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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Expanding the Chemical Structure Space of Opto-Electronic Molecular Materials: Unprecedented Push–Pull Chromophores by Reaction of a Donor-Substituted Tetracyanofulvene with Electron-Rich Alkynes

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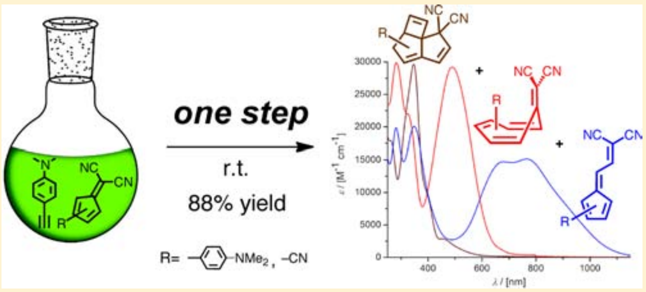
Ⓢ *Supporting Information*



ABSTRACT: The reaction of a 3,5-bis(*N*,*N*-dimethylanilino)-substituted 2,4,6,6-tetracyanopentafulvene (TCPF) with mono- and bis(*N*,*N*-dimethylanilino)acetylene provides facile access to push–pull chromophores with diverse new scaffolds. The starting TCPF reacts with bis(*N*,*N*-dimethylanilino)acetylene in a formal [2+2] cycloaddition at the exocyclic double bond, followed by retroelectrocyclization, to yield an ethenylene-extended push–pull pentafulvene. The transformation with 4-ethynyl-*N*,*N*-dimethylaniline also yields a similar extended pentafulvene as well as two other products that required X-ray analysis for their structure elucidation. One features an 8,8-dicyanoheptafulvene core formed by formal [2+2] cycloaddition, followed by ring opening via fragmentation. The second is a chiral cyclobutenylated tetrahydropentalene, resulting from a cascade of formal [6+2] and [2+2] cycloadditions. All new nonplanar push–pull chromophores display amphoteric redox behavior with both strong electron-donating and -accepting potency. Notably, the *N*,*N*-dimethylanilino-substituted extended pentafulvenes show remarkably low oxidation potentials (0.27/0.28 V vs Fc/Fc$^+$ reference) that are lower than those for *N*,*N*-dimethylaniline itself. The push–pull-substituted extended pentafulvenes feature intense electronic absorption bands, extending over the entire visible spectral range into the near infrared, and low highest occupied molecular orbital–lowest unoccupied molecular orbital gaps. These properties, together with high thermal stability and good solubility, suggest the potential use of the new chromophores as advanced materials in molecular electronics devices.

■ INTRODUCTION

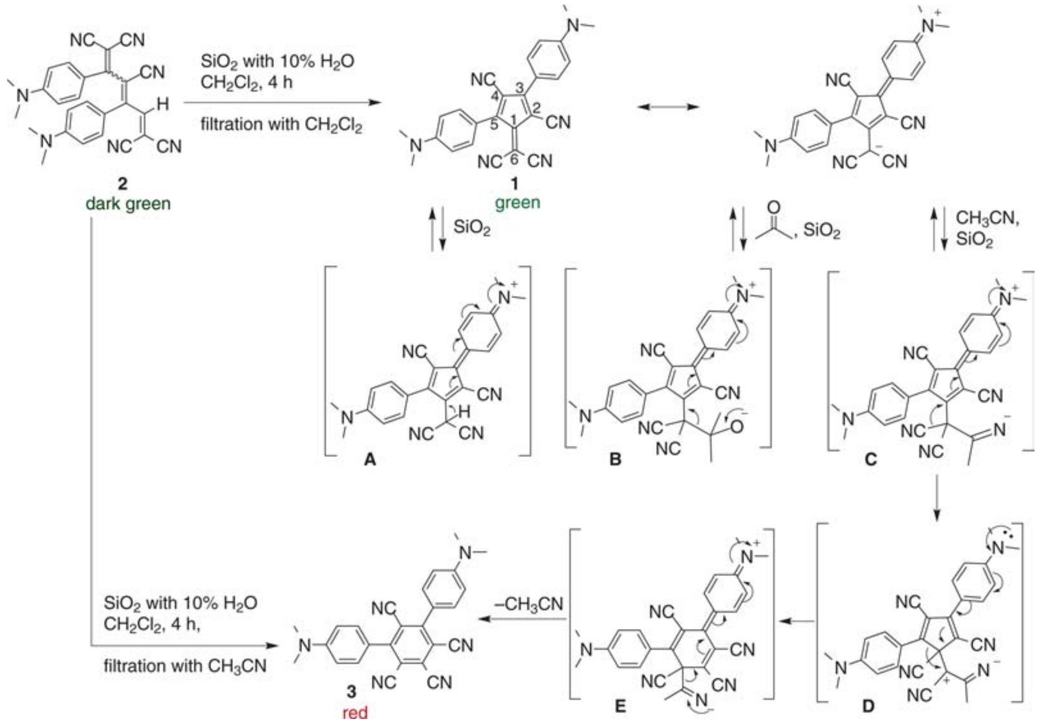
The performance of organic opto-electronic materials[1,2] relies on the ability to efficiently transfer electrons from a high-lying highest occupied molecular orbital (HOMO, an electron "donor") to a low-lying lowest unoccupied molecular orbital (LUMO, an electron "acceptor"). A low HOMO–LUMO gap is characteristic of conjugated π-chromophores substituted with strong electron donors (D) and acceptors (A), and such "push–pull" systems have been extensively investigated.[3] Additional interest in D–A chromophores arises from their electrochemically amphoteric behavior leading to a range of readily accessible redox states.[4]

