

Non-planar push–pull chromophores

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The development of a unique class of non-planar push–pull chromophores by means of [2 + 2] cycloaddition, followed by cycloreversion, of electron-deficient olefins, such as tetracyanoethene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ), as well as dicyanovinyl (DCV) and tricyanovinyl (TCV) derivatives, to donor-substituted alkynes is explored in this feature article. This high-yielding, “click-chemistry”-type transformation with acetylenic dendrimers affords dendritic electron sinks capable of multiple electron uptake within a narrow potential range. An [AB]-type oligomer with a dendralene backbone was synthesised by a one-pot, multi-component cascade reaction of polyne oligomers with TCNE and tetrathiafulvalene (TTF). In most cases, the resulting chromophores feature intense intramolecular charge-transfer bands extending far into the near infrared region and some of them display high third-order optical nonlinearities. Despite substitution with strong donors, the electron-withdrawing moieties in the new chromophores remain potent acceptors and a number of them display positive first reduction potentials (vs. the ferrocenium/ferrocene (Fc⁺/Fc) couple in CH₂Cl₂), which rival those of parent TCNE, TCNQ and F₄-TCNQ. The non-planarity of the chromophores strongly enhances their physical properties when compared to planar push–pull analogues. They feature high solubility, thermal stability and sublimability, which enables formation of amorphous, high-optical-quality thin films by vapour phase deposition and makes them interesting as advanced functional materials for novel opto-electronic devices.

1. Introduction

Intramolecular charge-transfer (CT) interactions are a fundamental property of π -systems that consist of strong

electron donors (D) and acceptors (A) connected *via* a π -conjugated spacer (D– π –A). The chemistry of planar push–pull chromophores has been extensively explored over the past decades,¹ and variation of the donor and acceptor substituents has become a popular approach for tuning their HOMO–LUMO gaps. Much effort has been devoted to their synthesis in order to define structure–property relationships and generate functional molecular components for next-generation

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François Diederich (born 1952) is a native of the Grand-Duchy of Luxembourg and studied chemistry at the University of Heidelberg, where he obtained his diploma (1977), doctoral (1979) and habilitation (1985) degrees. From 1979 to 1981, he was a Postdoctoral Fellow at UCLA, where he returned in 1985, after his Habilitation in Heidelberg, as an Acting Associate Professor. In 1989, he became Full Professor and in 1992, he moved to his current position at the ETH Zürich. His research interests are in carbon-rich molecular architectures and opto-electronic materials, supramolecular chemistry on surfaces, molecular recognition and structure-based drug design.

electronic and optical applications.² D- π -A chromophores featuring intense intramolecular CT interactions have received growing attention as active nonlinear optical (NLO) materials^{3–7} with a wide range of potential applications, such as in all-optical computing and signal processing. Most of these molecules are planar structures to retain efficient donor-acceptor π -conjugation.

Organic advanced materials are generally used in electronic and opto-electronic devices in the form of thin films. Controlling their morphology is a key issue in practical applications. Planar molecules, especially low-molecular-weight compounds, tend to crystallise readily and, hence, they usually undergo aggregation and crystallite formation which affects the optical properties. On the other hand, properly designed non-planar molecules add distinct advantages in physical properties: they are more soluble, less aggregating and more readily sublimable, forming amorphous thin films which are good candidates for potential use in opto-electronic devices because of their good processability, optical transparency and homogeneous properties. It is therefore not surprising that the development of π -chromophores, incorporated in non-planar, star-shaped, spiro-linked or branched architectures, has become a very active area of advanced materials research today.^{8–10}

In the early 2000s, we prepared a new class of planar CT chromophores,^{11–13} the donor-substituted cyanoethynylethenes (CEE), such as **1** and **2**, and demonstrated their outstanding opto-electronic properties (Fig. 1). These D- π -A chromophores display remarkably high two-photon absorption properties and third-order optical nonlinearities, as determined by their third-order polarisability γ_{rot} , relative to their small molecular mass.¹⁴ Considering the quotient $\gamma_{\text{rot}}/\text{number of } \pi\text{-electrons}$, the γ_{rot} value of $(12.0 \pm 1.5) \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$ for **1** exceeds the highest published value of $0.5 \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$ for poly(triacetylene) oligomers.¹⁵ CEE **1** forms crystalline thin films (20 nm thickness) on highly oriented pyrolytic graphite (HOPG) by vapour phase deposition. Nanoscale data recording on these crystalline thin film by scanning tunneling microscopy (STM) realised a storage density of $10^{13} \text{ bits cm}^{-2}$ of dots with a diameter of *ca.* 2.1 nm.¹⁶ The progress in this chemistry of acetylene-based, planar push-pull chromophores has recently been reviewed.¹⁷

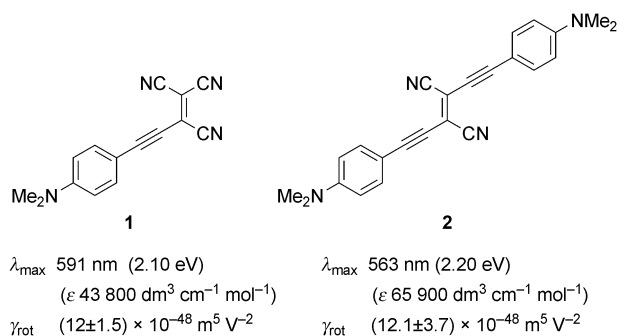


Fig. 1 Donor-substituted cyanoethynylethenes (CEEs). Given are the maxima of the intramolecular CT bands λ_{max} in CHCl_3 at 298 K and the third-order polarisability γ_{rot} measured by degenerate four-wave mixing (DFWM) experiments in CH_2Cl_2 .

