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Synthesis and Properties of Arylvinylidene-Bridged Triphenylamines

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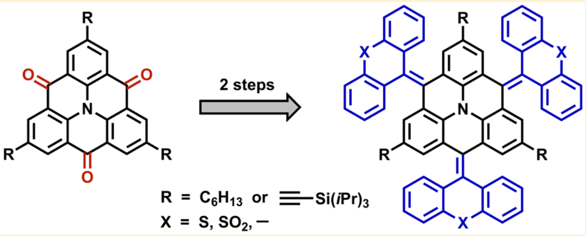
Supporting Information

ABSTRACT: A series of arylvinylidene-bridged triphenylamines were efficiently synthesized through the thionation/Barton−Kellogg olefination sequence from their corresponding carbonyl precursors. The electrochemical investigations identified these highly distorted scaffolds as fairly strong electron donors capable of several reversible oxidation steps with the first oxidation occurring at a potential comparable to that of ferrocene for the *n*-hexyl-substituted diphenylvinylidene-bridged compound.



Appealing π systems with a virtually planar nitrogen atom at the center, so-called heterotriangulenes, were realized by introducing various tethers into the originally propeller-shaped triphenylamine (TPA) moiety.[1] For example, compound **1** with the sp^3-hybridized dimethylmethylene tethers retains the electronic character of triphenylamine readily forming persistent radical cations (Figure 1).[2] Compound **1** and its diarylmethylene-bridged counterpart **2** were used as versatile building blocks for p-type materials to be used in organic electronics.[3−5] The replacement of the tetrahedral bridges with carbonyl moieties provided the perfectly planar electron-deficient scaffold **3**.[1a,6] Various derivatives of **3** with alkyl and alkoxy side chains of different lengths were synthesized, and their propensity for self-assembly was studied.[7] Star-shaped compounds comprising **3** with electron-rich carbazole moieties were reported as highly electroluminescent materials.[8] Additionally, efficient energy transfer in multichromophoric systems based on **3** with peripheral naphthalimides was identified.[9] Nevertheless, in all these undoubtedly interesting examples, solely the activated para positions of the phenyl moieties in **3** were functionalized.

Upon closer examination, the heterotriangulene **3** reveals its potential for the construction of a new type of nitrogen-centered π system via synthetic modifications of the bridging carbonyls. It was only recently during the conclusion of this work that such an approach appeared in the literature for the first time. Yamaguchi and co-workers prepared a series of heterotriangulenes **4** π-expanded at the bridging positions through the Ramirez−Corey−Fuchs dibromoolefination of pentafluorophenyl-substituted **3** followed by the Suzuki−Miyaura cross-coupling.[10] The ability of the obtained compounds to undergo oxidative cyclodehydrogenation toward nitrogen-doped polycyclic aromatic hydrocarbons (PAHs) was investigated.

Herein, we report on an alternative approach to related arylvinylidene-bridged triphenylamines **5**, i.e., olefinated heterotriangulenes, with the Barton−Kellogg reaction[11,12] as a key step and discuss the influence of the introduced C═C bonds on the optoelectronic properties of the resulting compounds.

The soluble precursor **6** was prepared from the iodinated heterotriangulene **7** via the Pd-catalyzed Negishi cross-coupling with *n*-hexylzinc bromide in 74% yield (Scheme 1).[7c,8] Because of the ability of the triisopropylsilyl (TIPS)-ethynyl moieties to facilitate the growth of single crystals, the TIPS-ethynyl-substituted analogue **8** was synthesized as well.[7c] After ketones **6** and **8** had been heated with Lawesson's reagent in toluene, the corresponding thioketones **9** and **10** were obtained as stable purple solids in almost quantitative yields.[13]

Both thioketones **9** and **10** were further subjected to the 3-fold Barton−Kellogg olefination with diphenyldiazomethane and 9-diazo-9*H*-thioxanthene.[11,14] The intermediate thioepoxides were used directly without purification for the subsequent reaction with triphenylphosphine because of their tendency to decompose during column chromatography. The desired olefinated heterotriangulenes **5a**−**5d** were obtained as yellow solids, stable at ambient temperature under air, and soluble in common organic solvents, in good yields between 46% (**5a**) and 58% (**5d**). To investigate the effect of the electron-withdrawing sulfone units on the optoelectronic properties of the π system, **5e** was synthesized in 94% yield by oxidation of **5c** with H_2O_2 and acetic acid.[15] We attempted to fuse the arylvinylidene-bridged triphenylamines **5a**−**5d** to the corresponding heteroatom-doped PAHs by oxidative cyclodehydrogenation.[16] Unfortunately, none of the inves-

