; found C 93.25, H 6.72.

Tetrakis[β-(*p*-*N*,*N*-dimethylphenyl)-*p*-styryl]methane (3c): This compound was prepared by the General Procedure; compound **1** (0.41 g, 0.50 mmol) and *p*-dimethylaminostyrene (**2c**, 1.5 g, 10 mmol)[38] furnished 0.21 g (47%) of **3c** as beige needles. M.p. > 250 °C. ^{1}H NMR (300 MHz, F_3CCOOD): δ = 3.36 (s, 24 H), 7.12 (d, ^3J = 16.4 Hz, 4 H), 7.22 (d, ^3J = 16.4 Hz, 4 H), 7.37 (d, ^3J = 8.3 Hz, 8 H), 7.47 (d, ^3J = 8.3 Hz, 8 H), 7.49 (d, ^3J = 8.9 Hz, 8 H), 7.72 (d, ^3J = 8.9 Hz, 8 H) ppm. ^{13}C NMR (75 MHz, F_3CCOOD): δ = 47.1 (CH_3), 64.9 ($C_{quat.}$), 119.5 (CH), 125.3 (CH), 125.9 (CH), 128.3 (CH), 131.3 (CH), 131.9 (CH), 134.3 ($C_{quat.}$), 139.7 ($C_{quat.}$), 141.5 ($C_{quat.}$), 147.1 ($C_{quat.}$) ppm. MS (70 eV, EI): *m*/*z* (%) = 900 (100) [$M^{\cdot+}$], 678 (86) [$(C_{16}H_{16}N)_3C^+$], 450 (15) [M^{2+}], 134 (41) [$C_7H_6NMe_2^+$]. IR (KBr): $\tilde{\nu}$ = 3021, 1609, 1522, 1443, 1356, 1186, 1164, 948, 816 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 364 nm (134900). FL ($CHCl_3$): λ_{max} = 431 nm. $C_{65}H_{64}N_4$ (901.3): calcd. C 86.42, H 7.47, N 6.11; found C 86.43, H 7.34, N 6.03.

Tetrakis[β-(thien-2-yl)-*p*-styryl]methane (3d): This compound was prepared by the General Procedure; compound **1** (0.82 g, 1.00 mmol) and 2-vinylthiophene (**2d**, 1.5 g, 14 mmol)[39] furnished 0.20 g (27%) of **3d** as yellow needles. M.p. > 250 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 6.93 (d, ^3J = 16.0 Hz, 4 H), 7.06 (dd, ^3J = 5.0, ^3J = 3.6 Hz, 4 H), 7.18 (d, ^3J = 8.2 Hz, 8 H), 7.20 (d, ^3J = 3.6 Hz, 4 H), 7.42 (d, ^3J = 16.0 Hz, 4 H), 7.46 (d, ^3J = 5.0 Hz, 4 H), 7.52 (d, ^3J = 8.2 Hz, 8 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 64.0 ($C_{quat.}$), 122.1 (CH), 125.3 (CH), 125.8 (CH), 126.7 (CH), 127.0 (CH), 127.9 (CH), 130.6 (CH), 134.4 ($C_{quat.}$), 142.2 ($C_{quat.}$), 145.4 ($C_{quat.}$) ppm. MS (70 eV, EI): *m*/*z* (%) = 752 (91) [$M^{\cdot+}$], 567 (100) [$(C_{12}H_9S)_3C^+$]. IR (KBr): $\tilde{\nu}$ = 3022, 1625, 1501, 945, 820, 695 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 338 nm (112200). FL ($CHCl_3$): λ_{max} = 398 nm, 425. $C_{49}H_{36}S_4$ (753.1): calcd. C 78.15, H 4.82, S 17.03; found C 77.88, H 4.70, S 16.84.

Tetrakis[β-(naphthalen-1-yl)-*p*-styryl]methane (3e): This compound was prepared by the General Procedure; compound **1** (0.82 g, 1.00 mmol) and 1-vinylnaphthalene (**2e**, 1.4 g, 9.1 mmol)[40] furnished 0.70 g (75%) of **3e** as a beige resin after chromatography on silica gel (chloroform/hexane, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35−7.59 (m, 28 H), 7.70−7.93 (m, 20 H), 8.17−8.24 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 64.8 ($C_{quat.}$), 124.0 (CH), 124.2 (CH), 126.1 (CH), 126.2 (CH), 126.3 (CH), 126.5 (CH), 127.5 ($C_{quat.}$), 128.4 (CH), 129.0 (CH), 131.4 (CH), 131.6 (CH), 131.8 (CH), 134.1 ($C_{quat.}$), 135.5 ($C_{quat.}$), 135.9 ($C_{quat.}$), 146.6 ($C_{quat.}$) ppm. MS (70 eV, EI): *m*/*z* (%) = 928 (57) [$M^{\cdot+}$], 699 (100) [$(C_{18}H_{13})_3C^+$]. IR (KBr): $\tilde{\nu}$ = 3055, 1628, 1505, 962, 811, 791, 773 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 334 nm (25100). FL ($CHCl_3$): λ_{max} = 389 nm (sh), 407. $C_{73}H_{52}$ (929.2): calcd. C 94.36, H 5.64; found C 94.02, H 5.38.