Fulvenes make up an interesting class of non-benzenoid chromophores[5] that in recent years have been decorated with donor and acceptor functionalities to tune the HOMO–LUMO gap.[6] Substituted 6,6-dicyanopentafulvenes and 8,8-dicyanoheptafulvenes were found to show promising optical nonlinearities.[7] Recently, phenylated 6,6-dicyanopentafulvenes were exploited as *n*-type additives in solar cells,[8] whereas the electronic properties of perphenylated and peralkynylated derivatives were investigated by electronic paramagnetic resonance spectroscopy of their radical anions.[9]

The formal [2+2] cycloaddition (CA) of donor-substituted alkynes to electron-deficient olefins, followed by retroelectrocyclization (RE) (CA–RE reaction), is a highly efficient, broadly applicable method[3e,g,10] for accessing stable, soluble, nonplanar push–pull chromophores with intense intramolecular charge-transfer absorptions (ICT) and high third-order optical nonlinearities. Some of these compounds have already found application in opto-electronic devices.[11] During investigations aimed at further extending the scope of this transformation, we serendipitously prepared 3,5-bis[(4-dimethylamino)phenyl]-substituted 2,4,6,6-tetracyanopentaful-

Received: December 11, 2012
Published: January 25, 2013

Scheme 1. A Possible Mechanism for the (Acidic) SiO_2/MeCN-Promoted Rearrangement of Pentacyanohexa-1,3,5-triene 2 via TCPF 1 to Tetracyanobenzene 3[a]



[a] The colors correspond to those of the solutions.

vene (TCPF) **1** (Scheme 1), a stable, high-melting solid featuring an intense, bathochromically shifted ICT band (λ_{max} = 782 nm; ε = 27500 M^{-1} cm^{-1}) expanding from 600 to ~1100 nm in CH_2Cl_2.[12] We subsequently became interested in exploring the reactivity of TCPF **1** in the CA–RE reaction and report here its transformation with activated, *N*,*N*-dimethylanilino (DMA)-substituted alkynes. These reactions led to the formation of a variety of unusual ICT chromophores, thereby expanding the chemical structure space for push–pull systems featuring opto-electronic properties of interest for potential device applications, such as in organic solar cells.[8b]

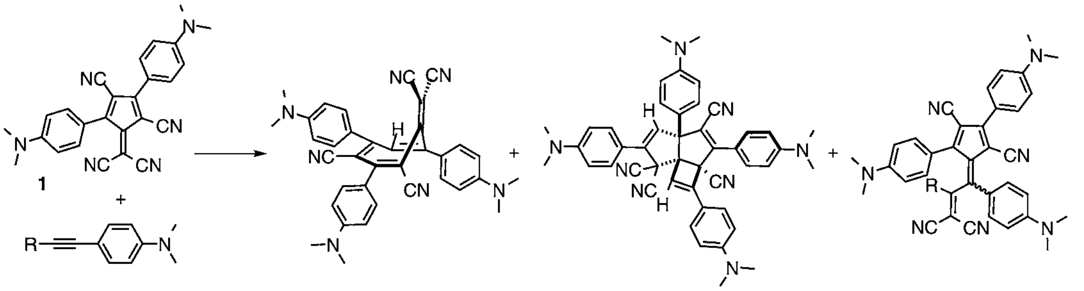
■ RESULTS AND DISCUSSION

Preparation of TCPF 1 and Its SiO_2-Promoted Rearrangement. The interesting opto-electronic properties of **1** mandated the development of an improved synthetic protocol starting from (*E*/*Z*)-1,1,3,6,6-pentacyanohexa-1,3,5-triene **2** (Scheme 1).[12] The latter compound is available in one step by CA–RE reaction of 3-DMA-1,1,2,4,4-pentacyanobuta-1,3-diene with 4-ethynyl-*N*,*N*-dimethylaniline. Treatment of **2** with acidic wet SiO_2 [10% (w/w) H_2O] in CH_2Cl_2 for 4 h, followed by filtration with a 2:1 CH_2Cl_2/Me_2CO mixture and column chromatography, afforded pure TCPF **1** in 70% yield. For reproducible high yields of **1**, the addition of water to SiO_2 is essential, as exposure of **2** to untreated SiO_2 yielded substantial amounts of the red-colored tetracyanobenzene **3** (for X-ray, see Figure 3SI of the Supporting Information). Independent of the treatment of SiO_2 with water, hexasubstituted benzene **3** was the exclusive product if MeCN was used instead of a 2:1 CH_2Cl_2/Me_2CO mixture for the filtration described above.

We monitored these transformations more carefully, with the following findings. The dark green-colored solution of pentacyanohexatriene **2** changed upon treatment with moisturized SiO_2 in CH_2Cl_2 to a maroon-colored solution after 45 min. Filtration after 4 h with a 2:1 CH_2Cl_2/Me_2CO mixture generated a purple filtrate, which adopted the green color of TCPF **1** upon dilution with CH_2Cl_2 and standing for ~5 h. This suggests an intermediate purple-colored complex **B** (Scheme 1), an addition product to acetone. In contrast, a brownish-maroon filtrate was obtained when the suspension was filtered with MeCN, and after 10 min, the red color indicated a complete transformation to **3**. These observations were confirmed by LC–MS, showing full consumption of **2** and formation of either **1** or **3** (Figure 1SI of the Supporting Information).

