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Acenequinocumulenes: Lateral and vertical π-extended analogs of tetracyanoquinodimethane (TCNQ)

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Text for Table of Contents



New synthetic methodology extends the basic skeleton of tetracyanoquinodimethane (**TCNQ**) along both the lateral and vertical axes, via benzoannulation and incorporation of a [3]cumulene, respectively. Terminal functionalization of the cumulenic core allows attachment of electron donor and acceptor functional groups.

Keywords pentacenes, donor-acceptor; organic materials; cumulenes; synthetic methodology

Abstract:

We have designed a series of molecules and developed synthetic methodology that allows for the inclusion of structural diversity along both the lateral and vertical axes of the basic **TCNQ** skeleton. In the lateral direction, benzoannulation extends the π -system through (hetero)acene formation, while incorporation of a [3]cumulene increases delocalization vertically. The potential of these new molecules as semiconductors is explored through UV-vis spectroscopy, cyclic voltammetry, X-ray crystallography, thin film formation, and mobility measurements (*via* space charge limited current measurements).

Introduction

The past few decades have seen spectacular achievements in the development of organic semiconductors in terms of stability, processability, and charge carrier mobility.^[1,2] This progress highlights the beauty of synthetic organic chemistry, which offers the tools to design, explore, and tune the properties of molecules for use in devices such as organic sensors,^[3,4] field effect transistors (OFETs),^[4–6] organic light-emitting diodes (OLEDs),^[7–9] and organic photovoltaics (OPVs).^[10–13] Organic semiconductors are often classified into two categories, p-type (donor, hole conducting) and n-type (acceptor, electron conducting). In the case of p-type organic semiconductors, many requisite properties have been fulfilled,^[1,2,6,14,15] while the realization of n-type organic materials remains troubled by issues such as complex synthesis, instability in air, poor solubility, large electron injection barriers, and low charge carrier mobilities.^[16–19]

One of the most common non-fullerene compound classes used as n-type semiconductors are cyano-based acceptors such as tetracyanoethylene (**TCNE**, Figure 1)^[20-23] and the more stable, π -extended analogue tetracyanoquinodimethane (**TCNQ**).^[24] First reported in 1960 by Acker *et al.*,^[25,26] pristine **TCNQ** has become one of the most extensively studied acceptor materials.^[26-29] The electron accepting abilities of **TCNQ** have been further fine-tuned through substitution,^[24,30-32] incorporation of heteroatoms,^[24,32-34] and, most commonly, extension of the π -system by lateral benzoannulation to give π -extended **TCNQ**

derivatives (**exTCNQs**).^[24,32,35–38] It was originally expected that **exTCNQs** could offer more stable and improved conducting materials.^[37,39] In reality, however, the π -expansion does not necessarily result in enhanced acceptor properties, and derivatives such as **TCAQ**, **TCTQ**, and **TCPQ**^[24,32,36–38] show non-planar structures that give rise to the so-called "butterfly" conformation and can hinder π -communication and effective charge transport.^[40,41] Despite lower electron accepting properties, **exTCNQs** have been remarkably adapted through structural modification.^[42] For example, **TCTQ** and **BDCNBA** undergo photoinduced electron transfer (PET) almost as efficiently as fullerene C₆₀,^[43,44] while **TCAQ** derivatives have demonstrated effectiveness in a range of PET processes.^[45–49] These results are significant, since they emphasize that device efficiency is not solely dictated by acceptor strength, and that shape and/or solid-state packing of the material are also crucial parameters.^[50]



Figure 1. Molecular structure of **TCNE**, **TCNQ**, a series of benzoannulated π -extended derivatives of the **TCNQ** family; inset, dicyanovinylacenequino[3]cumulenes (**1a–c** and **2**) and the corresponding keto derivatives (**3a–c** and **4**) introduced in this work.

To date, there are few **exTCNQ** derivatives that exceed the length of **TCTQ**,^[37,50–53] and most derive from the pioneering work of Martin and Hanack, including **5,14-TCPQ** and **6,13-TCPQ**,^[37,51] and Yamada *et al.* who reported **TBPQ**.^[52] In these cases, however, the

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poor solubility in common organic solvents restricts practical use, while large HOMO-LUMO gaps limit visible absorptions.^[51,52]

We became fascinated by the question of whether lateral and vertical substitution of **exTCNQ** derivatives could be used to augment desirable properties. We hypothesized that a [3]cumulene spacer at the "tail" position could be used to provide air-stable, soluble **exTCNQs** with more planar conformations.^[40,41,54] Furthermore, the cumulene moiety has been shown to have an effect of lowering the energy of LUMO,^[55] and it can be easily functionalized for the incorporation of electronically neutral, donor, or acceptor groups (Figure 1). On the other hand, the "head" position would allow tuning of the overall electron deficiency through incorporation of either a ketone or dicyanovinyl moiety. Finally, we expected that the "wings" of the butterfly could be varied through the formal exchange of the acene unit with a heteroacene.