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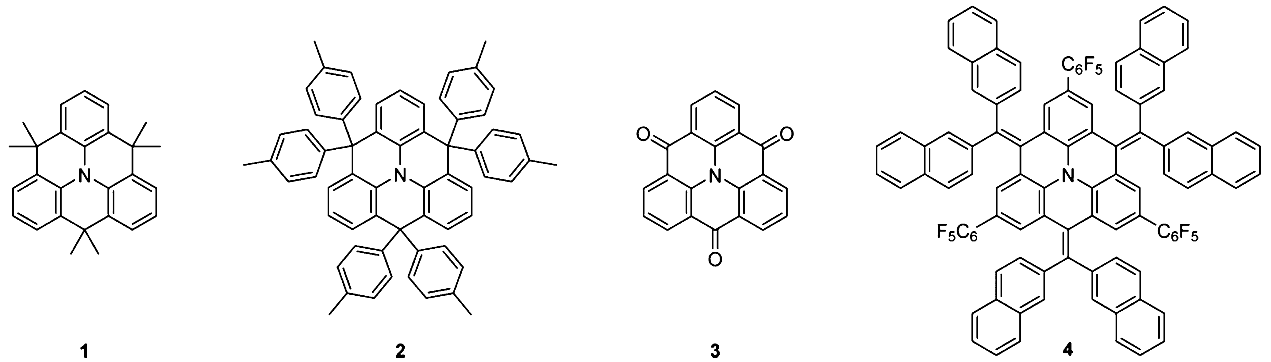
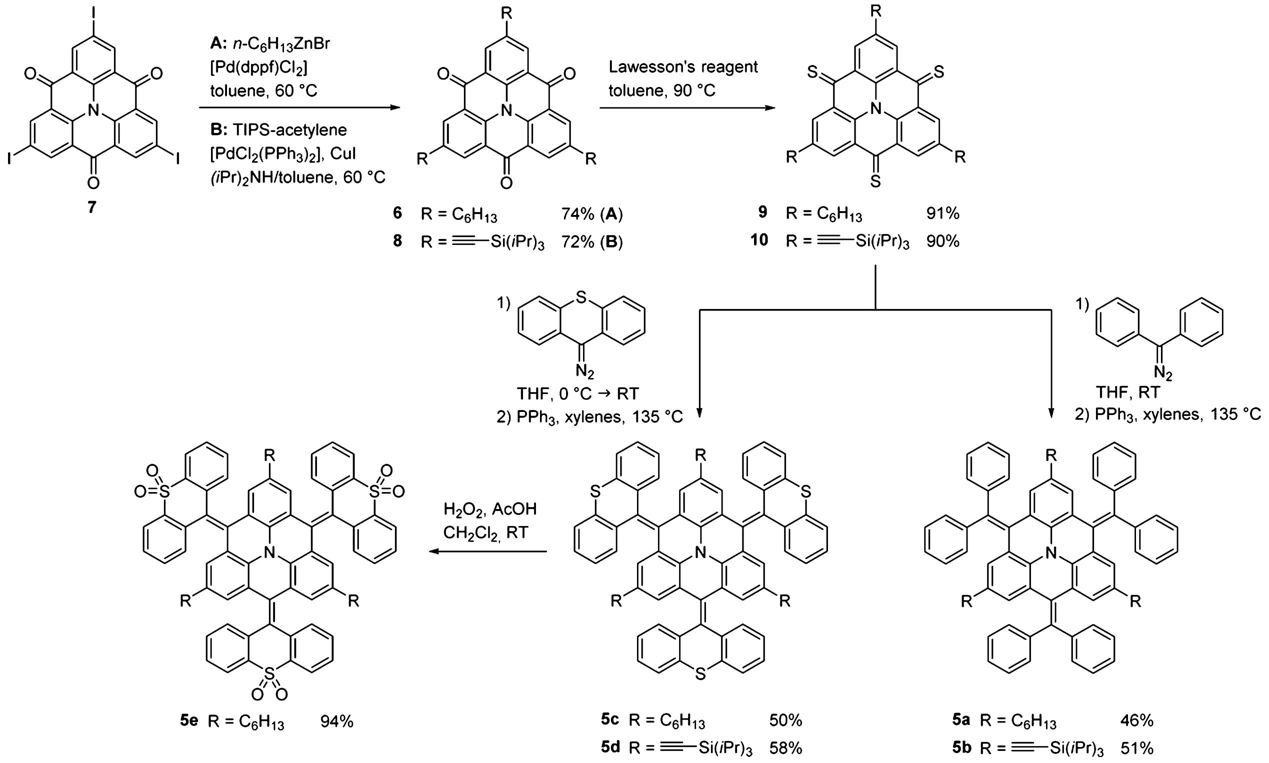


Figure 1. Examples of bridged triarylamine derivatives **1**−**4**.

Scheme 1. Synthesis of Arylvinylidene-Bridged Triphenylamines 5a−5e



tigated compounds delivered any cyclized species upon treatment with $FeCl_3$ in a CH_2Cl_2/CH_3NO_2 mixture or by exposure to any of the well-established oxidant/Lewis acid combinations (Scholl reaction), and extensive decomposition was observed instead. Also, various photocyclization setups (Mallory reaction) failed and afforded only complex mixtures of unidentifiable products.

Single crystals of **5b**, **5d**, and **5e** suitable for X-ray crystallographic analysis were obtained by various crystallization techniques (Figure 2 and the Supporting Information). In contrast to the previously reported perfectly planar N-centered heterotriangulenes,[6,7c] compounds **5b**, **5d**, and **5e** possess a bowl-shaped structure with a moderate pyramidalization at the nitrogen atom with the sum of the corresponding C−N−C angles ranging from 349.1° (**5e**) to 353.7° (**5b**). Correspondingly, the sulfonyl-substituted compound **5e** forms the deepest π bowl with the maximal deviation of the nitrogen atom from the mean plane passing through the three *para*-C(sp^2) atoms of 1.28 Å. For all compounds, the average N−C(sp^2) bond length of 1.42 Å is comparable to that in triphenylamine.[17]

As a result of pronounced steric crowding around the exocyclic C═C bonds, the three bridging arylvinylidenes in **5b**, **5d**, and **5e** are bent in the same direction pointing away from the bowl-shaped triphenylamine core. This unfavorable steric situation presumably leads to the observed deformation of the originally flat heterotriangulene π system and is responsible for the absence of π−π stacking in the crystal structures of these compounds. Consequently, structural characteristics of overcrowded alkenes can be observed.[18] For example, the thioxanthene dioxide-containing compound **5e** adopts an *anti*-folded conformation at the olefinic C═C bonds, which is commonly observed for related overcrowded olefins, such as dixanthylene and dithioxanthylene.[18a] The degree of nonplanarity of the thioxanthylidene moieties measured as folding dihedrals between the least-squares planes defined by the carbon atoms of the lateral benzene rings varies between 46.0° (S43 unit) and 56.3° (S57 unit). The folding of the acridane