TCPF **1** is stable in a CH_2Cl_2 solution but is completely transformed to hexasubstituted benzene **3** under the conditions for the preparation of **3** from **2**, suggesting **1** is a direct precursor of **3** (Scheme 1). A zwitterionic resonance structure of **1**, due to D–A conjugation, allows the formation of adducts to polar solvents containing electrophilic centers, such as **B** and **C** with acetone and acetonitrile, respectively. Similarly, **1** may be reversibly protonated at C(6) (intermediate **A**) by the acidic wet SiO_2. Adducts **A** and **B** revert to **1** upon dilution with CH_2Cl_2. MeCN adduct **C**, on the other hand, undergoes an irreversible 1,2-CN migration from C(6) to C(1) generating intermediate **D**, a carbocation stabilized by two π-substituents. Subsequent ring expansion of intermediate **D** to **E**, followed by elimination of MeCN, leads to hexasubstituted benzene **3**. Interestingly, Shoji et al. recently reported the isolation of a 3,5-bis-azulenyl-substituted 2,4,6,6-tetracyanopentafulvene by SiO_2 chromatography with a CH_2Cl_2/EtOAc mixture as the eluent.[13] They did not report a 1,2-CN rearrangement, probably because of the weaker electron-donating ability of the azulenyl versus the DMA substituents in **1**. To the best of our knowledge, such

Scheme 2. Transformations of TCPF 1 with Electron-Rich Alkynes[a]



4: R = H (i) **5** (±)-**6** **7**: R = H

8: R = 4-Me_2N–C_6H_4 (ii) **9**: R = 4-Me_2N–C_6H_4

10: R = *t*Bu (iii) no reaction

[a]Reagents and conditions: (i) for details see Table 1; (ii) 1:1 $(CH_2Cl)_2$/MeCN, 175 °C, microwave, 1 h, 85%; (iii) 1:1 $(CH_2Cl)_2$/MeCN, 175 °C, microwave, 1 h, no reaction.

a thermal rearrangement of 6,6-dicyanopentafulvenes is unprecedented. However, in theoretical studies of the thermal isomerization of unsubstituted pentafulvene to benzene, an intermediate "prefulvene", a bicyclo[3.1.0]hex-3-ene 2,6-diradical, has been postulated.[14]

Transformations of TCPF 1 with Electron-Rich Alkynes. The reaction of **1** in CH_2Cl_2 or MeCN with electron-rich alkynes was investigated. The transformation with 4-ethynyl-*N*,*N*-dimethylaniline (**4**) gave three new products in an 88% combined yield: ring expanded heptafulvene **5**, cyclobutene-fused tetrahydropentalene (±)-**6**, and extended pentafulvene **7** (Scheme 2). The isolation of all products (see entry 2 in Scheme 2) by column chromatography on SiO_2 was not possible because of the instability of (±)-**6** to SiO_2. This was overcome by using recycling preparative gel permeation chromatography, which allowed the separation of (±)-**6** (36%) from the mixture of **5** and **7**. Subsequent column chromatography on SiO_2 gave **5** (23%) and **7** (29%). The product distribution of this reaction depended moderately on solvent and stoichiometry. In MeCN, **7** was the preferred product (57%), whereas in less polar CH_2Cl_2 and with an equimolar amount of **4**, all three products were obtained in similar amounts. Doubling the amount of **4** favored slightly the formation of (±)-**6** (41%). Heating [e.g., for 5 min at 160 °C in MeCN (see Figure 2SI of the Supporting Information)] reduced the reaction time drastically but led to the formation of additional minor side products.

Table 1

entry	conditions for step i of Scheme 2	4 (equiv)	ratio (%)[a]		
			5	(±)-6	7
1	CH_2Cl_2, 20 °C, 60 h	1	34	32	34
2	CH_2Cl_2, 20 °C, 24 h	2	26 (23)	41 (36)	33 (29)
3	CH_3CN, 20 °C, 60 h	1	24	19	57

[a]The ratios were determined by both LC–MS and ^1H NMR spectroscopy. Isolated yields are given in parentheses.

The reaction of **1** with bis-DMA-acetylene **8** required much harsher conditions (175 °C for 1 h in a sealed tube) and gave selectively the diastereoisomeric mixture **9** in 85% yield (Scheme 2), in a 1:0, 1:1, or 0:1 $(CH_2Cl)_2$/MeCN mixture. The *tert*-butylated DMA-acetylene **10** did not react with TCPF **1**, even under forcing conditions (up to 175 °C and microwave irradiation). Apparently, steric hindrance renders the attack of **8** more difficult and even prevents the reaction of **10** entirely.

Structural Characterization. The structures of **5**, (±)-**6**, **7**, and **9** were evidenced by single-crystal X-ray analysis (Figure 1). Crystals suitable for X-ray analysis were obtained for **5**, (±)-**6**, and **7** by slow diffusion of pentane into CH_2Cl_2 or $CHCl_3$ solutions and for **9** by slow diffusion of pentane into a toluene solution. Single crystals of heptafulvene **5** contain three distinct molecules in the unit cell (Figure 4SI of the Supporting Information), differing mainly in the orientation of the DMA units. The cycloheptatriene ring of **5** adopts a boat-shaped conformation (a $^{4,5,1}B$ conformation according to Stoddart's notation for carbohydrates[15] in which atoms 4, 5, and 1 are above the reference plane). The double and single bonds in the heptafulvene ring are fully localized, showing that **5** does not display aromatic character (for bond lengths, see Figure 4SI of the Supporting Information).

The structure of (±)-**6** shows an enantiomeric pair in the unit cell. The DMA moiety at the ring junction and the annulated cyclobutene ring are in *exo* positions (Figure 1). The X-ray crystal structure of the extended pentafulvenes **7** and **9** shows *Z*- and *E*-configurations, respectively, at the exocyclic double bond. The *Z*-configuration of **7** is kept upon introduction of the DMA substituent at C(7), leading to **9** (note the change in the Cahn–Ingold–Prelog sequence upon introduction of the additional DMA substituent of **9**). The *E*-diastereoisomer of **7** is disfavored because of allylic $A^{(1,3)}$ strain.[16] Because **9** exists as an *E*/*Z* mixture in solution (see below), 10 different crystals of **9**, obtained from the same batch, were analyzed by X-ray diffraction. All single crystals analyzed had the same unit cell dimensions, suggesting that only the *E*-isomer had crystallized. Furthermore, the ^1H NMR spectrum of crystals of **9** recorded at −20 °C in CD_2Cl_2 showed exclusively signals of the *E*-isomer (Figure 18SI of the Supporting Information). When the sample was warmed to 20 °C, signals for a 3:1 *E*/*Z* mixture were observed (Figure 18SI of the Supporting Information), indicating that *E*/*Z*-isomerization in solution is facile at room temperature.

