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Proacetylenic Reactivity of a Push–Pull Buta-1,2,3-triene: New Chromophores and Supramolecular Systems

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Dedicated to the 150th anniversary of German-Japanese relations

Proaromaticity is an efficient concept for reducing HOMO–LUMO gaps in push–pull chromophores.[1–3] Experimental electrochemical and optical gaps of donor–acceptor-substituted (push–pull) quinoids (Figure 1) are much lower in energy, compared to acyclic or nonquinoid cyclic analogs, as a result of the significant charge-separated character of their ground state. The increase in aromaticity of quinoids induced by electronic asymmetry has been evidenced in extensive physical and theoretical studies[2] and the concept successfully applied to the development of chromophores with high optical nonlinearities.[3]

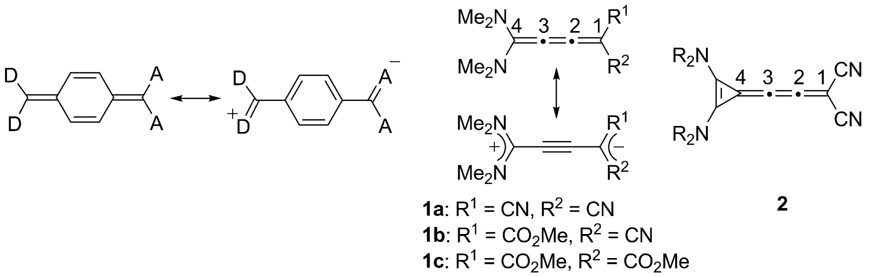

Figure 1. Left: Proaromatic donor–acceptor-substituted quinoids (D = electron-donating group, A = electron-accepting group). Right: Known donor–acceptor-substituted [3]cumulenes **1a–c**[4,8] and **2**[5] (R was not clearly defined in Ref. [5]).

Structural analysis of push–pull [3]cumulenes, such as **1** and **2** (Figure 1), revealed that the central cumulenic double bond is very short, similar in length to the C≡C bond in alkynes. The X-ray crystal structure of 1,1-bis(dimethylamino)-4,4-dicyanobutatriene (**1a**)[4] shows a short central C2−C3 bond of 1.201 Å, thus implying acetylenic character. Additionally, the ^{13}C NMR signal at 22.9 ppm ($CDCl_3$) indicates a highly shielded environment at the dicyano-substituted C1 in **1a** and suggests that this molecule might be best described by its charge-separated acetylenic form, rather than the [3]cumulenic form. Similarly, an upfield resonance at 19.0 ppm was found for the diaminocyclopropenylidene derivative **2**.[5] Based on topological resonance energy (TRE) analyses of annulenes and cyclynes, Chauvin and co-workers suggested that acetylene is "… ca. three times more topologically aromatic than … benzene",[6] which should also favor the acetylenic charge-separated state of donor–acceptor-substituted [3]cumulenes. Despite these experimental and theoretical findings, a proacetylenic, i.e. acetylene-like, reactivity of the central double bond in push–pull [3]cumulenes has not yet been observed. Only polar additions of nucleophiles/electrophiles to **1a**, converting the butatriene into buta-1,3-dienes have been reported.[4] Herein, we describe the synthesis of a new donor–acceptor-substituted butatriene and demonstrate the chameleonic reactivity of its central CC bond with respect to cycloadditions, undergoing both olefin-type and acetylene-type transformations. The opto-electronic and molecular recognition properties of the resulting new chromophores are discussed. It is noticeable that donor–acceptor-substituted cumulenes have been predicted to be even more