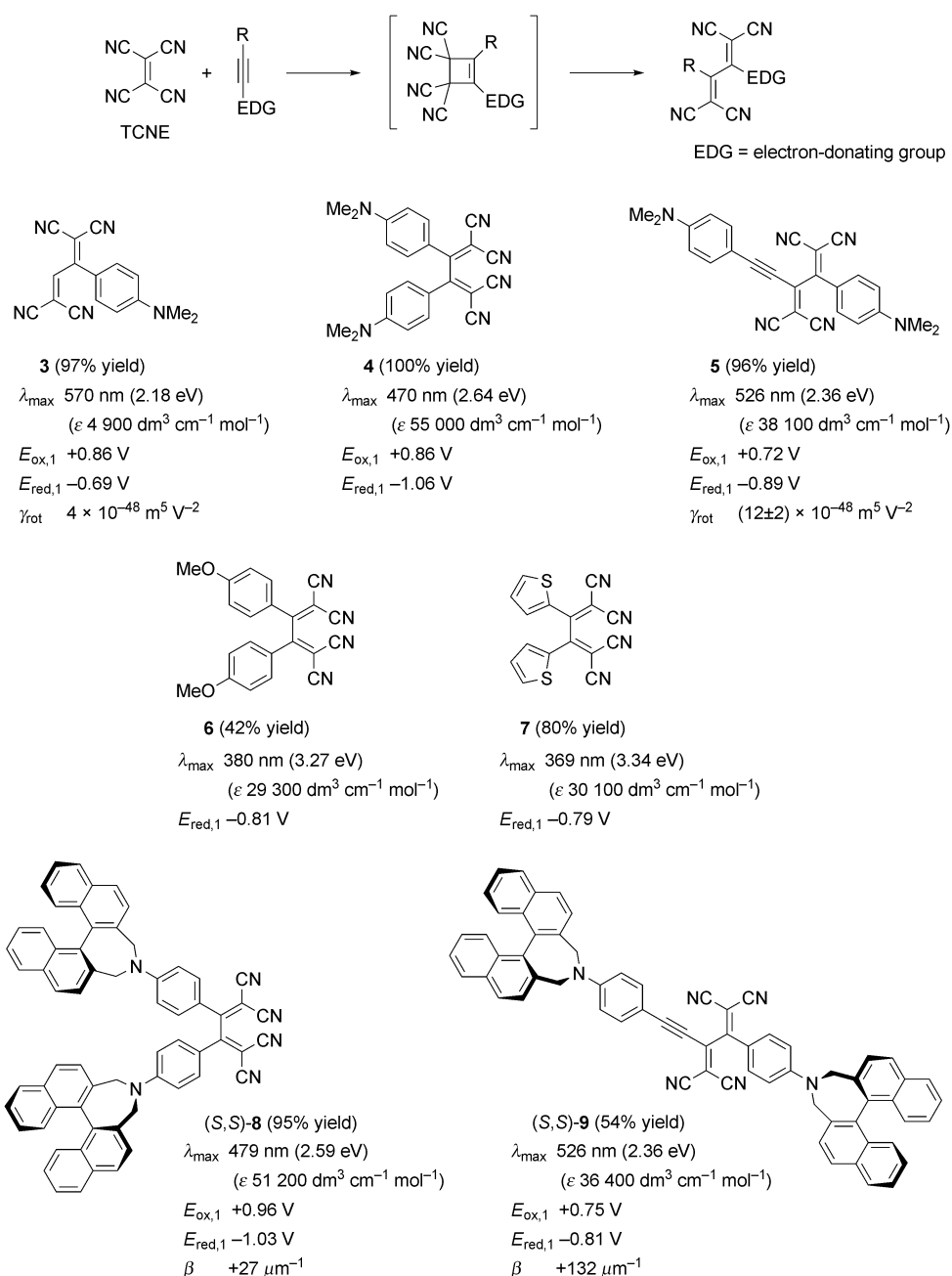
During the study on planar donor-substituted CEEs, it was found difficult to obtain high-optical-quality thin films (100 nm–1 μm thickness) by vapour deposition techniques, where deposition rate is a crucial factor in controlling the structure of the films. We rapidly envisaged that non-planarity of the D- π -A molecules would desirably reduce the long-range order of films and thereby lead to the formation of amorphous rather than crystalline thin films. Here, we describe our ongoing efforts to develop new non-planar D- π -A chromophores by means of single-step, high-yielding [2 + 2] cycloadditions of electron-withdrawing olefins, such as tetracyanoethene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ), as well as dicyanovinyl (DCV) and tricyanovinyl (TCV) derivatives, to electron-rich alkynes, followed by cycloreversion. These efficient, “click-chemistry”-type¹⁸ reactions proceed without need for catalysis and yield strong push-pull chromophores with substantially twisted π -systems, which are rather difficult to access by other chemical transformations. We review here how systematic study led to a deepened understanding of donor-acceptor conjugation in non-planar D- π -A systems and demonstrate their potential as advanced functional materials for device fabrication. It should be noted that several research groups recently also reported synthesis and properties of non-planar push-pull chromophores,^{19–22} their number however remains quite small when compared to planar D- π -A systems.

2. Donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes

Thermal [2 + 2] cycloaddition of the strong electron acceptor TCNE with electron-rich ruthenium-acetylide complexes, followed by ring opening of the initially formed cyclobutenes to form organometallic 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivatives, was first reported by Bruce and co-workers in 1981.^{23a} Subsequently, the preparation of organometallic TCBDs containing various metal atoms, such as platinum, tungsten, osmium, nickel, manganese and iron, has been explored.^{23–28} These results induced the synthesis of first metal-free TCBDs by cycloaddition of TCNE with organo-donor-substituted alkynes,^{29–35} some of which have been investigated as NLO chromophores.^{29,30} Nevertheless, a systematic study on the synthesis and electronic properties of such D- π -A systems had not been reported.

We described in 2005 that *N,N*-dimethylanilino (DMA)-substituted alkynes readily undergo a [2 + 2] cycloaddition with TCNE, followed by retro-electrocyclisation, to give non-planar CT chromophores, donor-substituted TCBDs, such as **3–5** (Scheme 1).³⁶ Transformations are very high-yielding, atom-economic and even proceed in high yield at ambient temperature without solvent, in a ballmill or by using mortar and pestle. The [2 + 2] cycloaddition with TCNE also works with weaker donors, activating the alkyne, such as anisole (in **6**) or thiophene (in **7**), although more forcing conditions are required.³⁷

A wide variety of X-ray crystal structures of donor-substituted TCBDs have been solved. They all reveal considerable non-planarity. A typical example is shown for **5** in Fig. 2.