Intramolecular D–A interactions, that is, the interaction between the π-conjugated DMA donor and the cyanated pentafulvene core, enhance the quinoid character (δr) of the DMA group (for a comprehensive summary of all δr values, see Table 1SI of the Supporting Information).[17,18] A high δr

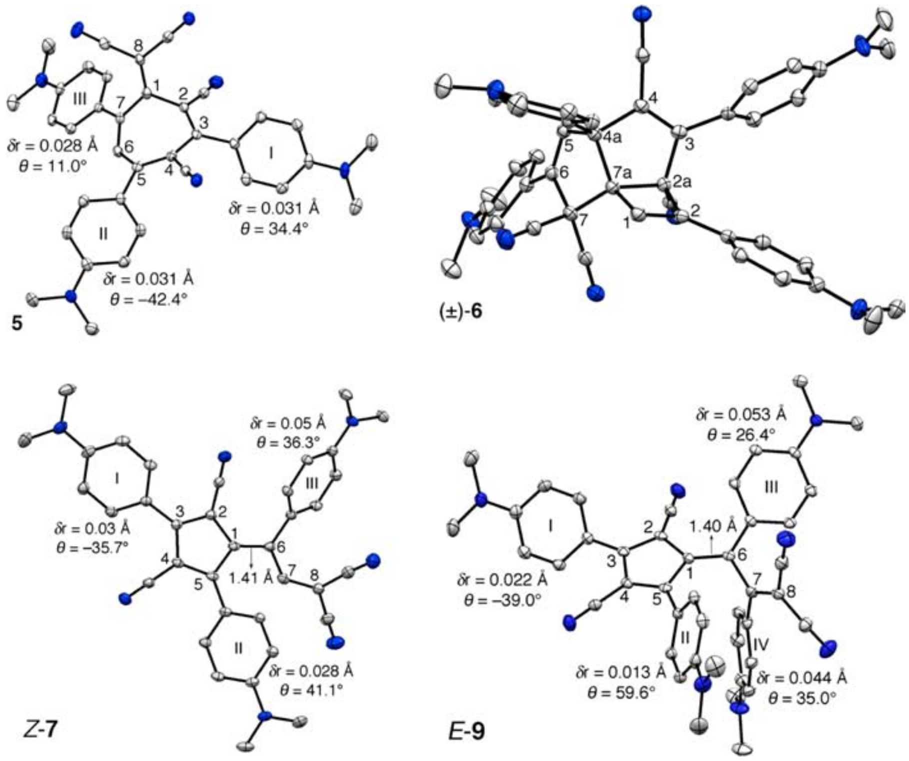


Figure 1. ORTEP plots of **5** (conformer A), (±)-**6**, *Z*-**7**, and *E*-**9** (arbitrary numbering; H atoms omitted for clarity). Atomic displacement parameter ellipsoids shown at the 50% probability level. T = 100 K. For details of the X-ray analyses, including selected bond lengths and angles, see Figures 4SI−7SI of the Supporting Information. Different DMA moieties in a molecule are marked as I−IV. The fulvene numbering is used for **5**, **7**, and **9** in the theoretical part; however, the numbering in the experimental part follows the systematic IUPAC nomenclature (as proposed by the ACD software). For the definition of the quinoid character (δr) of the DMA groups, see ref 17 and the text; θ is the torsional angle between the DMA planes and the acceptor moieties.

correlates with a low torsional angle θ between the π-planes of donor and acceptor moieties, as found for the DMA group at C(3) of **1** (δr_{I} = 0.065; θ_{I} = −13.6°).[12] For example, DMA group III (Figure 1) at C(6) in *E*-**9** (δr_{III} = 0.053; θ_{III} = 26.4°) has a better conjugation with the pentafulvene core than DMA group I at C(3) (δr_{I} = 0.022; θ = −39.0°). Similar to **1**, DMA group II at C(5) of *Z*-**7** and *E*-**9** has a low quinoid character (for *Z*-**7**, δr_{II} = 0.028 and θ_{II} = 41.1°; for *E*-**9**, δr_{II} = 0.013 and θ_{II} = 59.6°). Further proof of the efficient D−A interactions in both *Z*-**7** and *E*-**9** comes from the lengthening of the exocyclic double bond on the cyclopentadienyl core, found to be 1.41 and 1.40 Å, respectively (Figure 1), compared to the length of 1.35 Å for a 6-aryl-substituted 2,3,4,5-tetrachloropentafulvene.[19] The high quinoidal character of DMA group III at C(6) and the reduced double bond character of the exocyclic C(1)−C(6) bond together indicate a facile *E*/*Z* isomerization around this bond.