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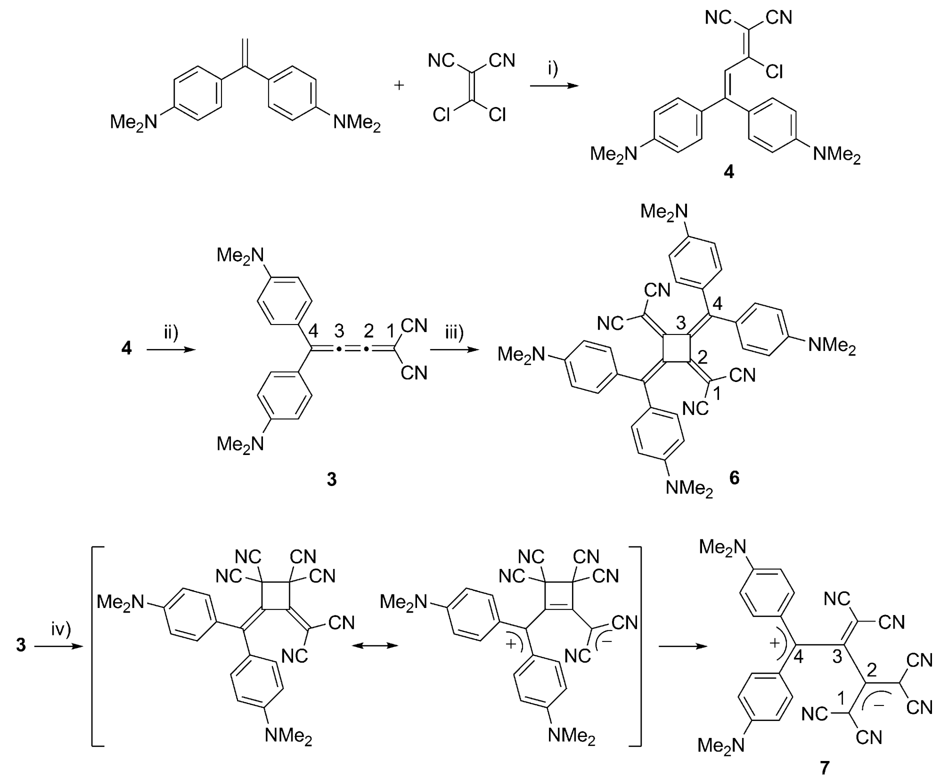

Scheme 1. Synthesis of push–pull butatriene **3** and chromophores **6** and **7**. Conditions: i) Et_3N, MeCN, 0 °C→r.t., 2.5 h, 97 %; ii) quinuclidine, THF, reflux, 17 h, 80 %; iii) $[Ni(CO)_2(PPh_3)_2]$, PPh_3, benzene, reflux, 4.5 h, 48 %; iv) tetracyanoethene, CH_2Cl_2 or MeCN, r.t., 30 min, 99 %.

potent non-linear optical chromophores than comparable push–pull oligo-enes and oligo-ynes.[7]

We synthesized 1,1-dicyano-4,4-bis(*N*,*N*-dimethylanilino)-butatriene **3** from the vinyl chloride precursor **4**, following protocols of Viehe and co-workers[4] and Gompper and Wolf[8] with a slight modification (Scheme 1). The X-ray diffraction analysis (see the Supporting Information) of **3** gave an average central C2–C3 bond length for the two symmetry-independent molecules in the crystal of 1.23(2) Å, shorter than in symmetric butatrienes[4a,9] but slightly longer than in **1a**. The ^{13}C NMR signal at 40 ppm (100 MHz, $CDCl_3$) implies a significant electron density at dicyano-substituted C1. This signal is, however, relatively downfield as compared to the comparable resonance in **1a** and **2**, which suggests that the charge-separated mesomeric contribution for **3** is smaller. This is in line with the weaker electron-donating power of a *N*,*N*-dimethylanilino (DMA) as compared to a *N*,*N*-dimethylamino (in **1a**) or a diaminocyclopropenylidene moiety (in **2**). The strong IR absorption at 2044 cm^{-1} for the central CC vibration is at the borderline between the positions of acetylene and cumulene bands, while the moderately strong absorption at 2213 cm^{-1} for the CN stretch is at higher energy than those reported for **1a** (2178 cm^{-1})[4] and proaromatic dicyano compounds (2168 and 2183 cm^{-1}).[2] Taken together, these data suggest that **3** might behave as a hybrid of cumulene and acetylene.