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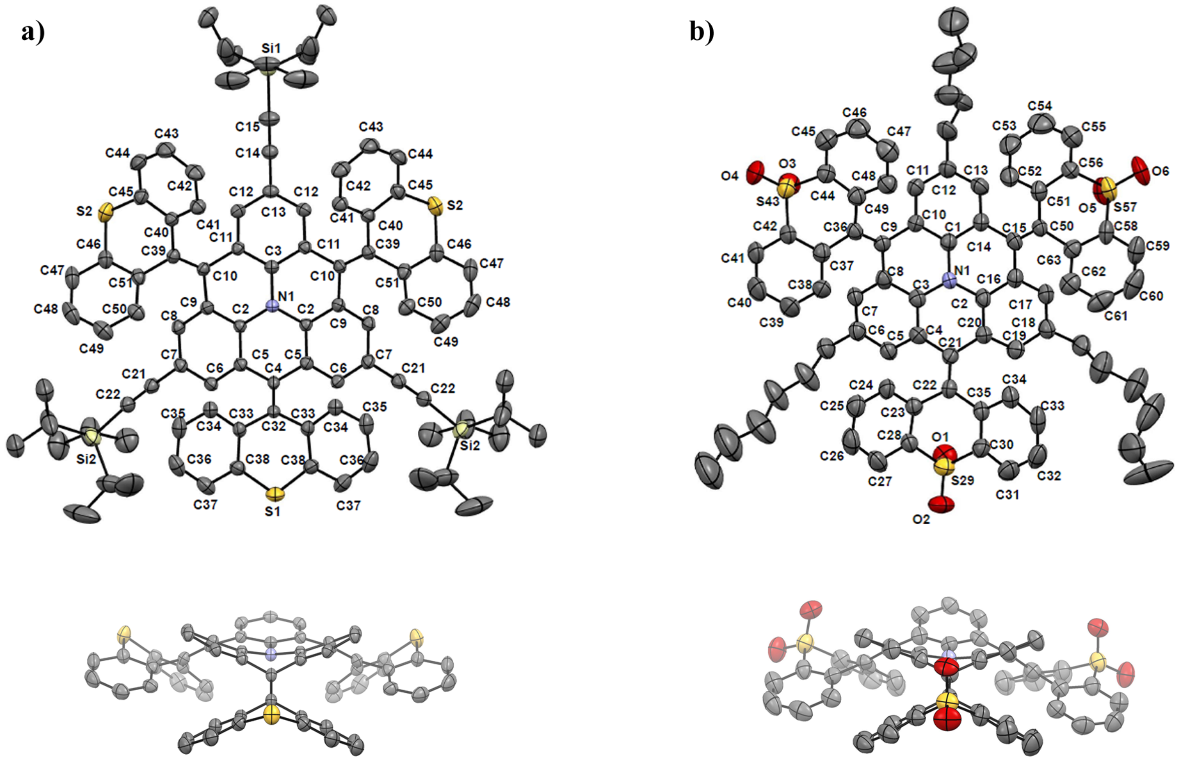

Figure 2. Top and side views (TIPS-ethynyl and *n*-hexyl moieties omitted) of the crystal structures of (a) **5d** and (b) **5e**. *T* = 173 K. Ellipsoids at 50% probability.

Table 1. Selected Photophysical and Electrochemical Data of Compounds 5a−5e, 6, 9, and 10

	$\lambda_{max}{}^{a}$ (nm)	ε^{b} (M^{-1} cm^{-1})	$\lambda_{em}{}^{c}$ (nm)	Stokes shift (cm^{-1})	$\Phi_F{}^{d}$	E^{oe} (V)	$E_g{}^{optf}$ (V)	$E_{HOMO}{}^{g}$ (eV)	$E_{LUMO}{}^{h}$ (eV)
5a	405	27700	*i*	–	–	+0.05	2.72 (2.98)	−4.85 (−4.67)	−2.13 (−1.16)
5b	404 (sh)^{m}	21650	*i*	–	–	+0.32	2.80^{n}	−5.12^{n}	−2.32^{n}
5c	430	30400	498	3175	0.57	+0.40^{j}	2.57 (2.79)	−5.20 (−4.92)	−2.63 (−1.58)
5d	428	27000	511	3795	0.46	+0.56^{j}	2.61^{n}	−5.36^{n}	−2.75^{n}
5e	449	40300	528	3332	0.47	+0.55, −2.07^{k}	2.47 (2.68)	−5.35 (−5.40)	−2.73 (−2.16)
6	424	33800	*i*	–	–	*n*	2.79 (3.12)	*n* (−6.02)	*n* (−2.28)
9	572	27900	*i*	–	–	*n*	2.01 (2.34)	*n* (−5.88)	*n* (−3.18)
10	577	25000	*i*	–	–	+1.18,^{l} −0.94	2.00^{n}	−5.98^{n}	−3.86^{n}