We report herein the development of an efficient synthetic pathway for the synthesis of stable and soluble dicyanovinylacenequino[3]cumulene derivatives (**1a–c** and **2**), as well as their corresponding keto analogs (**3a–c** and **4**).^[56] Our synthetic protocol is versatile and readily allows the modification of every part of the acenequino[3]cumulenic butterfly framework, namely the head, the wings, and the tail (Figure 1). The structural modifications are correlated by changes in physical and optoelectronic properties, as detailed *via* UV-vis spectroscopy, cyclic voltammetry (CV), X-ray crystallography, as well as thin-film formation, and charge mobility determination.

Synthesis

Ketoacenequino[3]cumulenes **3a–c** and **4** were formed in good yield using a two-step process of desymmetrization of pentacenequinone^[57,58] followed by reductive elimination (Scheme 1).^[59] Specifically, the nucleophilic addition of acetylides **5a–c** to pentacene-6,13quinone and subsequent recrystallization of the product from CH_2CI_2 gave alcohols **6a–c**.^[60] Reductive elimination using $SnCI_2$ and HCI yielded ketoacenequino[3]cumulenes **3a–c** as intensely red to purple colored products, following purification by recrystallization from CH_2CI_2 . With ketones **3a–c** in hand, dicyanovinyl derivatives **1a–c** were targeted. Direct conversion from **3a–c** to **1a–c** was attempted using standard Knoevenagel conditions, such as the Lehnert reagent (TiCl₄, pyridine).^[61,62] These reaction conditions, however, led to complex mixtures, and the desired products were not identified. Likewise, the conversion of alcohols **6a–c** to **7a–c** under standard Knoevenagel conditions was also unsuccessful and thus, these routes were abandoned.^[63] Ultimately, an adaption of the procedure reported by Hayashi and coworkers in 2005^[64] was successfully devised, which allowed for formation of **7a–c** *via* reaction of **6a–c** in neat malononitrile and Ti(O*i*-Pr)₄ (Scheme 1). The dicyanovinyl products **7a–c** could be isolated pure *via* crystallization (**7a–b**) or column chromatography (**7c**). Reductive elimination of **7a–c** using SnCl₂ and HCl gave [3]cumulenes **1a–c** in good yields.



Scheme 1. Synthetic pathway to ketoacenequino[3]cumulenes **3a–c** and their corresponding dicyanovinyl derivatives **1a–c**.

The synthetic transformations developed for **1a–c** were then used to vary the electronic constitution of the "wings" of the acene backbone (Scheme 2). Reaction of acetylide **5a** with antradithiophene-5,11-quinone gave **8** (as a diastereomeric mixture of *syn-* and *anti-*isomers; see SI for details). Reductive elimination easily transformed **8** to cumulene **4**. Once again, attempt conversions of ketone **4** to dicyanovinyl derivative **2** with e.g., the Lehnert reagent, failed. Thus, as described above, Knoevenagel condensation was accomplished using **8** in

neat malononitrile and Ti(O*i*-Pr)₄, giving **9** in good yield, which then allowed formation of **2** *via* reductive elimination.



Scheme 2. Synthetic pathway to ketoacenequino[3]cumulene **4** and the corresponding dicyanovinyl derivative **2**; all anthradithiophene products are a mixture of *syn-* and *anti-*isomers.

It is worth noting that, in spite of the fact that the target molecules feature large π -systems and dipole moments that might lead to insolubility, the products **3a–c**, **4**, **1a**, **1c**, and **2**, show good solubility (>10 mg/mL) in a variety of organic solvents such as CH₂Cl₂, CHCl₃, and THF (**1b** shows only modest solubility <5 mg/mL).

Stability.

Ketone derivatives **3a–c** and **4** show good "kinetic" stability under normal laboratory conditions, with no observed sensitivity to light, air, or water. Thermal stability is excellent, with decomposition points spanning from 255 °C (**3b**) to 301 °C (**3c**), as measured under nitrogen by differential scanning calorimetry (DSC, Figures S51–S54).^[65] Dicyanovinyl derivatives **1a–c** and **2** have slightly reduced thermal stability, and all four derivatives show decomposition points by DSC in the range of ca. 200–230 °C (Figures S55–S58).