In comparison to **1a**, which features a longest-wavelength absorption maximum at λ_{max} = 356 nm,[4] the additional phenylene rings in **3** induce a bathochromic shift of the absorptions. In the purple CH_2Cl_2 solution of **3**, maxima at λ_{max} = 588 nm (ε = 54 700 M^{-1}cm^{-1}) and 541 nm (ε = 48 500 M^{-1}cm^{-1}) were observed, and their intramolecular charge-transfer (CT) character was suggested by the disappearance of these bands upon protonation with trifluroacetic acid (TFA). The longest-wavelength maximum of **3** is bathochromically shifted by 90 nm (0.38 eV) relative to the analogous buta-1,3-diene **5**[10] (λ_{max} = 498 nm, Figure 2). According to rotating disk voltammetry (half-wave potentials $E_{1/2}$ vs. Fc$^+$/Fc, in CH_2Cl_2 containing 0.1 M nBu$_4$NPF$_6$), this reduction in optical gap is mainly due to the stabilization of the LUMO level of **3** (E_{red} = −1.35 for **3** and −1.71 V for **5**) and slightly due to a variation in the HOMO energy (E_{ox} = +0.57 for **3** and +0.52 V for **5**).

Thermal dimerization of **3** was not observed upon heating in MeCN at reflux for 2 days.[11] However, by applying the protocol developed by Iyoda and co-workers[12] for cyclooligomerization of cumulenes, **3** underwent a Ni(0)-mediated [2+2] cyclodimerization to give [4]radialene **6** in 48 % yield (Scheme 1). The reaction is highly regioselective: only the compound from head-to-tail dimerization at the central C2–

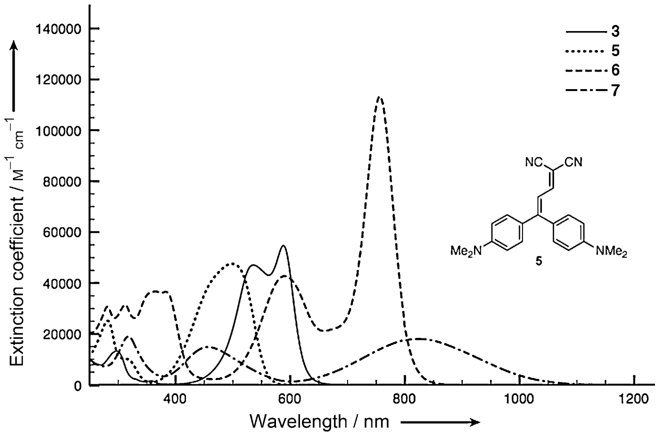

Figure 2. Electronic absorption spectra of **3** and **5**–**7** in CH_2Cl_2 at 25 °C (ca. 10^{-5} M).

C3 bond was isolated. In principle, this Ni(0)-mediated reaction could yield a [6]radialene[12d] that might be benzene-like due to three-fold push–pull interactions. However, such a compound was not observed in the crude mixture by mass spectrometry.

The X-ray crystal structure of **6** revealed two symmetry-independent, practically superimposable molecules in the unit cell ($P\bar{1}$ space group, Figure 3a). The nearly C_{2h} symmetric conformer found in the crystal is more stable than the other possible D_2-symmetric head-to-tail dimer by approximately 5 kJ mol^{-1} according to density functional theory calculations (B3LYP/6-31G+(d,p) in the gas phase; see the Supporting Information for the geometry of the D_2-symmetric conformer).[13] With the centroid of each molecule locating on a crystallographic center of symmetry and no disorder, according to the isotropic atomic displacement parameters, the four-membered ring of **6** is in effect a perfect square. By contrast, most reported [4]radialenes feature a puckered ring caused by steric repulsion between exocyclic substituents.[14] There is significant pyramidalization about the two cyano-substituted carbon atoms C1 and C1′ (POAV (π-orbital axis vector) angle[15] ~4°; for numbering, see Figure 3). The pyramidalization is indicative of negative charge density at these atoms and is consistent with the quinoid character δr[16] of 0.04 Å determined for the DMA donor rings (see Figure 3 for definition and determination of δr). This pyramidalization partially relieves the steric repulsion between the exocyclic substituents. Additionally, C1 and C1′ show a 0.24 Å deviation from the plane set by the central four-membered cycle, whereas C4 and C4′ are essentially located in this plane.