[a] Only the longest wavelength absorption maxima recorded in CH_2Cl_2 are shown. [b] Molar extinction coefficient at the longest wavelength absorption maximum. [c] Emission maxima in CH_2Cl_2. [d] Relative fluorescence quantum yields determined by using quinine bisulfate in aqueous 0.1 M H_2SO_4 as a standard. [e] The first oxidation and reduction potentials measured by cyclic voltammetry (0.1 M *n*-Bu_4NPF_6 in CH_2Cl_2; scan rate ν = 0.1 V s^{-1}) are given against the Fc^+/Fc couple as an internal standard. [f] $E_g{}^{opt} = h \times c/\lambda_{end}$. Computed values [B3LYP/6-31G(d,p)] in parentheses were estimated as the lowest-lying excited state with significant oscillator strength. [g] Estimated from the experimental first oxidation potential under the assumption that Fc^+/Fc is −4.8 eV vs vacuum;[19] computed values in parentheses. [h] Estimated from the experimental optical band gap $E_g{}^{opt}$ and the respective HOMO level (for **5a**−**5d**) or from the experimental first reduction potential under the assumption that Fc^+/Fc is −4.8 eV vs vacuum (for **5e** and **10**);[19] computed values in parentheses. [i] Not observed. [j] Reversible only at scan rates higher than 0.5 V s^{-1}. [k] Irreversible reduction. [l] Measured by rotating disc voltammetry. [m] Shoulder. [n] Not estimated.

subunits is caused by their incorporation within the rigid heterotriangulene core less pronounced and reaches the maximum of 39.9° for the C9═C36 bond. To further diminish the steric strain, the central C═C bonds in **5e** are slightly twisted as represented by the average of the dihedral angles ranging from −3.2° (C4−C21−C22−C23 and C20−C21−C22−C35) to −1.4° (C14−C15−C50−C51 and C16−C15−C50−C63). The C═C bond lengths between 1.332(7) and 1.367(7) Å are in the range observed for other overcrowded olefins,[18] while the olefinic C(sp^2) atoms show basically no pyramidalization as illustrated by the uniform sum of the angles around these atoms of 359.9°.

To evaluate the impact of different bridging moieties on the photophysical properties, UV−vis emission and absorption spectra of all new compounds were recorded (Table 1, Figure 3, and the Supporting Information).

Thiocarbonyl-bridged compounds **9** and **10** display the longest wavelength absorption maxima (λ_{max}) at 572 and 577 nm, respectively, which are bathochromically shifted by more than 140 nm compared to those of the respective triketones **6** and **8**. Such differences are characteristic and account for n−π* transitions that are accessible at lower energies in thiocarbonyl chromophores.[20] The introduction of the diphenylmethylene bridges in **5a** and **5b** leads to hypsochromic shifts of the lowest-energy absorption maxima that are found around 405 nm. This

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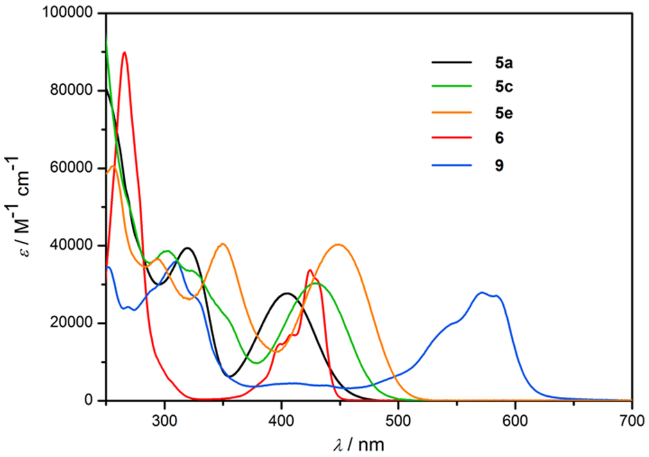

Figure 3. UV−vis absorption spectra of *n*-hexyl-substituted compounds **5a**, **5c**, **5e**, **6**, and **9** in CH_2Cl_2.

result is rather surprising as both *n*-hexyl-substituted (**5c**) and TIPS-ethynyl-substituted (**5d**) thioxanthylidene compounds show the respective absorption bands at 430 and 428 nm that are comparable to those of the parent triketones **6** and **8**. In addition, oxidation of the thioxanthene moiety in **5e** shifts the absorption maximum to 449 nm. Whereas the diphenylvinylidene-bridged compounds **5a** and **5b** do not show any detectable fluorescence in CH_2Cl_2, their more rigid thioxanthylidene-substituted analogues **5c**−**5e** display intense green emission with maximal wavelengths around 500 nm and the quantum yield reaching 0.57 for **5c** (Table 1).[21]

To elucidate the effects influencing the UV−vis absorption properties, density functional theory (DFT) calculations at the B3LYP/6-31G(d,p)[22] level of theory were performed for the *n*-hexyl-substituted compounds **5a**, **5c**, **5e**, **6**, and **9** (Table 1, Figure 4, and the Supporting Information). It is reasonable to assume behavior comparable to that of their TIPS-ethynyl-substituted counterparts. While the HOMO in **5a**, **5c**, and **5e** (and **6**) is mainly localized on the triphenylamine core, the LUMO is significantly delocalized over the arylvinylidene moieties. Hence, the UV−vis absorption bands observed for **5** are of a $\pi-\pi^*$ nature. In contrast to **6**, however, the HOMO in the thiocarbonyl-bridged **9** is localized on the S atoms leading to n−π^* transitions. Overall, the computed excitation energies are in good agreement with the experimental UV−vis absorption spectra, and it can be concluded that the introduction of the rigid thioxanthylidene moieties into **5c** and **5e** results in the lowering of HOMO and LUMO levels and decreases the band gaps compared to those of **5a** with diphenylmethylene bridges (Table 1 and the Supporting Information).