Proposed Mechanism for the Formation of the New Chromophores. The formation of **5** and (±)-**6** most probably proceeds first through attack at the C(5) position of **1** by the terminal C atom of the acetylene (pathway A, Figure 2), generating a stabilized zwitterion.[20] The latter may complete a formal [2+2] CA to yield a bicyclo[3.2.0]heptadiene derivative. Its *cis*-oriented DMA and cyano groups at the ring junctions are ideally located for ring opening via fragmentation and following isomerization afford the donor-substituted tetracyanoheptafulvene **5**. Alternatively, the zwitterion may react at C(6) to complete a formal [6+2] CA, generating the racemic dihydropentalene **11**. The more accessible of the two cyanovinyl units in the bicyclic core in **11** subsequently undergoes a second formal [2+2] CA with excess **4**.[21] The resulting cyclobutene (±)-**6** cannot undergo a RE reaction, because a thermally allowed conrotatory ring opening would generate a highly strained *cis,trans,cis*- or a *trans,cis,cis*-cycloheptatriene.[22−24] Indeed, a solution of (±)-**6** in $(CDCl_2)_2$ proved to be stable at 120 °C for 2 days. Pathway B corresponds to the expected regioselective CA−RE reaction, involving initial attack at C(6) under formation of an aromatic cyclopentadienyl anion-containing zwitterionic intermediate,[9] and leads to the ethenylene-extended pentafulvene **7**.

The reactivity profile of TCPF **1** is unique as it gives cycloaddition products at the endo- and exocyclic double bonds of the fulvene core that have not been seen with previously reported pentafulvenes.[9,25] For instance, the ring expansion of push−pull pentafulvene derivatives via [2+2] CA, followed by fragmentation, has been observed only with electron-deficient alkynes, such as dimethyl acetylenedicarboxylate, with the initial attack presumably occurring at C(2) of the endocyclic C(2)═C(3) bond.[25] 6-Aminopentafulvenes[26] and 5,6-dihydropentalenes[27] undergo intermolecular [6+2] cycloaddition, whereas no such addition is known for 6,6-dicyanopentafulvenes. Pentafulvenes bearing a terminal unsaturated substituent at C(6) undergo intramolecular [6+2] cycloaddition to afford tricyclic products.[28]

***E*/*Z* Isomerization of 7 and 9.** The *E*/*Z* isomerization of **7** and **9** in solution was investigated in detail by one- and two-dimensional (DQF-COSY, HSQC, and HMBC) NMR spectroscopy (section 6SI of the Supporting Information), complemented by density functional theory (DFT) calculations (section 7SI of the Supporting Information). A full account of

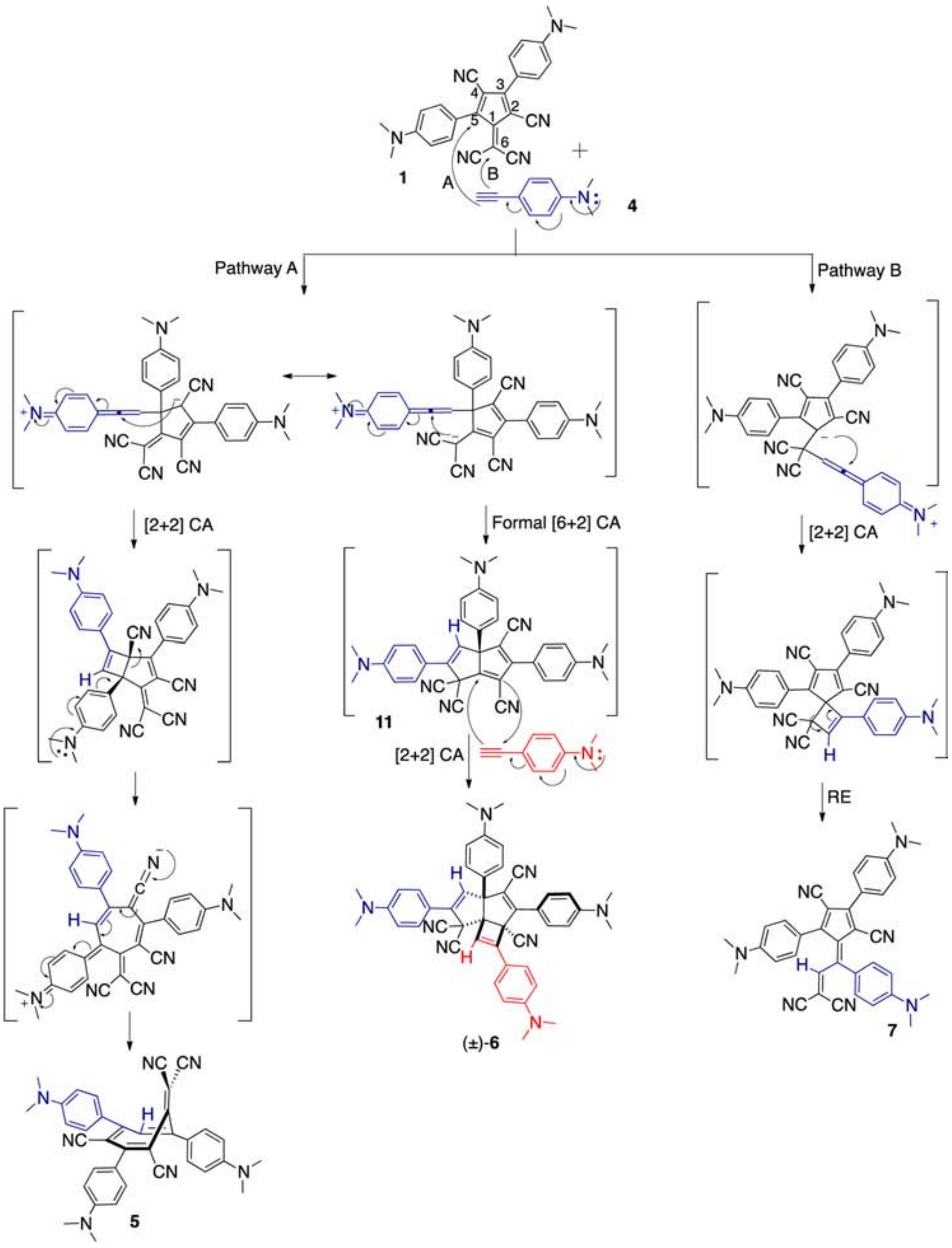


Figure 2. Possible pathways for the regioselective formal [2+2] and [6+2] cycloaddition reactions of TCPF **1** with DMA-acetylene **4**.