Figure 2. X-ray crystallographic structure and solid-state packing of a) **3a**, b) **3c**, c) **1a**, and d) **1c** (hydrogen atoms omitted for clarity).

X-ray analysis.

X-ray crystallographic analysis of four molecules has been achieved (**3a**, **3c**, **1a**, and **1c**) giving insight into the molecular structure, geometry, and solid-state order (Figure 2). Bond lengths of the four derivatives are unremarkable, showing neither substantial trends nor indication of distinct proacetylenic characteristics as described by Diederich and coworkers for donor-acceptor cumulenes.^[66]

The π -conjugated frameworks of keto derivatives **3a** and **3c** adopt a planar arrangement, including the acene and cumulene moieties. In the case of **3a**, the pendent aryl rings of the tail are rotated out of plane slightly by 19° and 32°, whereas the phenyl substituents of **3c** are twisted out of plane of the cumulene by 33–53°. There are no significant π - π -stacking interactions between neighboring acene units of **3a**, although the [3]cumulene chain is located at a distance of ca. 3.4 Å relative to the acenequinone moiety of the adjacent molecule (Figure S1a). Symmetry related molecules of **3c** stack "pair-wise" with nearly complete overlap of the acene groups at a distance of 3.5 Å (Figure S1b). Neighboring pairs are arranged to form a 1-D slipped stack, also at π - π -stacking distance of ca. 3.5 Å. Dicyanovinyl derivative **1a** crystallizes with two crystallographically unique molecules that form a dimeric arrangement, in which one molecule is located directly on top of the other.

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weak π - π -stacking interactions of adjacent naphthalene moieties that vary from 3.4 to 4.0 Å (Figure S1c). Compound **1c** shows a solid-state structure in which two molecules arrange as centrosymmetric pairs with minor direct overlap of the π -systems, *e.g.*, the cyclopentadienylidene (CPD) rings are separated by a distance of 4.6 Å (Figure S1d). Thus, unlike **1a**, the packing of **1c** appears dominated by CH- π interactions resulting from the pendent phenyl groups of the tetraphenyl-CPD group, rather than π -stacking.

Dicyanovinyl derivatives **1a** and **1c** feature a non-planar, so-called "butterfly" structure as a result of steric interactions between the *peri*-hydrogens of the acene core and the cyano groups (Figures S2, S3). The acene scaffold of both molecules is distorted from planarity by a little more than 30°, with angles between the wings for **1a** and **1c** of α = 146–148° (Table 1). Because the pendent substituents on the tail of **1a** and **1c** are distanced from the acene core by the [3]cumulene moiety, the bending is less that of **TCAQ** (α = 144.6°),^[35] **TCTQ** (α = 135.9°),^[50] and **TCPQ** (α = 132.4°)^[50] as summarized in Table 1. A similar trend can also be seen when comparing the deviation of the dicyanovinyl groups relative to the central ring of the acene skeleton, *i.e.*, the tilt angles (Table 1): **1a** (γ_i = 31.5, 37.9°) and **1c** (γ_i = 34.5°) versus **TCAQ** (γ_i = 34.7°; γ_i = 34.1°),^[35] **TCTQ** (γ_i = 38.8°),^[50] and **6,13-TCPQ** (γ_i = 39.6°; γ_i = 39.1°).^[50]

Cmpd	Structure front view (left) and side view (right)	Bend angle $lpha$ [°] ^[a]	Tilt angle γ ₁ [°] ^[a]	Tilt angle γ ₂ [°] ^[a]
1a ^[b, c]	γ_1 γ_2	147.2	31.5	23.2
Tu	γ_1 γ_2	146.2	37.9	12.7
1c ^[b]	γ1-8-72	147.6	34.5	19.3
TCAQ ^[35]	γ_1	144.6	34.7	34.1

Table 1. Comparison of bend and tilt angles of 1a and 1c to those of TCAQ, TCTQ, and 6,13-TCPQ.

9



^[a] For details on the determination of the bend and tilt angles, see Figures S2 and S3. ^[b] Aryl tailgroups omitted for clarity. ^[c] Two crystallographically independent molecules with different α - and γ angles are present in the unit cell.