Previously, the carbonyl-bridged heterotriangulene was identified as a fairly strong two-electron acceptor with the first reduction at approximately −1.40 V (vs Fc^+/Fc).[7c] To investigate the evolution of its redox properties in relation to the particular bridging moieties, electrochemical studies were performed (Table 1 and the Supporting Information). For thiocarbonyl-bridged **10**, the first reduction is observed at −0.94 V, which corresponds to an anodic shift of 500 mV when compared to its carbonyl counterpart **8**.[7c] On the other hand, the introduction of the arylvinylidene tethers imparts electron-donating character to the heterotriangulene scaffold.

Thus, the diphenylvinylidene-substituted derivatives **5a** and **5b** exhibit three reversible one-electron oxidations with the first nitrogen-centered electron transfer at +0.05 and +0.32 V, respectively. For comparison, the dimethylmethylene-bridged compound **1** forms the corresponding radical cation at +0.34 V and triphenylamine is oxidized at +0.53 V under similar conditions.[3c,5b] The potential difference of 270 mV between **5a** and **5b** may be ascribed to the electron-withdrawing effect of the acetylenic moieties in **5b**.[23] At first sight, it might appear somewhat surprising that compounds **5c** and **5d** decorated with the electron-rich thioxanthene moieties are not the strongest electron donors in the series. In agreement with the computational results, this observation can most likely be explained by rather inefficient electronic communication between the distorted heterotriangulene core and the lateral π systems (*vide supra*). Furthermore, only a limited anodic shift of 150 mV of the first oxidation potential is observed when going from **5c** to **5e** with the electron-withdrawing sulfones,[15] which further supports the anticipated limited conjugation between the nitrogen-centered core and the bridging π systems. In addition, **5e** accepts three electrons in two consecutive

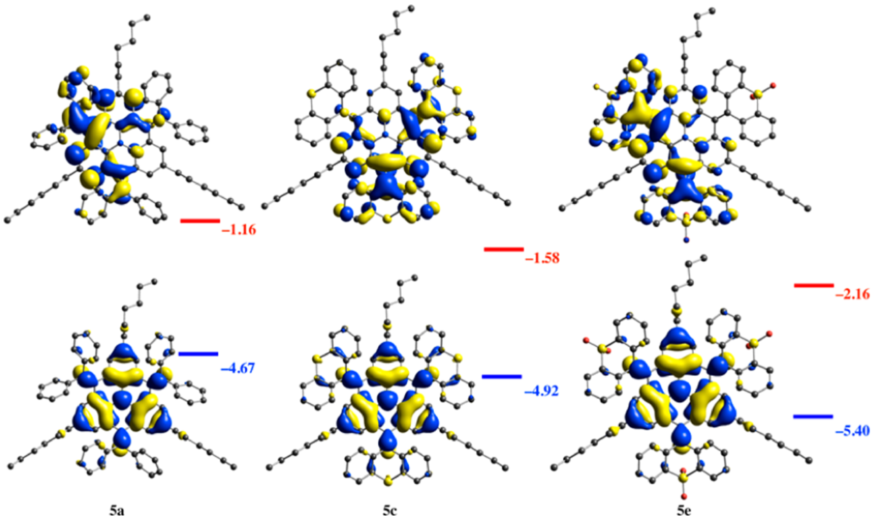

Figure 4. Frontier molecular orbitals of **5a**, **5c**, and **5e**. HOMO (blue bars) and LUMO (red bars) energies are given in eV at the B3LYP/6-31G(d,p) level of theory.

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reduction steps at −2.03 and −2.19 V located at the SO_2 groups.[24]

In conclusion, a versatile synthetic protocol allowing the transformation of electron-deficient carbonyl-bridged heterotriangulenes into their expanded electron-rich arylvinylidene counterparts has been elaborated. This method employing the thionation/Barton−Kellogg olefination sequence is complementary to the previously reported synthesis of related π systems in which prior introduction of the electron-withdrawing pentafluorophenyl substituents to increase the electrophilicity of the acridone-type carbonyls in **3** was crucial to the applied dibromoolefination.[10,25] Indeed, the newly developed approach afforded fairly strong electron donors capable of several reversible oxidation steps with the diphenylvinylidene-bridged compound **5a** undergoing the first oxidation at almost the same potential as ferrocene. Such compounds are of great interest for the formation of intermolecular charge-transfer complexes and/or mixed valence organic materials.[26]

EXPERIMENTAL SECTION

General. Reagents were purchased at reagent grade and used without further purification. Analytical TLC analysis was performed on aluminum plates coated with a 0.20 mm silica gel containing a fluorescence indicator. TLC plates were visualized by exposure to ultraviolet light (254 and 366 nm). Column chromatography was performed on silica gel (230−400 mesh). The syntheses of **7**,[8] **8**,[7c] (9*H*-thioxanthen-9-ylidene)hydrazine,[14a] 9-diazo-9*H*-thioxanthene,[14b] and diphenyldiazomethane[14a] were performed according to literature procedures. Melting points were determined in open capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent signal as an internal reference (^{1}H, $CDCl_3$ at 7.26 ppm and CD_2Cl_2 at 5.32 ppm; ^{13}C, $CDCl_3$ at 77.16 ppm and CD_2Cl_2 at 53.8 ppm) and recorded at ambient probe temperature. Chemical shift values are reported in parts per million relative to the signal of tetramethylsilane (TMS). Coupling constants (J) are given in hertz. The apparent resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Infrared spectra (IR) were recorded on an ATR mode spectrometer, and characteristic IR absorptions are reported in cm^{-1} and denoted as strong (s), medium (m), and weak (w). UV−vis absorption and emission spectra were recorded in a quartz cuvette (1 cm) at room temperature. The absorption maxima (λ_{max}) are reported in nanometers with the extinction coefficient (ε) in M^{-1} cm^{-1}; shoulders are indicated as sh. Relative fluorescence quantum yields were calculated using quinine bisulfate in aqueous 0.1 M H_2SO_4 (Φ = 0.54) as a standard.[27] Non-degassed, spectroscopic grade solvents and a quartz cuvette (1 cm) were used. Quantum yields were determined using the equation $\Phi_X = \Phi_S(I_S/I_X)(A_X/A_S)(n_X/n_S)^2$, where Φ_S is the reported quantum yield of the standard, I the integrated emission spectrum, A the absorbance at the excitation wavelength, and n the refractive index of the solvent being used [n_X = 1.424 (CH_2Cl_2), and n_S = 1.334 (0.1 M H_2SO_4)].[28] The quotient A_X/A_S = 1, because for the excitation wavelength the intersection of the absorption spectrum of the sample (X) and the standard (S) was used. Mass spectra were measured with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix or without any matrix. The signal of the molecular ion [M]$^+$ is reported in m/z units.