Scheme 1 Top: Reaction between TCNE and an alkyne, substituted with an electron-donating group (EDG). Bottom: Examples of donor-substituted TCBDs. Given are the maxima of the longest-wavelength CT bands λ_{\max} in CH₂Cl₂ at 298 K, cyclic voltammetry data in CH₂Cl₂ (+0.1 M *n*Bu₄NPF₆ vs. Fc⁺/Fc), third-order polarisabilities γ_{rot} measured by DFWM experiments in CH₂Cl₂ for DMA-substituted TCBDs, and helical twisting power β for *N*-phenyldinaphthazepine-appended TCBDs.

The TCBD framework is highly non-planar with the dihedral angle ($\theta = -96.7^\circ$) between the two DCV planes being nearly orthogonal. On the other hand, the donor-substituted TCBD chromophores show high quinoid character for the DMA moiety reflecting efficient intramolecular CT interactions in the ground state. They display intense low-energy intramolecular CT bands, and these can be tuned to cover the entire spectral range from the visible to the near infrared region (NIR). The λ_{\max} values of the intramolecular CT bands in donor-substituted TCBDs are variable in a range between 369 nm (3.34 eV, $\epsilon = 30\,100$ dm³ cm⁻¹ mol⁻¹) for **7** and

570 nm (2.18 eV, $\epsilon = 4900$ dm³ cm⁻¹ mol⁻¹) for **3**. Interestingly, centrosymmetric molecules **4**, **6** and **7** show substantial solvatochromic effects; the λ_{\max} value of **6** shifts from 379 nm (3.27 eV) in CHCl₃ to 358 nm (3.46 eV) in hexane. The observed solvatochromism is best explained by the increase in electric moment from the ground to the excited state through a change in the quadrupole moment or octupole moment.³⁸

In agreement with the strong intramolecular CT interactions and the resulting low HOMO–LUMO gap, donor-substituted TCBDs show large third-order optical nonlinearities,

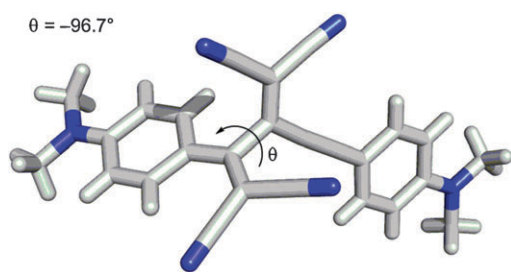


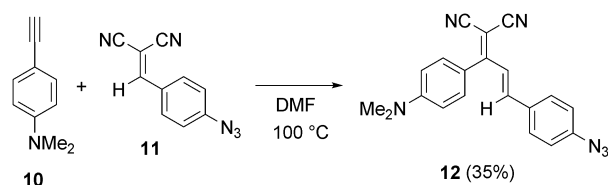
Fig. 2 X-Ray crystal structure of DMA-substituted TCBD **5**.

reaching a high γ_{rot} value of $(12 \pm 2) \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$ for **5**, comparable to those for donor-substituted CEEs.³⁶ Importantly, TCBDs are thermally stable up to 300 °C, which was confirmed by thermal gravimetric analysis (TGA), and can be sublimed without decomposition. As hoped for, their non-planarity enables the formation of high-optical-quality amorphous films (80–850 nm thickness), rather than crystalline films, by vapour deposition.³⁹ Degenerate four-wave mixing (DFWM) measurements for the films of **5** revealed an exceptionally high third-order susceptibility with the $\chi^{(3)}_{1111}$ value of $(2 \pm 1) \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$ at the off-resonant wavelength of 1.5 μm . This value is $\sim 10^3$ times larger than that of fused silica ($1.9 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$). In the meanwhile, **5** has found first application in silicon-organic-hybrid (SOH) waveguides.⁴⁰

In another study, we have recently prepared the optically active *N*-phenyldinaphthazepine-appended TCBDs (*S,S*)-**8** and (*S,S*)-**9** and investigated their potential to induce cholesteric phases in nematic liquid crystals.⁴¹ The remarkably high value of the helical twisting power β ($+132 \mu\text{m}^{-1}$), that describes the ability of a chiral dopant to twist a nematic phase, for (*S,S*)-**9** is due to the presence of skewed aromatic planes. Only a limited number of dopants have been reported with β values of the order of hundreds of μm^{-1} so far.⁴² On the other hand, (*S,S*)-**8** displays a significantly lower β value of $+27 \mu\text{m}^{-1}$ despite its structural similarity to (*S,S*)-**9**. This is explained as a consequence of comparable contributions from conformers with approximately opposite values of the torsional angle around the central TCBD bond that feature oppositely handed twisting ability. Moreover, X-ray diffraction analyses and electrochemical and UV/Vis measurements revealed that the introduction of chiral *N*-phenyldinaphthazepine donors in place of the achiral DMA moiety does not decrease the strong intramolecular CT interactions: the donor strength of both moieties is nearly identical. As an additional benefit, however, the chiral *N*-phenyldinaphthazepine donors add exceptionally large chiroptical responses: Cotton effects in the circular dichroism (CD) spectra show $\Delta\epsilon$ values up to $1294 \text{ M}^{-1} \text{ cm}^{-1}$. These findings indicate that the *N*-phenyldinaphthazepine moiety is a very interesting building block for the construction of chiral push–pull systems.