Tetrakis[β-(naphthalen-2-yl)-*p*-styryl]methane (3f): This compound was prepared by the General Procedure; compound **1** (0.82 g, 1.00 mmol) and 2-vinylnaphthalene (**2f**, 1.4 g, 9.1 mmol)[40] furnished 0.35 g (38%) of **3f** as beige needles. M.p. > 250 °C. ^{1}H NMR

(400 MHz, [D$_6$]DMSO, 90 °C): δ = 7.30 (d, ^3J = 8.6 Hz, 8 H), 7.38 (s, 8 H), 7.45−7.52 (m, 8 H), 7.62 (d, ^3J = 8.6 Hz, 8 H), 7.82 (dd, ^3J = 8.7, ^4J = 1.7 Hz, 4 H), 7.86−7.90 (m, 12 H), 8.00 (s, 4 H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$, 90 °C): δ = 64.1 (C$_{\text{quat.}}$), 123.4, 125.5, 125.8, 127.0, 127.3, 127.6, 127.7, 128.1, 128.3, 128.4, 130.3, 132.2, 132.9, 134.4, 134.7, 145.3 ppm. MS (70 eV, EI): *m/z* (%) = 928 (40) [M$^{\cdot+}$], 699 (100) [(C$_{18}$H$_{13}$)$_3$C$^+$]. IR (KBr): ṽ = 3054, 3024, 1595, 1507, 959, 846, 814, 744 cm^{-1}. UV/Vis (CHCl$_3$): λ$_{\max}$ (ε) = 333 nm (177800). FL (CHCl$_3$): λ$_{\max}$ = 383 nm, 498. C$_{73}$H$_{52}$ (929.2): calcd. C 94.36, H 5.64; found C 94.26, H 5.56.

Tetrakis(β-ferrocenyl-*p*-styryl)methane (3g): This compound was prepared by the General Procedure; compound **1** (0.82 g, 1.00 mmol) and vinylferrocene (**2g**, 2.0 g, 9.4 mmol) furnished 0.84 g (73%) of **3g** as an orange powder after chromatography on silica gel (chloroform/hexane, 1:1). M.p. > 250 °C (dec.). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.13 (s, 20 H), 4.27 (t, ^3J = 1.8 Hz, 8 H), 4.45 (t, ^3J = 1.8 Hz, 8 H), 6.68 (d, ^3J = 16.1 Hz, 4 H), 6.85 (d, ^3J = 16.1 Hz, 4 H), 7.27 (d, ^3J = 8.4 Hz, 8 H), 7.32 (d, ^3J = 8.4 Hz, 8 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 64.9 (C$_{\text{quat.}}$), 66.8 (CH), 69.0 (CH), 69.2 (CH), 83.5 (C$_{\text{quat.}}$), 125.0 (CH), 125.6 (CH), 127.1 (CH), 131.2 (CH), 135.5 (C$_{\text{quat.}}$), 145.3 (C$_{\text{quat.}}$) ppm. MS (70 eV, EI): *m/z* (%) = 1160 (79) [M$^{\cdot+}$], 873 (14) [(C$_{18}$H$_{13}$Fe)$_3$C$^+$], 580 (15) [M^{2+}], 186 (100) [(C$_5$H$_5$)$_2$Fe$^+$]. IR (KBr): ṽ = 3090, 3023, 2924, 1631, 1506, 1411, 1106, 1001, 959, 806, 754, 484 cm^{-1}. UV/Vis (CHCl$_3$): λ$_{\max}$ (ε) = 270 nm (47900), 318 (83200). C$_{73}$H$_{60}$Fe$_4$ (1160.7): calcd. C 75.54, H 5.21; found C 75.29, H 5.10.