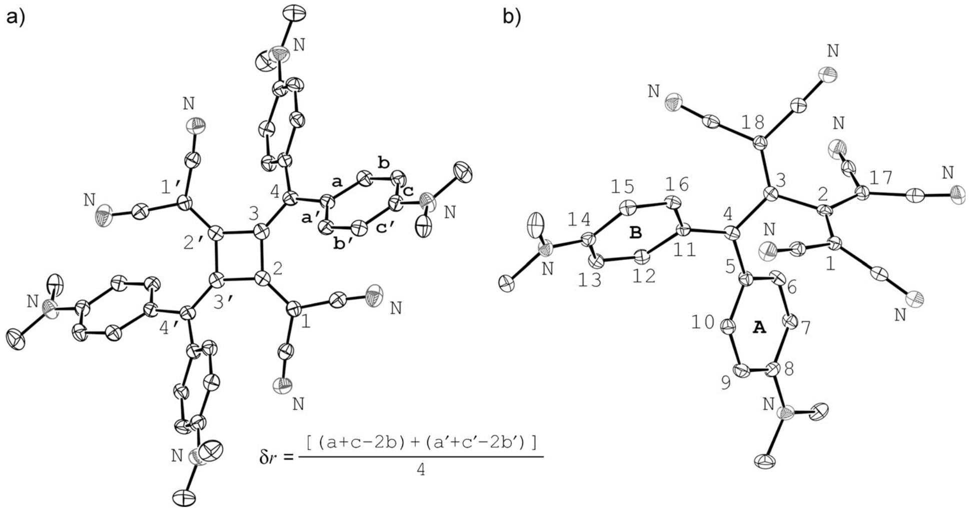

Figure 3. a) ORTEP representation of **6**, $T = 273$ K, anisotropic displacement ellipsoids are shown at the 50% probability level. Only one of two almost superimposable, symmetry-unrelated molecules is shown; see the Supporting Information for the other one and their relative orientation in the crystal. Selected bond lengths [Å] and angles [°]: C2–C3 = C2′–C3′ 1.474(3), C2–C3′ = C2′–C3 1.473(3), C2–C3–C2′ = C2–C3′–C2′ 89.19(17), C3–C2′–C3′ = C3′–C2–C3 90.81(17). The quinoid character δr[16] is calculated as shown, from the bond lengths in the DMA moieties (see the Supporting Information); average δr [Å] for all four DMA rings = 0.041 (in benzene, δr = 0; in fully quinoid rings, δr would be on the order of 0.10–0.12 Å). b) ORTEP representation of **7**, $T = 100$ K, anisotropic displacement ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and δr [Å]: C1–C2 1.399(3), C2–C3 1.497(4), C3–C4 1.468(3), C2–C17 1.401(3), C3–C18 1.369(3), C5–C6 1.409(4), C5–C10 1.417(4), C6–C7 1.365(4), C7–C8 1.420(5), C8–C9 1.417(4), C9–C10 1.368(4), C11–C12 1.427(4), C11–C16 1.434(3), C12–C13 1.350(4), C13–C14 1.426(4), C14–C15 1.436(4), C15–C16 1.350(4), δr (ring A) 0.050, δr (ring B) 0.081.

[4]Radialene **6** has a metallic copper luster in the solid-state and is blue-colored in solution. The UV/Vis spectrum shows two strong intramolecular CT bands at $\lambda_{max} = 589$ nm ($\varepsilon = 42700$ M^{-1} cm^{-1}) and 756 nm ($\varepsilon = 113300$ M^{-1} cm^{-1}) in CH_2Cl_2 (Figure 2). Although it is a structural dimer of **5**, the absorption profiles of the two chromophores have no similarity. The sharp, intense absorption of **6** in the deep-red region is reminiscent of those of squaraines, a class of squaric acid-derived, zwitterionic cyanine dyes.[17] Electrochemically, four oxidation events at +0.31, +0.64 (2e$^-$), and +0.89 V and two reductions at −1.22 and −1.97 V were recorded, consistent with the apparent number of electrochemically active moieties (four aniline and two dicyanovinyl groups). The unique π-system of **6** is further evidenced by the fact that its first oxidation and reduction events are more favorable by 200 and 500 mV, respectively, as compared to **5**. The two reduction steps in **6**, on the other hand, are expectedly much less favorable than in octacyano[4]radialene which features positive potential values for the reduction to the dianion.[18]