3. Donor-substituted 1,1-dicyanobuta-1,3-dienes

We recently reported the synthesis of planar push–pull chromophores with 1,2,3-triazoles as versatile π -linkers allowing variation of the position of DMA donor and 1,1-dicyanovinyl (DCV) acceptor moieties and showed the importance of the



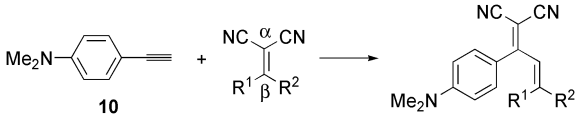
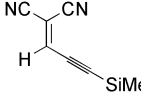
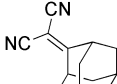
Scheme 2 Unexpected reaction between **10** (DMAA) and **11** to yield the 1,1-dicyanobuta-1,3-diene (DCBD) **12**.

positioning of the donor and acceptor on the 1,2,3-triazole ring for the opto-electronic properties.⁴³ During this investigation, we discovered that thermal 1,3-dipolar cycloaddition—the Huisgen reaction—of 4-ethynyl-*N,N*-dimethylaniline (DMAA, **10**) and DCV-substituted phenyl azide **11** did not take place; instead the 1,1-dicyanobuta-1,3-diene (DCBD) derivative **12** was isolated in 35% yield as a result of a formal [2 + 2] cycloaddition/cycloreversion (Scheme 2). This unexpected reactivity of the electronically less activated DCV electrophile, as compared to TCNE, motivated us to investigate the full scope of the reaction of **10** with various DCV derivatives.

As summarised in Table 1, a wide range of DCVs **13–22** and the tricyanovinyl (TCV) derivative, CEE **1**, undergo [2 + 2] cycloaddition/cycloreversion with **10** in DMF at 100 °C to provide the corresponding donor-substituted DCBDs **23–33** in high yield.⁴⁴ The DMA moiety is selectively introduced at the β -carbon of the DCV moiety in the resulting DCBDs (X-ray analyses). The transformation shows excellent functional group tolerance, as aromatic DCVs with electron-withdrawing (entries 1–3), electronically “neutral” (entries 4 and 5) and electron-donating (Entries 6 and 7) substituents in *para*-position, as well as non-aromatic DCVs (entries 8–10), are transformed to DCBDs in good to excellent yield. Reactions with DCVs bearing electron-withdrawing substituents on the phenyl ring are generally rapid (Entries 1–3). The presence of electron-donating phenyl substituents or sterically-bulky groups does not decrease the yield but slows the reaction. As a typical example, DCV **19** bearing a strong DMA donor is not completely consumed even after 1 week. However by using an excess amount of DMAA, DCV **19** was totally consumed under the standard conditions after 70 h to afford **29** in 97% yield. Contrary to the reaction of **19**, TCV derivative **1** gives the corresponding 1,1,4-tricyanobuta-1,3-diene **33** in high yield after 3 d. The specific advantage of this new reaction is obviously the functional diversity of the resulting donor-substituted DCBDs, indicating the possibility of further structural modification of the resulting chromophores. This post-modification strategy for donor-substituted DCBD chromophores is currently pursued.

The entire reaction profile for the transformation of DMAA with the simplest model system, 1,1-dicyanoethene, has been computed by gas-phase and solvated (MeCN) DFT calculations (B3LYP/6-31G(d)) using the polarisable continuum model (PCM) (Scheme 3).⁴⁴ The transformation consists of four basic steps, and there are five minima along the reaction coordinate. From starting materials (**A**), nucleophilic addition of the γ -carbon of the terminal alkyne to the β -position of the electrophile occurs to produce a zwitterionic high-energy intermediate (**B**) through the bond-forming transition state (**TS**) (**AB**[‡]). Subsequently, bond formation between the α and δ

Table 1 Yields and reaction times for the cycloaddition/cycloreversion reaction of DCV derivatives with **10** in DMF at 100 °C

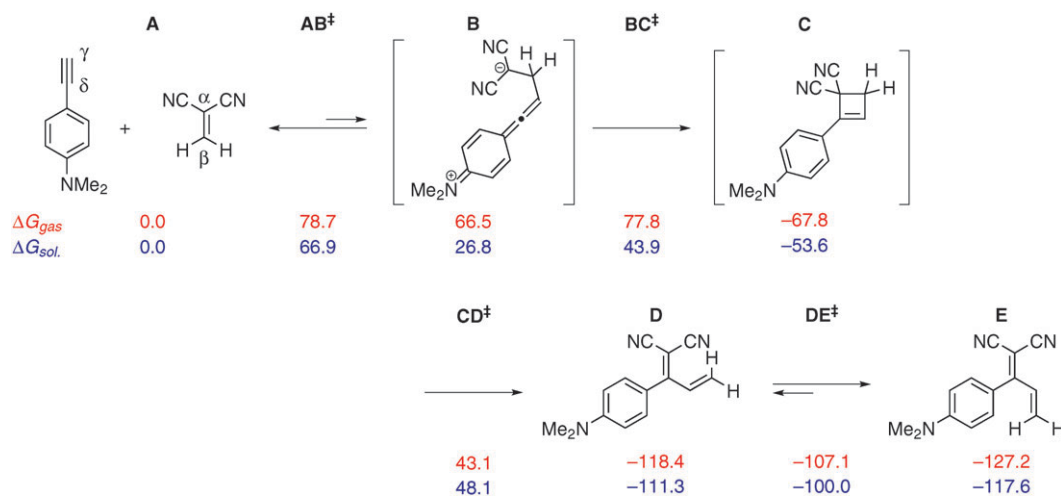
					
Entry		Acceptor	Time	Product	Yield ^a (%)
1	13	R ¹ = H, R ² = <i>p</i> -C ₆ H ₄ NO ₂	20 min	23	98
2	14	R ¹ = H, R ² = <i>p</i> -C ₆ H ₄ CHO	40 min	24	90
3	15	R ¹ = H, R ² = <i>p</i> -C ₆ H ₄ CCH	1.1 h	25	95
4	16	R ¹ = H, R ² = <i>p</i> -C ₆ H ₄ Br	4 h	26	91
5	17	R ¹ = H, R ² = Ph	1.5 h	27	85
6	18	R ¹ = H, R ² = <i>p</i> -C ₆ H ₄ OMe	7 h	28	92
7	19	R ¹ = H, R ² = <i>p</i> -C ₆ H ₄ NMe ₂	3 d	29	97 ^b
8	20		80 min	30	63
9	21	R ¹ = H, R ² = cyclohexyl	3 h	31	90
10	22		40 h	32	80
11	1	R ¹ = CN, R ² = <i>p</i> -C ₆ H ₄ NMe ₂	3 d	33	89

^a Isolated yield. ^b 3 Equiv. **10**.

carbons through TS **BC**[‡] occurs to afford the ring-closed cyclobutene product (**C**). It should be noted that a concerted [2 + 2] TS **AC**[‡] for the process from **A** to **C**, where the β–γ and α–δ bonds form directly, could not be located. Large and stabilising solvation energies (Δ*G*_{gas}–Δ*G*_{sol.}) for **AB**[‡], **B** and **BC**[‡] strongly support the zwitterionic mechanism of the [2 + 2] cycloaddition of DMAA and DCVs. Moving forward, the ring-opening cycloreversion step breaks the α–β bond to give initially the *s*-*cis* product (**D**) and eventually the *s*-*trans* conformer (**E**) by *s*-*cis*-to-*s*-*trans* isomerisation with a small barrier.