Photocyclization of Tetrakis[β-(aryl)-*p*-styryl]methanes 9 (General Procedure): A solution of tetrakis[β-(aryl)-*p*-styryl]methane **3** (0.16 mmol) and the indicated amount of iodine in 150 mL of toluene was irradiated with a mercury-pressure lamp (Philips HPK 125 W) for 5 h under a constant stream of air. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (chloroform/hexane, 1:1) to give the analytically pure product.

Tetrakis(phenanthren-3-yl)methane (9a): This compound was prepared by the General Procedure; compound **3a** (0.13 g, 0.18 mmol) and iodine (12 mg, 94 μmol) furnished 21 mg (16%) of **9a** as a colorless powder. M.p. > 250 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.45 (ddd, ^3J = 8.0, ^4J = 1.5 Hz, 4 H), 7.53 (ddd, ^3J = 8.0, ^4J = 1.5 Hz, 4 H), 7.68 (dd, ^3J = 8.7, ^4J = 1.8 Hz, 4 H), 7.79 (s, 8 H), 7.87 (d, ^3J = 8.7 Hz, 4 H), 7.89 (dd, ^3J = 8.0, ^4J = 1.5 Hz, 4 H), 8.28 (d, ^3J = 8.0 Hz, 4 H), 8.99 (d, ^4J = 1.8 Hz, 4 H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 66.7 (C$_{\text{quat.}}$), 122.6 (CH), 124.1 (CH), 126.5 (CH), 126.6 (CH), 126.7 (CH), 127.3 (CH), 127.8 (CH), 128.6 (CH), 129.8 (C$_{\text{quat.}}$), 130.3 (C$_{\text{quat.}}$), 130.5 (C$_{\text{quat.}}$), 131.4 (C$_{\text{quat.}}$), 132.3 (C$_{\text{quat.}}$), 144.9 (C$_{\text{quat.}}$) ppm. MS (70 eV, EI): *m/z* (%) = 720 (48) [M$^{\cdot+}$], 543 (100) [(C$_{14}$H$_9$)$_3$C$^+$], 366 (19) [(C$_{14}$H$_9$)$_2$C$^+$], 365 (19) [C$_{29}$H$_{17}{}^+$]. IR (KBr): ṽ = 2923 cm^{-1}, 2852, 1628, 822, 746 cm^{-1}. UV/Vis (CHCl$_3$): λ$_{\max}$ (ε) = 265 nm (112200), 284 (69200), 304 (42700). FL (CHCl$_3$): λ$_{\max}$ = 364 nm, 384. FL (solid state): λ$_{\max}$ = 416 nm, 443. C$_{57}$H$_{36}$ (720.9): calcd. C 94.97, H 5.03; found C 94.88, H 4.89.

Tetrakis(6-methylphenanthren-3-yl)methane (9b): This compound was prepared by the General Procedure; compound **3b** (0.20 g, 0.26 mmol) and iodine (15 mg, 0.12 mmol) furnished 30 mg (15%) of **9b** as a colorless powder. M.p. > 250 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.30 (s, 12 H), 7.36 (d, ^3J = 8.0 Hz, 4 H), 7.64 (dd, ^3J = 8.5, ^4J = 1.5 Hz, 4 H), 7.71 (d, ^3J = 8.8 Hz, 4 H), 7.74 (d, ^3J = 8.8 Hz, 4 H), 7.77 (d, ^3J = 8.0 Hz, 4 H), 7.85 (dd, ^3J = 8.5, ^4J = 1.5 Hz, 4 H), 8.06 (s, 4 H) 8.98 (d, ^4J = 1.5 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.9 (CH$_3$), 65.0 (C$_{\text{quat.}}$), 122.2 (CH), 124.4(CH), 125.4 (CH), 126.3 (CH), 126.9 (CH), 127.5 (CH), 128.2 (CH), 128.3(CH), 129.3 (C$_{\text{quat.}}$), 130.1 (C$_{\text{quat.}}$), 130.4 (C$_{\text{quat.}}$), 131.0 (C$_{\text{quat.}}$), 136.3 (C$_{\text{quat.}}$), 144.6 (C$_{\text{quat.}}$) ppm. MS (70 eV, EI): *m/z* (%) = 776 (49) [M$^{\cdot+}$], 585 (100) [(C$_{15}$H$_{11}$)$_3$C$^+$], 394 (16) [C$_{31}$H$_{21}{}^+$]. IR (KBr): ṽ = 3019 cm^{-1}, 2920, 1604, 1514, 842 cm^{-1}. UV/Vis (CHCl$_3$): λ$_{\max}$ (ε) = 266 nm (120200), 286 (77600), 306 (57500). FL (CHCl$_3$): λ$_{\max}$ = 376 nm. C$_{61}$H$_{44}$ (777.0): calcd. C 94.29, H 5.71; found C 94.32, H 5.61.