Introduction of tetracyanoethene (TCNE) to a solution of **3** in CH_2Cl_2 or MeCN at 25 °C resulted in an immediate color change from purple to brownish orange. A stable and highly polar molecule was isolated by column chromatography on SiO_2 in nearly quantitative yield (99%). X-ray diffraction analysis revealed a zwitterionic molecule (**7**, Figure 3b), which presumably forms by a formal [2+2] cycloaddition–cycloreversion process via a cyclobutene intermediate (Scheme 1).[19] Since this reaction is known to occur between cyanoolefins and strongly polarized electron-rich acetylenes, the isolation of **7** signifies that the central CC bond of push–pull butatriene **3** may have a reactivity similar to a triple bond, corroborating the structural results described above.

The charges are permanently separated by the central, cross-conjugated dicyanoethenylidene moiety in the zwitterionic molecule. The positive terminus is stabilized by two electron-donating DMA moieties and the negative terminus by a tetracyanoallyl system. According to NMR studies, the two DMA rings are magnetically identical in solution and the two terminal carbons (C1 and C17, Figure 3b) of the tetracyanoallyl group are equivalent as well. These observations agree with X-ray data that indicate single-bond character in the C2–C3 (1.497(4) Å) and C3–C4 (1.468(3) Å) bonds, which allows rapid rotation. On the other hand, this equivalency implies that the charges are delocalized. In the solid-state, the C1–C2 and C2–C17 bonds have the same length within experimental precision; however, the two DMA rings show different degrees of quinoid character δr of 0.050 and 0.081 Å; the latter number approaches that of 7,7,8,8-tetracyanoquinodimethane (TCNQ, $\delta r = 0.102$).[20]

The electrochemistry ($E_{1/2}$ vs. Fc^+/Fc) of zwitterion **7** differs substantially from that of other neutral push–pull chromophores containing DMA donors and cyanoolefin acceptors.[21] Two oxidation and two reduction processes were observed. The first oxidation was observed at a high potential of 0.85 V and the first reduction at −0.26 V. The small electrochemical gap (1.11 eV) correlates well to the low-energy absorption band in the near-IR (NIR) region ($\lambda_{max} = 825$ nm; absorption onset ~1150 nm, or 1.08 eV; Figure 2). The absorption band became less intense upon addition of TFA; similar spectral changes have been found for other DMA-based chromophores, but the protonation site in the present case is more likely to be on the allyl anion moiety. During the course of neutralizing the added acid with Et_3N, we observed that the absorption profile of **7** was first restored, and then irreversibly changed with an excess of base.

We investigated the capability of the positively polarized DMA moieties to interact with supramolecular receptors that strongly bind cationic species. We selected tetraphosphonate cavitand **8** (Figure 4) as the host,[22] for its well-known tendency to engulf positively charged molecules within the upper cavity.[22,23]

By addition of **7** to **8** (3.3 mM) in $CDCl_3$, a ^{31}P NMR signal at 9.72 ppm (cf. 6.81 ppm for free **8**) was recorded for the resulting deep-green solution.[24] Such a downfield shift is consistent with ion-dipole interactions between a strongly positively polarized, nearly cationic DMA moiety of **7** and the P=O dipoles in **8**. A similar ^{31}P NMR shift was reported for tetraphosphonate cavitands encapsulating other positively charged species.[22,23] In the ^1H NMR spectra, the DMA signals of **7** moved upfield and broadened until disappearance upon complexation by **8**, suggesting that the DMA units experience a shielding effect from the cavity of the host, and that their rotational freedom becomes reduced by inclusion. From the signals of **8**, we noticed upfield shifts of the $ArCH_3$ ($\Delta\delta = -0.10$ ppm) and Ph-H_{ortho} signals ($\Delta\delta = -0.09$ ppm), indicative of their interaction with a bound cationic DMA moiety. By contrast, the signals from the H_{down} protons ($\Delta\delta = 0.14$ ppm) and the nearby $ArCHCH_2$ protons exhibited downfield shifts, suggesting the presence of an anionic moiety at the bottom of **8**. A complete disassembly of the **7·8** aggregate was achieved by addition of *N*-octylammonium bromide (**9**), which has a higher affinity to **8** due to additional ionic H-bonding with the P=O groups.[22,23] The brownish-orange color characteristic for unbound **7** was immediately restored, and a ^{31}P signal at 10.86 ppm was recorded, diagnostic for the binding of the octylammonium guest (see the Supporting Information for these NMR spectra).