The UV/Vis spectra of **23–33** feature intense intramolecular CT bands between 300 and 600 nm, depending on the

functional groups on the DCBD moiety. Despite the DMA functionality, DCBDs remain good electron acceptors. They display mainly an irreversible 1 e[–] reduction step between –1.20 and –1.88 V for the DCV moiety (all redox potentials in this feature article are measured in CH₂Cl₂ + 0.1 M *n*Bu₄NPF₆ and referenced vs. the ferrocenium/ferrocene couple (Fc⁺/Fc). The first reduction potentials would be more anodic by *ca.* 400 mV if given against saturated calomel electrode (SCE)). They also show a reversible 1 e[–] oxidation step at 0.69 ± 0.02 V centred on the DMA moiety. This oxidation potential is nearly unaffected by the nature of the substituents R¹ and R² (Table 1).



Scheme 3 Schematic representation of the proposed mechanism of the reaction of 1,1-dicyanoethene (DCE) with **10**. Given are the B3LYP/6-31G(d) free energy profiles in the gas phase (Δ*G*, kJ mol^{–1}) (in red) and using PCM solvation in acetonitrile (in blue). All data are normalised to the free energies of the starting materials.

4. Multivalent charge-transfer chromophores and novel cascade reactions

Monomeric DMA-substituted TCBDs display two reversible, well-resolved 1 e^- reduction steps between -0.69 and -1.29 V in CH_2Cl_2 . The two first reduction steps for TCBDs are facilitated, compared with those of DCBDs, as a result of the two DCV moieties in the TCBD framework (Scheme 1). The DMA- or *N,N*-dialkylanilino (DAA)-substituted TCBDs also feature reversible 1 e^- oxidation steps located on the donor moieties, which is indicative of their potential use as ambipolar-transporting materials.⁴⁵ We found that the trimeric DAA-substituted TCBD **34** shows six reversible 1 e^- reduction steps in the narrow potential range of 1 V (from -0.69 to -1.69 V), identifying that the DCV moieties do not behave as independent redox-active centres (Fig. 3).³⁷ Note that fullerene C_{60} displays the six 1 e^- reductions in a much wider potential range between -0.98 and -3.26 V in MeCN–toluene.⁴⁶

Inspired by this result, we focused on the synthesis of dendrimer-type multivalent CT chromophores, such as **35–38**, that are capable of taking up an exceptional number of electrons under electrochemical conditions (Fig. 3).⁴⁷ In contrast to **34**, buta-1,3-diyne-1,4-diyl fragments were used to attach the DAA moieties to the central core to reduce the steric encumbrance and enhance the distance between pairs of DCV acceptor moieties, thereby bringing the individual reduction potentials even closer. The multivalent DAA-substituted TCBDs **35–38** were synthesised by means of multiple TCNE addition to the corresponding oligoalkyne precursors in excellent yields (77–98%), which means nearly quantitative conversion in each individual cycloaddition/cycloreversion step. Electrochemical measurements revealed that the chromophores display reversible oxidation behaviour in a single, multi-electron transfer, strongly indicating that all the DAA moieties in a multivalent system behave as independent redox centres.⁴⁸ Multivalent TCBDs undergo several reversible 1 e^- reduction steps centred on the DCV units in a very narrow potential range. It is particularly remarkable that dendrimer **38** accepts 24 electrons in two reversible 12 e^- reduction steps at -0.70 and -1.10 V , respectively. This system acts as a potent “molecular battery”, featuring exceptional electron uptake and storage capacity.⁴⁹ Electron paramagnetic resonance/electron nuclear double resonance (EPR/ENDOR) spectroscopic measurements for multivalent TCBDs **35** and **36** revealed that spin and charge in both one-electron-reduced and -oxidised species, generated by chemical methods, are confined to individual single electron-withdrawing TCBD and the electron-donating DAA moieties, respectively, on the hyperfine EPR time scale.⁵⁰ These results are best explained by substantial deviation of the π -system from planarity, limited π -electron delocalisation and counterion effects. In some cases, EPR spectra could be obtained from the solutions of donor-substituted TCBDs even before contact with the reducing metal took place, which illustrates the exceptional electron-accepting properties of these chromophores.

While studying the reactivity of the multivalent TCBDs, we found that the $\text{C}\equiv\text{C}$ triple bonds adjacent to the

electron-accepting TCBD moieties in **35** undergo $[2 + 2]$ cycloaddition with tetrathiafulvalene (TTF), followed by retro-electrocyclisation, to yield **39** containing 1,2-di(1,3-dithiol-2-ylidene)ethane fragments. Upon heating **35** in MeCN with TTF, tris-adduct **39** was obtained in 47% yield which corresponds to a yield of 78% for each TTF addition (Scheme 4).⁴⁷ Similar transformations of TTF had previously been reported with CEEs by Hopf *et al.*⁵¹ and with 1,6-dicyano-1,3,5-hexatriyne by Hirsch and co-workers.⁵² This initial finding stimulated us to construct a new family of [AB]-type oligomers with a dendralene backbone^{53,54} by sequential TCNE/TTF additions to the end-capped polyynes.⁴⁷ Gratifyingly, one-pot, multi-component cascade reactions of DMA-donor-activated octatetrayne **40** with TCNE and TTF afforded [AB]-type oligomer **41** in 21% yield, which means 68% conversion in each cycloaddition/retro-electrocyclisation sequence.⁴⁷ This protocol is based on the remarkable electronic control during the entire transformation. TCNE adds first to the electron-rich $\text{C}\equiv\text{C}$ triple bond next to the DMA moiety in the octatetrayne. The $\text{C}\equiv\text{C}$ triple bond next to the formed TCBD moiety is now electron-deficient, and thus adds electron-rich TTF. The resulting 1,2-di(1,3-dithiol-2-ylidene)ethane renders the adjacent $\text{C}\equiv\text{C}$ triple bond electron-rich, and TCNE adds again. The last $\text{C}\equiv\text{C}$ triple bond becomes electron-deficient, and the second TTF molecule adds.