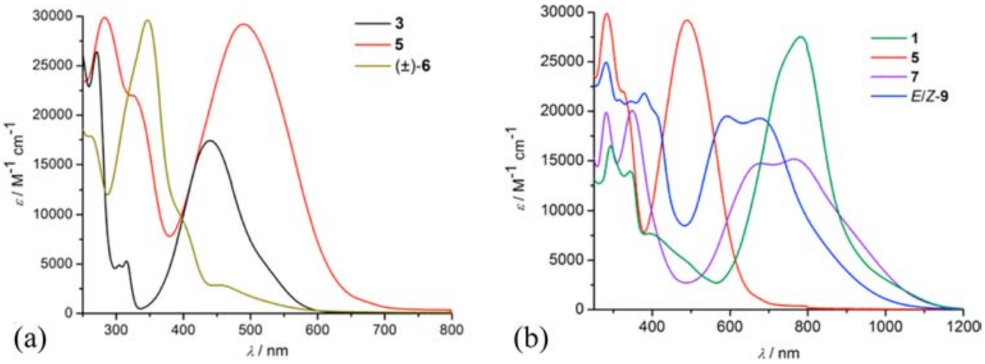


Figure 3. Electronic absorption spectra in CH_2Cl_2 at 293 K. (a) Hexasubstituted benzene **3**, heptafulvene **5**, and cyclobutene-annulated pentalene (±)-**6**. (b) Pentafulvenes **1**, **7**, and *E*/*Z*-**9** and heptafulvene **5**. Solutions of **7** and *E*/*Z*-**9** were equilibrated for 24 h at 293 K prior to measurement.

this elaborate analysis can be found in the Supporting Information, and the most important findings are summarized here. In agreement with the solid state X-ray analysis, the joint experimental−computational analysis revealed that compound

Table 2. Electrochemical and Optical Properties of Compounds 1,[12] 3, 5, (±)-6, 7, and *E*/*Z*-9 Observed by Cyclic Voltammetry

	cyclic voltammetry				optical	
compd	$E°$ (V)[a]	ΔE_p (mV)[b]	$\Delta(E_{ox,1} - E_{red,1})$ (V)	EA[c] (eV)	λ_{max} (nm) (log ε)	λ_{end} (nm) [E (eV)]
1[d]	0.90[e]		1.12	4.35	782 (4.4)	1100 (1.13)
	0.67 (1e$^-$)	60				
	−0.45 (1e$^-$)	60				
	−0.96[e]					
3	0.76[e]		2.08	3.48	440 (4.2)	600 (2.07)
	−1.32 (1e$^-$)	70				
	−2.21 (1e$^-$)[e]					
5	0.72[e,f]		1.78	3.47	490 (4.5)	675 (1.84)
	0.60 (1e$^-$)	60				
	−1.18 (1e$^-$)	80				
	−1.30 (1e$^-$)	80				
(±)-**6**	0.82[e]		2.88	2.46	465 (3.5)	550 (2.26)
	0.64[e]					
	0.54[e]					
	−2.34[e]					
7	0.85 (1e$^-$)[e]		0.94	4.13	765 (4.2)	1150 (1.07)
	0.27 (2e$^-$)	45				
	−0.67 (1e$^-$)	75				
	−0.89 (1e$^-$)	100				
E/*Z*-**9**	0.81[e]		1.16	3.92	710 (4.4)	1000 (1.24)
	0.28 (2e$^-$)	70				
	−0.88 (1e$^-$)	60				
	−1.05 (1e$^-$)	80				

[a] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. Values measured by cyclic voltammetry in a CH_2Cl_2 solution (with 0.1 M Bu_4NPF_6), where ν = 0.1 V/s. Values reported vs Fc/Fc$^+$. [b] $\Delta E_p = E_{pa} - E_{pc}$. [c] EA = E_{red} (V vs Fc$^+$/Fc) + 4.8 eV.[29] [d] Taken from ref 12. [e] E_p is the irreversible peak potential. [f] A redissolution peak was observed on the reverse scan at 0.55 V.

7 is almost exclusively present (>98:2) in the *Z*-configuration in CD_2Cl_2 and in $(CDCl_2)_2$ in the temperature range from −50 to 100 °C. On the other hand, compound **9** exists at room temperature as a mixture of *E*- and *Z*-diastereoisomers with an *E*:*Z* ratio of 3:1 in CD_2Cl_2 and 1:1 in CD_3CN. This is in contrast to the solid-state analysis, which provided X-ray crystals of only the *E*-isomer of **9**. As stated previously, crystals of *E*-**9** dissolved at −20 °C showed only ^{1}H NMR signals of the *E*-isomer; increasing the temperature to 20 °C led to a partial isomerization (Figure 18SI of the Supporting Information). The described NMR analysis allowed us to unambiguously assign the resonances and attachment points of all three DMA groups in *Z*-**7**, and of all four DMA groups in *E*- and *Z*-**9**.

Electronic Absorption Spectroscopy. Tetracyanobenzene **3**, heptafulvene **5**, and the extended pentafulvenes **7** and *E*/*Z*-**9** are dark metallic-shiny solids that are stable at ambient temperature under air and soluble in common organic solvents such as CH_2Cl_2, toluene, acetone, and acetonitrile. The electronic absorption spectra (CH_2Cl_2) of the penta- and heptafulvenes feature intense, bathochromically shifted ICT transitions, as shown in Figure 3.