The binding mode deduced from NMR studies is corroborated by the X-ray crystal structure of the chain-like **7·8** assembly (Figure 4), which highlights the four P=O groups in an all-inward configuration,[23] establishing ion-dipole interactions with a positively charged imminium-type center of **7**

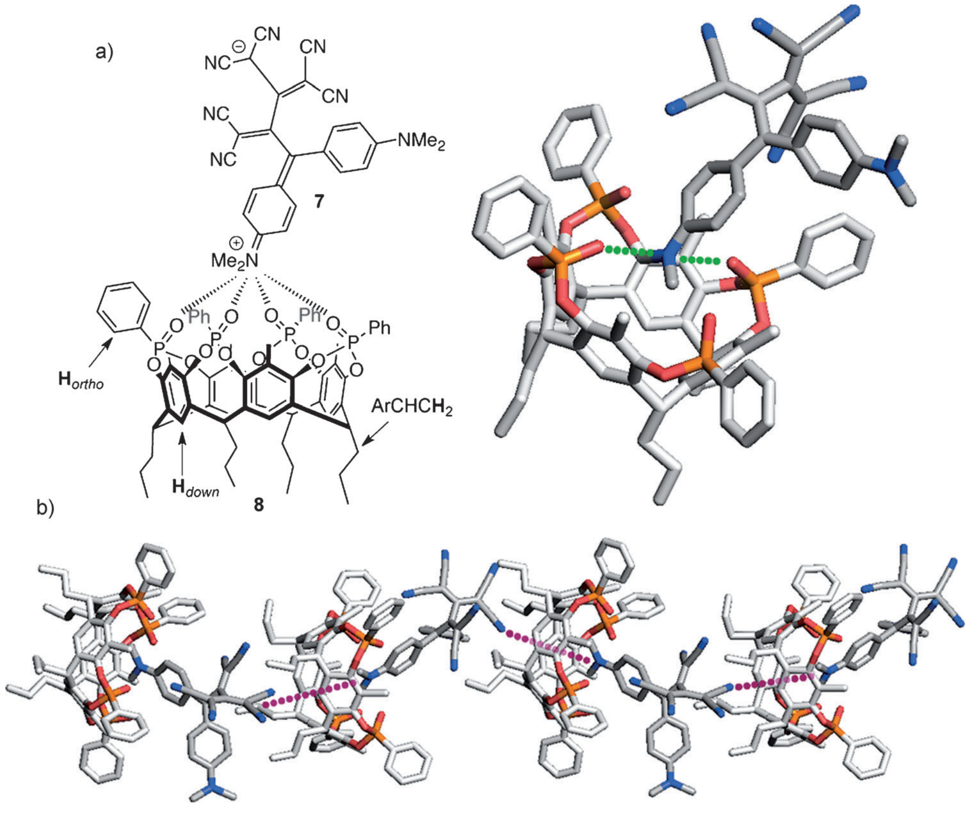

Figure 4. Solid-state geometry of the complex between zwitterion **7** and cavitand **8** based on X-ray diffraction analysis, $T = 100$ K. Included solvent molecules and hydrogen atoms are omitted for clarity. Color code: gray = carbon (darker for **7**, lighter for **8**), blue = nitrogen, red = oxygen, and orange = phosphor. a) The 1:1 complex **7·8**. The short P=O···$N(CH_3)_2$ distances of 2.9–3.0 Å are shown by the dotted green lines. b) Supramolecular co-polymeric arrangement of **7·8**; the attractive electrostatic interactions are shown by the dotted purple lines.