UV-vis analysis

TCPQ derivatives are typically colorless or yellow, and they feature absorptions in the UV or high-energy visible regions.^[51] Dicyanovinylacenequino[3]cumulenes **1a–c** and **2**, on the other hand, are dark red to black solids in the solid state and show brownish-red to dark purple colors in solution. Ketoacenequino[3]cumulenes **3a–c** and **4** are similarly dark red to black as solids, but are less absorbing in solution, giving bright red colors. On the basis of UV-vis spectroscopy, both keto (**3a–c** and **4**) and dicyanovinyl (**1a–c** and **2**) derivatives show attractive panchromatic absorption behavior with intense absorption bands in the UV region and broad absorptions in the visible region out to ca. 700 nm (Figure 3, Table 2).



Figure 3. Absorption spectra of a) ketoacenequino[3]cumulenes **3a–3c**, and **4** and b) dicyanovinylacenequino[3]cumulenes **1a–c**, and **2**, recorded in THF.

Cmpd	λ _{max} [nm]	ε [L mol ⁻¹ cm ⁻¹]	λ _{cutoff} [nm/eV] ^[a]	Cmpd	λ _{max} [nm]	ε [L mol ⁻¹ cm ⁻¹]	λ _{cutoff} [nm/eV] ^[a]
3a	538	32 700	582/2.13	1a	555 ^[b]	14 400	650/1.91
3b	547	20 300	616/2.01	1b	579 ^[b]	_[c]	686/1.81
3c	563	36 000	634/1.96	1c	551	36 100	629/1.97
4	536	38 900	582/2.13	2	562	26 800	642/1.93

Table 2. UV-vis spectroscopic data for 3a-c, 4, 1a-c, and 2, recorded in THF.

^[a] As estimated from the intercept of a tangent line to the lowest energy absorption of the UV-vis spectrum with the x-axis (at ε = 0). ^[b] Shoulder absorption. ^[c] Not determined due to limited solubility.

As a result of the broadening of low energy absorptions, it is easier to use the values for λ_{cutoff} in comparisons versus structure (*i.e.*, the lowest energy of measurable absorption for each molecule, Table 2). Using **3a** as an "unfunctionalized" molecule for comparison, it is clear that a more electron-rich acene framework (**4**) has almost no influence on λ_{cutoff} values (Figure 3a). Formal exchange of the tail-group for a weak donor (**3b**) or an acceptor (**3c**) leads to a distinct red-shift of ca. 0.1 eV and 0.2 eV, respectively, versus **3a**. Changes in absorptions are also correlated by DFT calculations (Figure S6).

Dicyanovinyl derivatives **1a–c**, and **2** exhibit a similar absorption pattern as the ketones (Figure 3b). The λ_{cutoff} values of the dicyanovinyl derivatives are consistently redshifted versus the analogous ketones by 0.2 eV, confirming the influence of the more electron deficient head group. Unlike the keto-derivatives, where the CPD tail group gives the most significant change in λ_{cutoff} (as a result of a lowering of the LUMO energy, Figure S6), dicyanovinyl derivative **1b** shows the largest change in λ_{cutoff} as a result of the addition of a donor tail group and the associated increase in HOMO energy (Figure S6). Thus, both the head and tail groups play a pivotal role in the absorptivity.

CV analysis

Calculations have established that the bending of the **exTCNQs** is one of two major factors giving rise to lower acceptor strength compared to parent **TCNQ** (the second factor is the introduction of new antibonding interactions induced by the additional fused benzene 11

rings).^[40,41] Thus, planarized compounds **1a** and **1b** (relative to other **exTCNQs**) were expected to exhibit comparable reduction potentials versus *e.g.*, **TCPQ**, even though the former feature only a single dicyanovinyl acceptor group. It was also hypothesized that the presence of the CPD group in **1c** should show a lowered LUMO energy level versus **1a** and **1b** (Figure S6). Cyclic voltammetry was used to explore these predictions (Tables 3 and S1; Figures S4 and S5).

CV analysis shows that, unlike other **exTCNQ** derivatives, compounds **1–4** show clear oxidation events (Table 3), and only the oxidation potential of **1b** and **3b** is significantly affected by substitution. Keto-derivatives **3a**, **3b**, and **4** show reduction potentials in a similar range of $-1.41 \vee to -1.55 \vee$, while the reduction of dicyanovinyl derivatives **1a**, **1b**, and **2** show facilitated reduction events in the range of $-1.19 \vee to -1.25 \vee$. This observation clearly demonstrates the influence of the dicyanovinyl head group on the LUMO levels of these compounds, while in the acene backbone ("wings") had little effect within each series (Figure S6). Dicyanovinyl derivative **1c** ($E_{red1} = -0.98 \vee$) and ketone **3c** ($E_{red1} = -1.06 \vee$), on the other hand, show lower reduction potentials, facilitated by the CPD moiety.^[67] Thus, the acceptor strength of **1c** is similar to that of **6,13-TCPQ** and **5,14-TCPQ** ($E_{red1} = -0.95 \vee$ and $-0.88 \vee$, respectively), but not to the level of other **exTCNQs** such as **TCAQ** and **TCTQ** (Table 3).