5. Donor-substituted expanded 7,7,8,8-tetracyanoquinodimethanes

Strong organic electron acceptors, such as TCNE, TCNQ, $\text{F}_4\text{-TCNQ}$ and their numerous derivatives, are highly attractive due to their opto-electronic properties. They form intermolecular CT complexes and salts with various organic and organometallic electron donors, and these materials frequently exhibit interesting properties such as electrical conductivity⁵⁵ and magnetism.⁵⁶ Environmentally stable acceptors are applied as *p*-dopants for organic light-emitting diodes (OLEDs) and solar cells.⁵⁷ Furthermore, cyano-based organic acceptors can act as non-chelating polydentate ligands and bridge metal centers, thus forming oligonuclear complexes and coordination polymers.⁵⁸ The electrochemistry of donor-substituted DCBDs and TCBDs clearly showed that $[2 + 2]$ cycloadditions of donor-substituted alkynes with electron-withdrawing olefins, followed by cycloreversion, provide a particularly effective method for the construction of strong organic acceptors and we next explored TCNQ as electron-deficient olefin component in this transformation.

Needless to say, TCNQ is one of the most important organic acceptors in the field of both synthetic chemistry and materials science. In 1972, Hagihara and co-workers reported the reactions of Pt(II) alkynyls derivatives and TCNQ to give intense red–purple products which were ascribed to intermolecular CT complex formation.⁵⁹ Later, one of these products was identified by X-ray analysis to be a buta-1,3-dienyl derivative resulting from formal $[2 + 2]$ cycloaddition of TCNQ to the alkyne moiety, followed by cycloreversion.⁶⁰ However in sharp contrast to TCNE, the reactivity of TCNQ toward donor-substituted alkynes remained unexplored in both organometallic and organic chemistry, although various

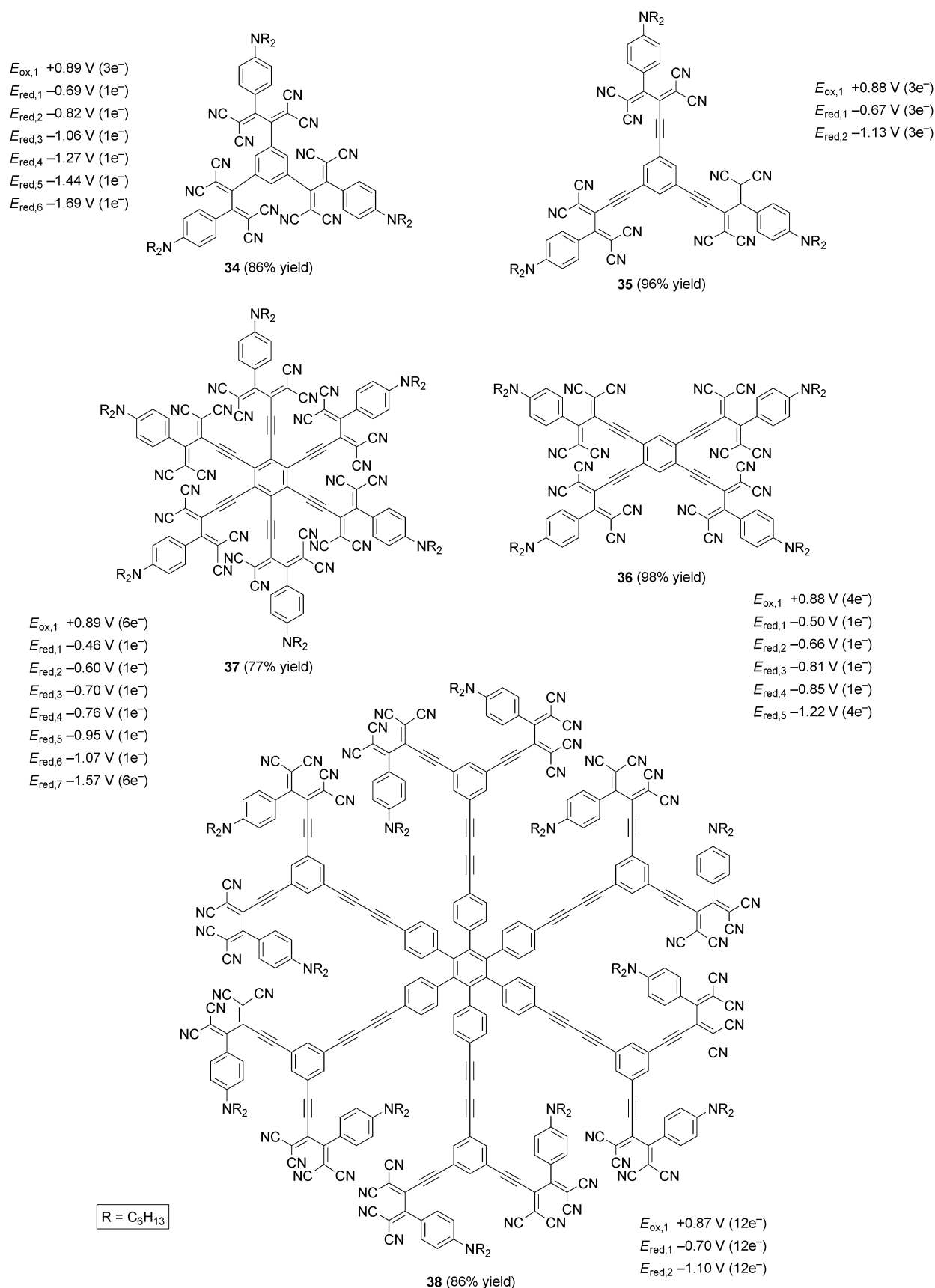
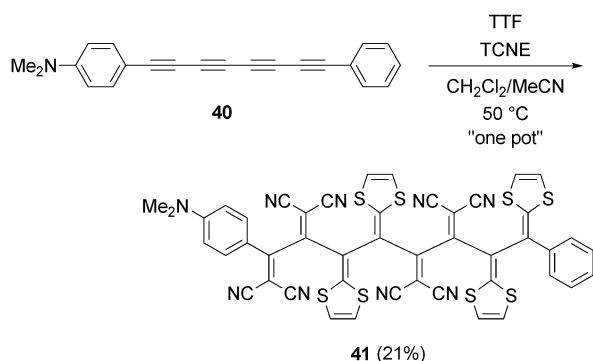
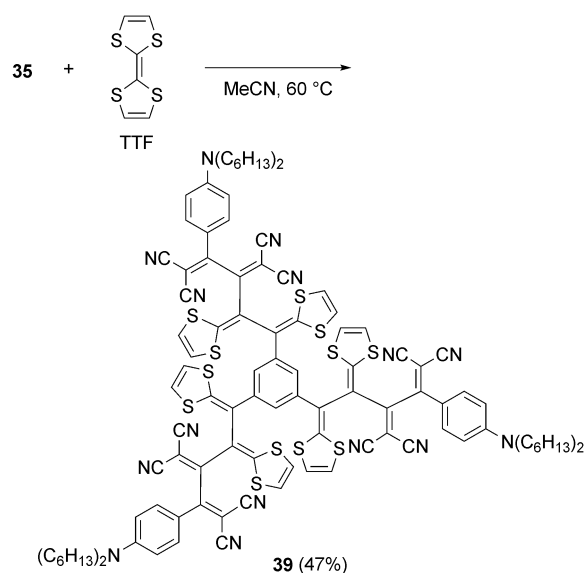