(short heavy-atom distances of $P{=}O\cdots N(CH_3)_2 = 2.9–3.0$ Å and $P{=}O\cdots(CH_3)_2N = 3.1–3.3$ Å). Notably, the anionic motif ($C(CN)_2$) of a neighboring zwitterion **7** is positioned at the lower rim of **8**, possibly due to the electrostatic attraction toward the nearby, bound cationic imminium center ($CN\cdots NMe_2$ distance: 6.9 Å) and C-H···anion interactions with the propyl legs of the cavitand. This arrangement leads to the formation of linear, AB-type co-polymeric arrays in the solid state (Figure 4b).

The association constant for a 1:1 host-guest complex **7·8**, $K_{\mathrm{ass}}^{303\mathrm{K}} = (2.13 \pm 0.04) \times 10^4\,\mathrm{M}^{-1}$, was determined by isothermal titration calorimetry (ITC) in nitrobenzene for reasons of solubility.[25] Interestingly, the process is both enthalpically and entropically driven, thus highlighting the key role played by solvation[22] ($\Delta H = -17.6 \pm 0.5\,\mathrm{kJ\,mol^{-1}}$, $T\Delta S = +7.6 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$, $\Delta G = -25.1 \pm 0.1\,\mathrm{kJ\,mol^{-1}}$).

In summary, we demonstrated the acetylene-like (proacetylenic) reactivity of a push–pull butatriene **3** in a formal [2+2] cycloaddition–cycloreversion reaction to give zwitterion **7**, in which charges are separated through cross-conjugation and stabilized by DMA rings (cation) and cyano groups (allyl anion). The positive charge on the DMA rings, and in particular their NMe_2 centers, is evidenced by complexation with a tetraphosphonate cavitand. The startling and unexpected optical similarity between squaraines and **6**, formed via a cumulene-like cyclodimerization of **3**, indicates the potential application of push–pull [4]radialenes as a new class of dyes with absorptions close to or in the NIR, but with lower polarity and higher solubility. The synthesis of higher, donor–acceptor-substituted [2n+1]cumulenes and the investigation of their reactivity and optoelectronic properties are currently being pursued. Additionally, the visible color changes of **7** upon complexation with **8** suggest the employment of this host system for the colorimetric detection of other highly polarized push–pull guest chromophores.

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Keywords: proacetylenic · push–pull chromophore · radialene · self-assembly · zwitterions

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[24] In this experiment, **7** was added in solid form. Dissolution of **7** in $CDCl_3$ is a very slow process, usually resulting in a heterogeneous, brownish-orange suspension due to the poor solubility. Remarkably, the complete dissolution of **7** is, however, possible in the presence of **8**.

[25] ITC experiments were carried out at $c = 0.5$ mM (for **8**); the formation of oligomers is assumed to be negligible at this dilute concentration. Thermodynamic parameters are evaluated according to a simple 1:1 host–guest complexation process.

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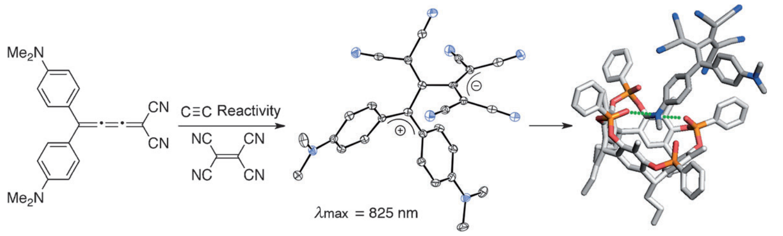

Proacetylenic: An aniline-based donor–acceptor-substituted butatriene exhibits not only cumulene-like dimerization to give a [4]radialene (λ_{max} = 756 nm), but also acetylene-like (proacetylenic) reactivity towards tetracyanoethene, affording via [2+2] cycloaddition–cycloreversion a NIR-absorbing zwitterionic chromophore (λ_{max} = 825 nm). The cationic charge on the imminium-type nitrogen in the zwitterion is evidenced by host–guest complexation with a tetraphosphonate cavitand.

Push–Pull Chromophore

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Proacetylenic Reactivity of a Push–Pull Buta-1,2,3-triene: New Chromophores and Supramolecular Systems