2,6,10-Trihexyl-4*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine-4,8,12-trione (6). To a degassed suspension of **7** (77.0 mg, 0.110 mmol) and [Pd(dppf)Cl_2] (7.3 mg, 0.010 mmol) in dry toluene (11 mL) was added *n*-hexylzinc bromide (0.5 M in THF, 1.0 mL, 0.36 mmol), and the mixture was stirred for 23 h at 60 °C. After the mixture had cooled, saturated aqueous $NaHCO_3$ (10 mL) was added and the mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with H_2O (1 × 20 mL), dried ($MgSO_4$), and filtered, and the solvents were removed under reduced pressure. Column chromatography (SiO_2, hexanes/CH_2Cl_2 1:2) and recrystallization from CH_2Cl_2/MeOH provided **6** as a yellow solid (38.2 mg, 60%): mp 219−220 °C; R_f = 0.39 (SiO_2, hexanes/CH_2Cl_2 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 6H), 2.93 (t, J = 7.7 Hz, 6H), 1.80 (q, J = 7.5 Hz, 6H), 1.44−1.29 (m, 18H), 0.90 (t, J = 6.9 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 140.8, 135.9, 134.4, 123.3, 35.3, 31.8, 31.3, 29.1, 22.7, 14.2; IR (ATR) 2927 (m), 2856 (w), 1652 (s), 1596 (m), 1468 (m), 1346 (w), 1293 (w), 801 cm^{-1} (w); UV−vis (CH_2Cl_2) λ_{max} (ε) 424 (33800), 266 nm (89800); HRMS (ESI-TOF) [M + H]$^+$ calcd for $C_{39}H_{46}NO_3{}^+$ m/z 576.3472, found m/z 576.3448. Anal. Calcd for $C_{39}H_{45}NO_3$: C, 81.35; H, 7.88; N, 2.43. Found: C, 81.10; H, 7.86; N, 2.45.

2,6,10-Trihexyl-4*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine-4,8,12-trithione (9). A solution of **6** (160 mg, 0.278 mmol) and Lawesson's reagent (404 mg, 1.00 mmol) was stirred in anhydrous toluene (8 mL) for 10 min at rt. The mixture was heated to 90 °C for 1.5 h until TLC analysis indicated consumption of **6**. Purification via column chromatography (SiO_2, hexanes/CH_2Cl_2 3:1) gave **9** as a magenta solid (158 mg, 91%): mp 218−219 °C dec; R_f = 0.95 (SiO_2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.13 (s, 6H), 2.86 (t, J = 7.8 Hz, 6H), 1.82−1.72 (m, 6H), 1.46−1.34 (m, 18H), 0.92 (t, J = 6.9 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 142.0, 138.3, 130.6, 126.1, 35.2, 31.8, 31.1, 29.3, 22.8, 14.3; IR (ATR) 2921 (s), 2854 (m), 1578 (s), 1456 (s), 1422 (m), 1222 (m), 1173 (s), 1209 (w), 911 cm^{-1} (w); UV−vis (CH_2Cl_2) λ_{max} (ε) 572 (27900), 310 (36000), 252 nm (34500); HRMS (ESI-TOF) [M]$^+$ calcd for $C_{39}H_{45}NS_3$ m/z 623.2709, found m/z 623.2711. Anal. Calcd for $C_{39}H_{45}NS_3$: C, 75.07; H, 7.27; N, 2.24; S, 15.42. Found: C, 74.07; H, 7.29; N, 2.29; S, 15.00.

2,6,10-Tris[(triisopropylsilyl)ethynyl]-4*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine-4,8,12-trithione (10). A solution of **8** (60.0 mg, 0.0694 mmol) and Lawesson's reagent (101 mg, 0.250 mmol) were stirred in dry toluene (8 mL) at rt for 10 min and subsequently heated to 90 °C for 1 h. After complete consumption of **8**, the reaction mixture was purified via filtration through a plug (Al_2O_3, CH_2Cl_2) that gave **10** as a purple solid (57.1 mg, 90%): mp >350 °C dec; R_f = 0.97 (SiO_2, hexanes/CH_2Cl_2 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36 (s, 6H), 1.19 (s, 63H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 140.7, 131.3, 127.7, 123.6, 103.8, 95.9, 18.8, 11.4; IR (ATR) 2941 (m), 2855 (m), 1558 (m), 1425 (s), 1153 (m), 1026 (m), 880 (m), 714 (s), 663 cm^{-1} (s); UV−vis (CH_2Cl_2) λ_{max} (ε) 577 (25000), 316 (47500), 272 nm (77200); HRMS (ESI-TOF) [M]$^+$ calcd for $C_{54}H_{69}NS_3Si_3$ m/z 911.3894, found m/z 911.3893. Anal. Calcd for $C_{54}H_{69}NS_3Si_3$: C, 71.07; H, 7.62; N, 1.53; S, 10.54. Found: C, 70.74; H, 8.03; N, 1.64; S, 10.62.