Fig. 3 Dendritic donor–acceptor systems acting as “molecular batteries”. Given are the yields of [2 + 2] cycloaddition/cycloreversion sequences of TCNE with the corresponding alkyne precursors and the cyclic voltammetry data in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M nBu}_4\text{NPF}_6$ vs. Fc^+/Fc .

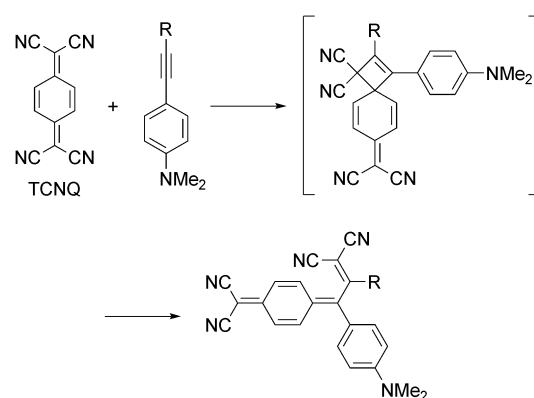


Scheme 4 Thermal [2 + 2] TCNE/TTF additions to donor-substituted alkynes, followed by retro-electrocyclisation, to give [AB]-type oligomers.

reactions with TCNQ, in particular nucleophilic additions, were thoroughly investigated over the past three decades.⁶¹

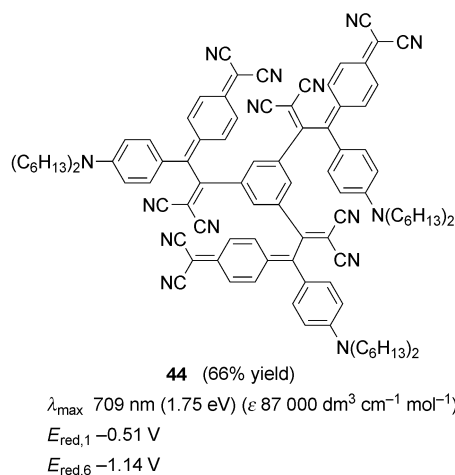
We showed that TCNQ undergoes [2 + 2] cycloaddition with a variety of DAA-substituted alkynes to afford non-planar, cyclohexa-2,5-diene-1,4-diylidene-expanded TCBDs, such as **42–44**, as environmentally and thermally stable products in good to high yield (66–100%) (Scheme 5).⁶² Since this initial report, several other examples of TCNQ-derived expanded TCBDs have been reported.^{63–68} Importantly, the reaction is completely regioselective with respect to TCNQ, occurring exclusively at one exocyclic C=C double bond adjacent to the DCV moiety and not at the endocyclic double bonds. A similar regioselectivity was previously observed in the Diels–Alder reaction of TCNQ with *in situ* generated *ortho*-quinodimethane, reported by Martín and Hanack.⁶⁹

Electrochemical studies showed that donor-substituted expanded TCNQs are potent electron acceptors, that undergo two reversible 1 e[−] reduction steps centred on the two DCV moieties, as in the case of TCBDs. The TCNQ-derived acceptor moiety in **42** (−0.50 V) facilitates the first reduction step by 190 mV when compared to TCBD **3**, which is reversibly reduced at −0.69 V. The difference between the first



42 R = H (81% yield)
 λ_{max} 759 nm (1.63 eV) (ϵ 27 800 dm³ cm^{−1} mol^{−1})
 $E_{\text{red},1}$ −0.50 V

43 R = *n*Bu (100% yield)
 λ_{max} 655 nm (1.89 eV) (ϵ 50 300 dm³ cm^{−1} mol^{−1})
 $E_{\text{red},1}$ −0.72 V



44 (66% yield)
 λ_{max} 709 nm (1.75 eV) (ϵ 87 000 dm³ cm^{−1} mol^{−1})
 $E_{\text{red},1}$ −0.51 V
 $E_{\text{red},6}$ −1.14 V

Scheme 5 Thermal [2 + 2] cycloaddition of TCNQ with donor-substituted alkynes, followed by cycloreversion. Given are the maxima of the intramolecular CT bands λ_{max} in CH₂Cl₂ at 298 K and the cyclic voltammetry data in CH₂Cl₂ + 0.1 M *n*Bu₄NPF₆ vs. Fc⁺/Fc.

and the second reduction potentials for expanded TCNQs are much smaller than that for corresponding donor-substituted TCBDs (230–570 mV). This finding is explained by the larger distance between the two redox centres, as a result of the insertion of the cyclohexa-2,5-diene-1,4-diylidene moiety, resulting in less electrostatic repulsion. The stepwise reduction of trimeric TCNQ adduct **44**, undergoing six reversible 1 e[−] steps, occurs in a narrower range between −0.51 and −1.14 V than that for trimeric TCBD **34** ($E_{\text{red},1}$ = −0.69 V, $E_{\text{red},6}$ = −1.69 V).