Tetrakis(naphtho[2,1-*b*]thien-8-yl)methane (9c): This compound was prepared by the General Procedure; compound **3d** (0.12 g, 0.16 mmol) and iodine (12 mg, 94 μmol) furnished 28 mg (23%) of **9c** as a beige powder. M.p. > 250 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.45 (d, ^3J = 5.5 Hz, 4 H), 7.54 (dd, ^3J = 8.8, ^4J = 1.8 Hz, 4 H), 7.60 (d, ^3J = 5.5 Hz, 4 H), 7.76 (d, ^3J = 8.4 Hz, 4 H), 7.87 (d, ^3J = 8.8 Hz, 4 H), 7.92 (d, ^3J = 8.4 Hz, 4 H), 8.53 (d, ^4J = 1.8 Hz, 4 H) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 66.4 (C$_{\text{quat.}}$), 121.4 (CH), 122.4 (CH), 124.9 (CH), 125.2 (CH), 126.4 (CH), 127.9 (CH), 129.3 (C$_{\text{quat.}}$), 129.7 (C$_{\text{quat.}}$), 130.7 (CH), 136.6 (C$_{\text{quat.}}$), 138.1 (C$_{\text{quat.}}$), 144.8 (C$_{\text{quat.}}$) ppm. MS (70 eV, EI): *m/z* (%) = 744 (47) [M$^{\cdot+}$], 561 (100) [(C$_{12}$H$_7$S)$_3$C$^+$], 377 (52) [C$_{25}$H$_{13}$S$^+$]. IR (KBr): ṽ = 2923, 2853, 1618, 1468, 1375, 1193, 1152, 1053, 904, 836, 817, 716 cm^{-1}. UV/Vis (CHCl$_3$): λ$_{\max}$ (ε) = 265 nm (100000), 297 (32400), 308 (30900). FL (CHCl$_3$): λ$_{\max}$ = 431 nm. C$_{49}$H$_{28}$S$_4$ (745.0): calcd. C 79.00, H 3.79, S 17.22; found C 78.69, H 3.70, S 16.98.

Tetrakis(chrysen-3-yl)methane (9d): This compound was prepared by the General Procedure; compound **3e** (0.30 g, 0.32 mmol) and iodine (20 mg, 0.16 mmol) furnished 35 mg (12%) of **9d** as a beige powder. M.p. > 250 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.59 (dd, ^3J = 8.0 Hz, 4 H), 7.68 (dd, ^3J = 8.0 Hz, 4 H), 7.79 (d, ^3J = 8.9 Hz, 4 H), 7.80 (d, ^3J = 9.3 Hz, 4 H), 7.89 (d, ^3J = 8.0 Hz, 4 H), 8.00 (d, ^3J = 8.9 Hz, 4 H), 8.06 (d, ^3J = 9.3 Hz, 4 H), 8.33 (d, ^3J = 9.3 Hz, 4 H), 8.77 (d, ^3J = 8.0 Hz, 4 H), 8.79 (d, ^3J = 9.3 Hz, 4 H), 9.15 (s, 4 H). IR (KBr): ṽ = 3051, 2922, 2851, 1618, 1489, 822, 834, 749 cm^{-1}. UV/Vis (CHCl$_3$): λ$_{\max}$ (ε) = 282 nm (208900), 299 (sh, 64600), 310 (41700), 326 (34700). FL (CHCl$_3$): λ$_{\max}$ 372 nm (sh), 388, 408 (sh). FL (solid state): λ$_{\max}$ 416 nm, 443. C$_{73}$H$_{44}$ (921.2) calcd.: C 95.19, H 4.81; found C 95.23, H 4.81.

Tetrakis(benzo[*c*]phenanthren-2-yl)methane (9e): This compound was prepared by the General Procedure; compound **3f** (0.20 g, 0.22 mmol) and iodine (20 mg, 0.16 mmol) in 1.5 l of toluene furnished 1 mg (0.5%) of **9e** as a colorless powder after irradiation for 15 h. IR (KBr): ṽ = 2922 cm^{-1}, 2852, 1628, 842, 746. MS (70 eV, EI): *m/z* (%) = 920 (38) [M$^{\cdot+}$], 693 (100) [(C$_{18}$H$_{11}$)$_3$C$^+$], 465 (20) [C$_{37}$H$_{21}{}^+$]. HRMS calcd. for C$_{73}$H$_{44}$ (921.2): 920.3443; found 920.3468.

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