The ICT band of heptafulvene **5** (Figure 3a) is intense but substantially hypsochromically shifted [λ_{max} = 490 nm (2.53 eV); ε = 29000 M^{-1} cm^{-1}] compared to the corresponding bands in the spectra of the pentafulvene derivatives. We ascribe this hypsochromic shift largely to the reduced planarity of the central core in the 8,8-dicyanoheptafulvene, which reduces its electron accepting ability. The spectra of the extended pentafulvenes are quite exciting, as they show broad, intense ICT bands spanning from ~500 nm over nearly the entire visible spectral region into the near infrared (NIR). Extended pentafulvene **7** features two ICT transitions at λ_{max} = 680 nm (1.82 eV; ε = 15000 M^{-1} cm^{-1}) and 760 nm (1.63 eV; ε = 15200 M^{-1} cm^{-1}), whereas the bands of *E*/*Z*-**9** appear at λ_{max} = 600 nm (2.07 eV; ε = 20000 M^{-1} cm^{-1}) and 700 nm (1.77 eV; ε = 20000 M^{-1} cm^{-1}), respectively. In contrast, TCPF **1** features a single, more narrow transition (1.59 eV; λ_{max} = 782 nm, and ε = 27500 M^{-1} cm^{-1}).[12] The appearance of a second ICT band in the spectra of **7** and *E*/*Z*-**9** reflects the presence of the additional DMA donors at C(6) that can undergo push−pull interactions with the electron-accepting, 2,4-dicyanopentafulvene core.

Acid−base titration with CF_3COOH and Et_3N gave further insight into the nature of the ICT interactions in the new compounds (see Figures 30SI−34SI of the Supporting Information). Treatment of the solution of tetracyanobenzene **3** with CF_3COOH led to a change in color from red to colorless and a complete disappearance of the intense CT band at 440 nm. Similarly, treatment of heptafulvene **5** with CF_3COOH led to a change in color from maroonish red to colorless and again a complete disappearance of the intense CT band at 490 nm. Neutralization with Et_3N regenerated the original spectra of **3** and **5** completely, with a slight decrease in the absorbance due to dilution. When a solution of **7** or *E*/*Z*-**9** was acidified with CF_3COOH, the color changed from bluish green to green and the bands at longer wavelengths (for **7**, λ_{max} = 760 nm; for *E*/*Z*-**9**, λ_{max} = 700 nm) remained intact, whereas the bands at shorter wavelengths (for **7**, λ_{max} = 680 nm; for *E*/*Z*-**9**, λ_{max} = 600 nm) completely disappeared. Neutralization with Et_3N regenerated the original absorption profile almost quantitatively as well as the color of the solution. Protonation in **7** and *E*/*Z*-**9** occurs at the most basic DMA moiety, which presumably is attached to the exocyclic allylidene moiety, and therefore, the ICT band involving these donor groups disappears in the presence of acid. This leaves a spectral trace (Figures 33SI and 34SI of the Supporting Information) that resembles much more the spectrum of TCPF **1** that lacks these additional DMA moieties. We therefore conclude that the lower-energy ICT band in **7** and *E*/*Z*-**9** arises from the transfer of charge from DMA moieties on the cyclopentadienyl ring to the electron-accepting extended pentafulvene core, whereas the higher-energy ICT band originates from charge transfer involving the DMA donor at C(6) on the exocyclic allylidene fragment.

Electrochemistry. The redox properties of the new chromophores **3**, **5**, (±)-**6**, **7**, and *E*/*Z*-**9** were investigated by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV) in CH_2Cl_2 (with 0.1 M Bu_4NPF_6, all potentials vs Fc^+/Fc). The CV data together with a comparison of optical and electrochemical HOMO−LUMO gaps are listed shown in Table 2, whereas Table 7SI of the Supporting Information includes the RDV data and Figure 36SI of the Supporting Information the raw CV traces.

Bis-1,4-DMA-substituted tetracyanobenzene **3** shows a single reversible one-electron reduction at −1.32 V, an irreversible one-electron reduction at −2.21 V, and an irreversible oxidation at 0.76 V. A comparison of the redox properties of 8,8-dicyanoheptafulvene **5** and 6,6-dicyanopentafulvene **1** demonstrates the inherent drastic changes in the electronic configurations possible for fulvene-based materials when the ring size is modified. Both pentafulvene **1** ($E_{\mathrm{red},1} = -0.45$ V)[12] and heptafulvene **5** ($E_{\mathrm{red},1} = -1.18$ V) display two reversible one-electron reductions. However, the electron affinity of **5** is much lower than that of **1** ($\Delta E_{\mathrm{red},1} = 0.73$ V). DFT calculations suggest that the LUMOs are located on the fulvene moiety of both **1** and **5** (Figure 29SI of the Supporting Information). The HOMO−LUMO gap for heptafulvene **5** is quite large (1.78 V) compared to that of the parent pentafulvene **1** (1.12 V). The cyclic voltammogram of cyclobutene-fused tetrahydropentalene (±)-**6** shows one irreversible reduction step at −2.34 V as well as several irreversible oxidation steps at 0.54, 0.64, and 0.82 V. The potential difference between the first oxidation and the first reduction corresponds to 2.88 V, which is roughly in agreement with the energetics of the intramolecular CT band of (±)-**6** ($\lambda_{\mathrm{end}} = 550$ nm, 2.26 eV).