4,8,12-Tris(diphenylmethylene)-2,6,10-trihexyl-8,12-dihydro-4*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine (5a). To a solution of thioketone **9** (75.0 mg, 0.120 mmol) in anhydrous THF (7 mL) was added in portions diphenyldiazomethane (77.1 mg, 0.397 mmol) in dry THF (3 mL), and the mixture was stirred at rt for 2 h. The solvent was removed under reduced pressure, the residue redissolved in anhydrous xylenes (7 mL), and PPh_3 (104 mg, 0.397 mmol) added. After the mixture had been stirred at 135 °C for 16 h, column chromatography (Al_2O_3, hexanes/CH_2Cl_2 4:1) and recrystallization from CH_2Cl_2/MeOH provided **5a** as yellow needles (56.3 mg, 46%): mp 265−271 °C; R_f = 0.74 (SiO_2, hexanes/CH_2Cl_2 2:1); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.34−7.24 (m, 24H), 7.19−7.14 (m, 6H), 6.68 (s, 6H), 1.87 (t, J = 7.7 Hz, 6H), 1.28−1.19 (m, 6H), 1.15−1.08 (m, 6H), 0.93−0.80 (m, 15H), 0.74−0.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.5, 136.5, 134.7, 130.0, 129.0, 128.4, 128.0, 126.5, 121.0, 35.0, 31.9, 31.3, 28.9, 22.7, 14.3; IR (ATR) 3055 (w), 2922 (s), 2854 (m), 1601 (w), 1432 (m), 1276 (m), 750 (m), 700 cm^{-1} (s); UV−vis (CH_2Cl_2) λ_{max} (ε) 405 (27700), 320 nm (39400); HRMS (ESI-TOF) [M]$^+$ calcd for $C_{78}H_{75}N$ m/z 1025.5894, found m/z 1025.5913. Anal. Calcd for $C_{78}H_{75}N$: C, 91.27; H, 7.36; N, 1.36. Found: C, 91.25; H, 7.47; N, 1.35.

4,8,12-Tris(diphenylmethylene)-2,6,10-tris[(triisopropylsilyl)ethynyl]-4*H*,8*H*,12*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine (5b). To a solution of thioketone **10** (103 mg, 0.113 mmol) in dry THF (5 mL) was added in portions a solution of diphenyldiazomethane (72.4 mg, 0.373 mmol) in dry THF (2 mL). The reaction mixture was stirred at rt for 2 h, and the solvent was removed under reduced pressure. The residue was dissolved in anhydrous xylenes (7 mL), PPh_3 (97.8 mg, 0.373 mmol) added, and the mixture stirred at 135 °C for 16 h. Column chromatography (SiO_2, hexanes/CH_2Cl_2 4:1) provided **5b** as an orange powder (75.8 mg, 51%): mp 369−371 °C; R_f = 0.30 (SiO_2, hexanes/CH_2Cl_2 4:1); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.32−7.26 (m, 24H), 7.21−7.17 (m, 6H), 6.89 (s, 6H), 1.01 (s, 63H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 142.7, 140.7, 136.1, 131.7, 129.9, 128.9, 127.5, 126.8, 121.6, 117.8, 106.7, 89.6, 18.8, 11.6; IR (ATR) 3057 (w), 2944 (m), 2862 (m), 2148 (w), 1439 (s), 1270 (m), 883 (m), 702 (s), 684 cm^{-1} (s); UV−vis (CH_2Cl_2) λ_{max} (ε) 404 (sh, 21600), 363 (40900), 306 nm (27900); HRMS (ESI-TOF) $[M]^+$ calcd for $C_{93}H_{99}NSi_3$ m/z 1313.7080, found m/z 1313.7069. Anal. Calcd for $C_{93}H_{99}NSi_3$: C, 84.94; H, 7.59; N, 1.07. Found: C, 84.87; H, 7.63; N, 1.04.

2,6,10-Trihexyl-4,8,12-tris(9*H*-thioxanthen-9-ylidene)-8,12-dihydro-4*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine (5c). To a solution of freshly prepared 9-diazo-9*H*-thioxanthene (269 mg, 1.20 mmol) in dry THF (3 mL) was added **9** (122 mg, 0.200 mmol) in dry toluene (10 mL) at 0 °C. After the mixture had been stirred at 0 °C for 1.5 h, the solvent was removed under reduced pressure. The residue was dissolved in dry xylenes (5 mL), PPh_3 (202 mg, 0.771 mmol) added, and the mixture stirred at 135 °C for 21 h. The resulting solution was purified via filtration through a plug (SiO_2, CH_2Cl_2/hexanes 3:1) followed by column chromatography (SiO_2, CH_2Cl_2/hexanes 2:1) to provide **5c** as a yellow solid (112 mg, 50%): mp 310−314 °C; R_f = 0.79 (SiO_2, hexanes/CH_2Cl_2 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.61 (m, 6H), 7.22−7.16 (m, 12H), 7.12−7.10 (m, 6H), 6.62 (s, 6H), 1.96 (t, J = 7.3 Hz, 6H), 1.29−1.22 (m, 6H), 1.19−1.11 (m, 6H), 1.07−1.01 (m, 12H), 0.90 (t, J = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 137.2, 137.1, 136.1, 129.7, 129.1, 128.6, 128.1, 126.6, 126.5, 126.1, 120.3, 35.0, 31.8, 31.0, 29.2, 22.6, 14.3; IR (ATR) 3058 (w), 2921 (s), 2854 (m), 1454 (s), 1428 (s), 1271 (s), 762 (m), 740 (s), 699 cm^{-1} (w); UV−vis (CH_2Cl_2) λ_{max} (ε) 430 (30400), 323 (sh, 33600), 302 nm (38600); HRMS (ESI-TOF) $[M]^+$ calcd for $C_{78}H_{69}NS_3$ m/z 1115.4587, found m/z 1115.4577. Anal. Calcd for $C_{78}H_{69}NS_3$: C, 83.90; H, 6.23; N, 1.25; S, 8.62. Found: C, 83.75; H, 6.25; N, 1.22; S, 8.40.