Cmpd	E _{red1} (V)	E _{ox1} (V)	Cmpd	E _{red1} (V)	E _{ox1} (V)
3a	-1.47 ^[a]	0.59 ^[d]	1a	-1.23 ^[b]	0.63 ^[d]
3b	-1.55 ^[b]	0.40 ^[c]	1b	-1.25 ^[c]	0.53 ^[c]
3c	-1.06 ^[d]	0.61 ^[b]	1c	-0.98 ^[d]	0.63 ^[d]
4	-1.41 ^[a]	0.59 ^[d]	2	-1.19 ^[c]	0.63 ^[d]
TCAQ ^[35]	-0.67 ^[e]	_[f]	5,14-TCPQ ^[37]	-0.88 ^[e]	_[f]
TCTQ ^[37]	-0.82 ^[e]	_ ^[f]	6,13-TCPQ ^[37]	-0.95 ^[e]	_[f]

Table 3. First electrochemical reduction (E_{red1}) and oxidation (E_{ox1}) potentials (measured in CH₂Cl₂, versus Fc⁺/Fc) for **1a–c**, **2**, **3a–c**, **4**, in comparison to **TCAQ**,^[35] **TCTQ**,^[37] and **TCPQs**.^[37]

^[a] Peak potential used due to closely spaced reduction potential. ^[b] Estimated half-wave potential taken from a quasi-reversible redox event. ^[c] Peak potential taken from an irreversible redox event. ^[d] Reversible redox event, half-wave potential.^[e] Measured in acetonitrile with tetraalkylammonium perchlorate as the supporting electrolyte. ^[f] To our knowledge, oxidation events for **TCAQ**, **TCTQ**, and **TCPQs** by electrochemical analysis have not been reported.

Thin-film formation and electron mobility characterization

Compounds **1a**, **2**, **3a**, and **4** showed nice film formation and films with thicknesses of 85–110 nm were achieved from chloroform. In the case of **1c** and **3c**, limited solubility in chloroform and *o*-DCB did not allow for smooth films to be formed and, consequently, mobilities could not be measured. Testing of **1a**, **2**, **3a**, and **4** for their hole-only mobility revealed weak mobilities ranging from $2.1 \cdot 10^{-7}$ (**3a**) to $5.8 \cdot 10^{-6}$ (**4**) cm² V⁻¹ s⁻¹ (Table S2). In spite of the low mobilities, this result is, perhaps, counter intuitive in view of the ketone and dicyanovinyl functionality that are both acknowledged acceptor groups. Investigations of the n-type mobility for **1a**, **2**, **3a**, and **4** were unsuccessful in this standard architecture due to the higher lying LUMO levels.

Conclusions

To conclude, we have designed, synthesized, and characterized a series of new dicyanovinylacenequino[3]cumulenes **1a–c** and **2** and their corresponding keto analogs **3a–c** and **4**. The target molecules are assembled *via* a sequence of nucleophilic addition, Knoevenagel condensation, and reductive elimination reactions. The nature of the acene wings of the molecule have little effect on the electronic make up, while both the head and tail can be used to modify the structure and HOMO-LUMO energy gaps. The overall effect of functionalization is demonstrated by panchromatic absorption for all molecules (1–4), with λ_{cutoff} values reaching nearly 700 nm for compound **1b**. Notably, inclusion of the [3]cumulene group provides the desired result of a more planarized acene structure relative to other **exTCNQs**, through distancing the tail functionalization from the acene core. Only the CPD group serves as a reasonable acceptor, and LUMO energies of compound **1c** are similar to the two largest known **exTCNQs**, **6,13-TCPQ** and **5,14-TCPQ**. The combination of the two motifs, a [3]cumulene and CPD moiety is, however, insufficient to provide the acceptor strength comparable to "smaller" **exTCNQs** such as **TCAQ** and **TCTQ**. The suitability of **1c**,

2, **3a**, and **4** as semiconductors in solar cells was evaluated *via* examination of thin film formation and charge carrier mobilities (films of **1c** and **3c** were limited by solubility, preventing analysis). Films showed hole mobilities, in spite of the presence of the acceptor groups, albeit mobilities were universally disappointing. Thus, it seems clear fundamental design changes are necessary in order to obtain a promising next generation of n-type materials based on the extended **exTCNQ** framework.

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