Electrochemical investigations of the extended pentafulvenes **7** and *E*/*Z*-**9** give further insight into the electronics of these systems. The oxidation potentials of **7** and *E*/*Z*-**9** are quite similar, with a first unresolved step corresponding to one reversible two-electron transfer at 0.27 and 0.28 V for **7** and *E*/*Z*-**9**, respectively, and a second oxidation wave of **7** (0.85 V) and *E*/*Z*-**9** (0.81 V). The low first oxidation potential is quite remarkable. *N*,*N*-Dimethylaniline itself shows an irreversible oxidation potential at 0.44 V (in CH_2Cl_2, Fc^+/Fc reference).[30] In contrast, DMA moieties in D−A systems participating in efficient ICT interactions show poor electron donating ability and high oxidation potentials ($E_{\mathrm{ox}} \approx 0.7$−1.1 V).[10] The first two-electron oxidation step in **7** and *E*/*Z*-**9** is preferred compared to the oxidation of pure *N*,*N*-dimethylaniline, whereas the second oxidation wave is closer to the oxidation potentials measured for the two DMA groups in **1** and other push−pull systems (Table 2). A DFT computational study [B3LYP/6-31(d) level of theory] of *Z*-**7**, *Z*-$\mathbf{7}^{+}$, and *Z*-$\mathbf{7}^{2+}$ and *E*-**9**, *E*-$\mathbf{9}^{+}$, and *E*-$\mathbf{9}^{2+}$ proposes a solution for the remarkably facile first two-electron oxidation of **7** and **9**. According to the calculations, the five-membered ring in the dication features two separate π-systems in a nearly orthogonal conformation to each other, each presumably bearing one positive charge (Figures 25SI−28SI of the Supporting Information). One is an allylic cation stabilized by the two DMA residues I and II on the ring. The other is the exocyclic allylidene with the DMA residues at position C(6) (DMA III in **7**) and positions C(6) and C(7) (DMA III and IV in *E*/*Z*-**9**). Such a finding obviously requires much further experimental and computational research, beyond this study.

The reduction potentials for both **7** and *E*/*Z*-**9** occur in two well-defined, reversible, one-electron reductions at −0.67 and −0.89 V for **7** and −0.88 and −1.05 V for *E*/*Z*-**9**. The difference in reduction potentials of **7** and *E*/*Z*-**9** results from the presence of one more DMA donor in *E*/*Z*-**9**, which also induces a twist around the C(6)−C(7) bond of the exocyclic allylidene moiety. This twisting reduces the level of conjugation between the dicyanovinyl and the pentafulvene ring, resulting in a significant cathodic shift of the reduction potentials.

The optical HOMO−LUMO gaps, determined from the λ_{end} of the longest-wavelength absorption band, correlate well ($R^2 = 0.999$) with the electrochemical gaps $\Delta(E_{\mathrm{ox},1} - E_{\mathrm{red},1})$, suggesting that the same orbitals are involved in both the optical and electrochemical band-gaps for **3**, **5**, (±)-**6**, **7**, and *E*/*Z*-**9** (Table 2). To the best of our knowledge, the small optical band gap of **7** (0.94 V) is the smallest in pentafulvene-based scaffolds and is quite remarkable for a small chromophore such as **7**.[31] Therefore, it is worthwhile to modify the pentafulvene at position C(6) to obtain amphoteric redox chromophores with small HOMO−LUMO gaps.

■ CONCLUSIONS

We report an optimized synthesis of push−pull-substituted pentafulvene **1** (TCPF), which avoids unexpected SiO_2- and solvent-promoted 1,2-CN shifts leading to 1,3-bis-DMA-substituted tetracyanobenzene **3**. A mechanism for this unprecedented rearrangement is proposed on the basis of experimental observations. TCPF **1** reacts in one step with DMA-acetylene to yield a series of new nonplanar push−pull chromophores of substantial complexity, featuring heptafulvene **5**, cyclobutene-fused tetrahydropentalene (±)-**6**, and extended pentafulvene cores **7** and *E*/*Z*-**9**. The elucidation of their structures required X-ray analysis, but they were also investigated and confirmed by advanced NMR spectroscopy in solution. Mechanisms for their formation are proposed. Interestingly, steric hindrance makes the addition of bis-DMA-acetylene to TCPF **1** much more selective, and only the extended pentafulvene *E*/*Z*-**9**, resulting from formal [2+2] cycloaddition, followed by retroelectrocyclization (CA−RE reaction), was isolated. While X-ray analysis of a series of crystals revealed only the *E*-**9** isomer in the solid state, the two *E*- and *Z*-isomers are present in solution to different extents, which is dependent on solvent polarity. The extended pentafulvenes **7** and *E*/*Z*-**9** feature outstanding opto-electronic properties. The electronic absorption spectra show broad ICT bands expanding from ~500 nm into the NIR, with maxima (λ_{max}) at 680 and 760 nm (**7**) and 600 and 700 nm (*E*/*Z*-**9**). Electrochemical investigations revealed exceptionally high electron donating ability of these chromophores (first oxidation waves at 0.27/0.28 V), which together with their strong electron accepting property [first reduction waves at −0.67 V (**7**) and −0.88 V (*E*/*Z*-**9**)] affords very small HOMO−LUMO gaps of 0.94 eV (**7**) and 1.16 eV (*E*/*Z*-**9**). The study demonstrates that the functionalization of the exocyclic C(6) position in push−pull pentafulvenes provides an excellent tool for influencing and fine-tuning the amphoteric redox behavior and the HOMO−LUMO gap of pentafulvene-based molecular materials. In view of their stability, solubility, and facile availability, adding to the beneficial opto-electronic properties, the reported chromophores warrant future exploration for use as organic electronic materials, such as in organic solar cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of all new compounds, details of the DFT calculations, spectroscopic and electrochemical data, computational details, energies, Cartesian coordinates, and crystallographic data in CIF format. 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.

■ ACKNOWLEDGMENTS

This work was supported by ERC Advanced Grant 246637 ("OPTELOMAC"). O.D. acknowledges the Fonds der Chemischen Industrie for a Kekulé scholarship. We thank Dr. Marc-Olivier Ebert (ETH Zürich) for helpful discussions regarding NMR and Dr. Aaron Finke and Dr. Adam Lacy for reading the manuscript.

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