4,8,12-Tris(9*H*-thioxanthen-9-ylidene)-2,6,10-tris-[(triisopropylsilyl)ethynyl]-8,12-dihydro-4*H*-benzo[1,9]-quinolizino[3,4,5,6,7-*defg*]acridine (5d). A solution of **10** (71.2 mg, 0.078 mmol) in dry toluene (3 mL) was added to freshly prepared 9-diazo-9*H*-thioxanthene (105 mg, 0.468 mmol) in dry THF (3 mL) at 0 °C. After the mixture had been stirred at this temperature for 1.5 h, the solvent was removed under reduced pressure. The residue was dissolved in dry xylenes (5 mL), PPh_3 (61.4 mg, 0.234 mmol) added, and the mixture stirred at 135 °C for 21 h. The crude product was purified via column chromatography (SiO_2, hexanes/EtOAc 12:1) to provide **5d** as a yellow solid (63.1 mg, 58%): mp 312−317 °C; R_f = 0.85 (SiO_2, hexanes/CH_2Cl_2 3:1); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.62 (d, J = 7.6 Hz, 6H), 7.27−7.20 (m, 6H), 7.17−7.16 (m, 12H), 6.80 (s, 6H), 1.02 (s, 63H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 137.23, 137.19, 136.1, 132.2, 132.1, 128.7, 128.0, 127.6, 126.2, 124.0, 120.7, 118.3, 106.2, 90.8, 18.9, 11.6; IR (ATR) 3061 (w), 2942 (m), 2861 (m), 1592 (w), 1430 (s), 1265 (s), 882 (m), 761 (m), 742 (m), 702 (m), 671 cm^{-1} (m); UV−vis (CH_2Cl_2) λ_{max} (ε) 428 (27000), 357 nm (50100); HRMS (ESI-TOF) $[M]^+$ calcd for $C_{93}H_{93}NS_3Si_3$ m/z 1403.5772, found m/z 1403.5778. Anal. Calcd for $C_{93}H_{93}NS_3Si_3$: C, 79.49; H, 6.67; N, 1.00; S, 6.84. Found: C, 79.34; H, 7.00; N, 0.97; S, 6.47.

4,8,12-Tris(10,10-dioxido-9*H*-thioxanthen-9-ylidene)-2,6,10-trihexyl-4*H*,8*H*,12*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]-acridine (5e). To a solution of **5c** (10.0 mg, 0.090 mmol) in CH_2Cl_2 (3 mL) were added H_2O_2 (30 wt %, 0.4 mL) and glacial acetic acid (0.1 mL). After the mixture had been stirred for 3 days at rt, the solution was washed repeatedly with an excess of H_2O, dried ($MgSO_4$), and passed through a short plug (SiO_2, CH_2Cl_2). Precipitation from CH_2Cl_2/hexanes gave **5e** as yellow crystals (10.2 mg, 94%): mp >350 °C dec; R_f = 0.54 (SiO_2, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.14 (dd, J = 7.8, 1.0 Hz, 6H), 7.49 (td, J = 7.7, 1.1 Hz, 6H), 7.35 (td, J = 7.6, 1.2 Hz, 6H), 7.26 (d, J = 7.8 Hz, 6H), 6.94 (s, 6H), 2.10 (t, J = 7.4 Hz, 6H), 1.30−1.23 (m, 6H), 1.19−1.12 (m, 6H), 1.10−1.04 (m, 12H), 0.91 (t, J = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 140.4, 140.2, 138.8, 135.6, 131.1, 130.4, 130.3, 129.4, 127.8, 124.8, 119.8, 35.0, 32.0, 31.9, 29.5, 22.9, 14.3 (17 signals of 18 expected); IR (ATR) 2928 (m), 2854 (w), 1607 (w), 1456 (m), 1314 (s), 1166 (s), 1126 (w), 765 cm^{-1} (m); UV−vis (CH_2Cl_2) λ_{max} (ε) 449 (40300), 350 (40400), 293 (36600), 256 nm (60600); HRMS (ESI-TOF) $[M]^+$ calcd for $C_{78}H_{69}NO_6S_3$ m/z 1211.4282, found m/z 1211.4278; Anal. Calcd for $C_{78}H_{69}NO_6S_3 \cdot 2H_2O$: C, 75.03; H, 5.89; N, 1.12; S, 7.70. Found: C, 75.44; H, 6.27; N, 1.01; S, 6.95.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra, crystal structure data for compounds **5b** (CCDC 1023082), **5d** (CCDC 1023084), and **5e** (CCDC 1023083), photophysical properties, detailed electrochemistry, and theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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