Expanded TCNQ chromophores feature intense low-energy intramolecular CT bands with maxima between 655 nm (1.89 eV, ϵ = 50 300 dm³ cm^{−1} mol^{−1}, **43**) and 759 nm (1.63 eV, ϵ = 27 800 dm³ cm^{−1} mol^{−1}, **42**) despite the considerable non-planarity (X-ray). Insertion of the cyclohexa-2,5-diene-1,4-diylidene moiety between the two DCV moieties in expanded TCNQs strongly reduces the optical

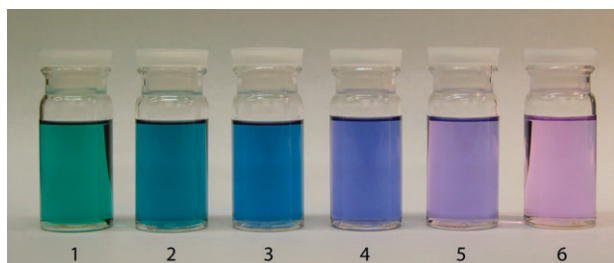


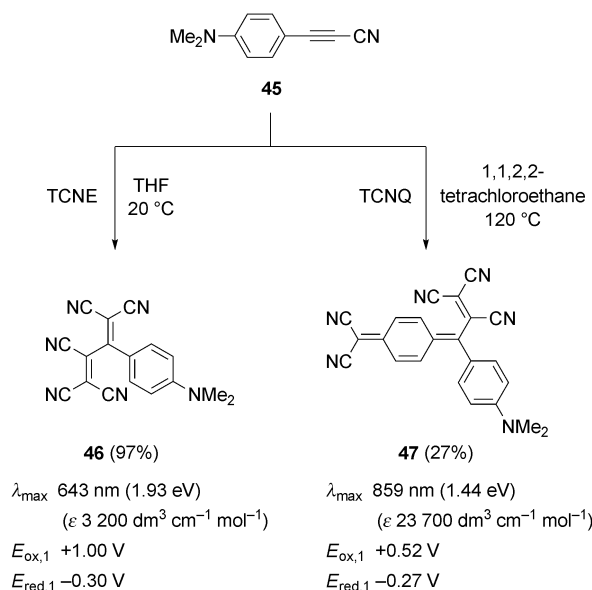
Fig. 4 Solvatochromism of **43** at 298 K. A solution of **43** in CH_2Cl_2 (1), CH_2Cl_2 –hexane 1 : 1 (2), CH_2Cl_2 –hexane 1 : 3 (3), CH_2Cl_2 –hexane 1 : 9 (4), CH_2Cl_2 –hexane 1 : 19 (5) and hexane (6).

HOMO–LUMO gap: the absorption maximum of the CT band for expanded TCNQ **42** occurs at 759 nm (1.63 eV), whereas that for corresponding TCBD **3** is 570 nm (2.18 eV, $\epsilon = 4900 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$). It is worth noting that expanded TCNQs feature remarkable solvatochromism owing to their large electric dipole moment; the CT band for **43** shifts from 559 nm (2.22 eV) in hexane to 655 nm (1.89 eV) in CH_2Cl_2 , changing the color from purple to green (Fig. 4).

6. Organic “super-acceptors” by [2 + 2] cycloaddition of TCNE, TCNQ and F_4 -TCNQ with electronically confused alkynes

While exploring the chemistry of [2 + 2] cycloadditions of TCNE or TCNQ with donor-substituted alkynes, we found that the reaction of TCNE or TCNQ with “electronically confused” alkyne **45**, which has one electron-donating DMA group and one electron-withdrawing CN group, furnished donor-substituted 1,1,2,4,4-pentacyanobuta-1,3-diene (PCBD) **46** and cyclohexa-2,5-diene-1,4-diylidene-expanded PCBD **47**, respectively (Scheme 6).⁷⁰ Expanded PCBD **47** features a remarkably low-energy intramolecular CT band with the maximum of 859 nm (1.44 eV, $\epsilon = 23\,700 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$) accompanied by a tail reaching to 1300 nm (0.95 eV). One of the most striking characteristics of **46** and **47** is their pronounced propensity for reversible electron uptake as a consequence of the additional CN group. Electrochemical measurements revealed that the two reduction steps become significantly more favored. TCBD **3** is reduced at -0.69 and -1.26 V, as described above, whereas the two electron transfers in PCBD **46** occur at -0.30 and -0.85 V, respectively. It is noteworthy that the first reduction potentials of these PCBDs are similar to those of TCNE (-0.32 V) or TCNQ (-0.25 V), despite the substitution with the potent DMA electron donor.

Interestingly, expanded PCBD **47** spontaneously forms an intermolecular CT salt with the strong electron donor dcamethylferrocene ($[\text{FcP}^*_2]$; $E_{\text{ox},1} = -0.59$ V) in MeCN (Scheme 7).⁷¹ The radical anion undergoes immediate reductive σ -dimerisation to afford the solid CT salt **48** ($[\{\text{FcP}^*_2\}_2]^{2+} [\text{47}]_2^{2-}$, X-ray). In accord with the new σ -bond formation, no EPR signal was observed even at 290 K in the solid state. On the other hand, dissociation of the σ -bond takes place in solution to form radical anion $\text{47}^{\bullet-}$, as indicated by EPR and IR investigations. This first observation of intermolecular CT salt formation is now followed by

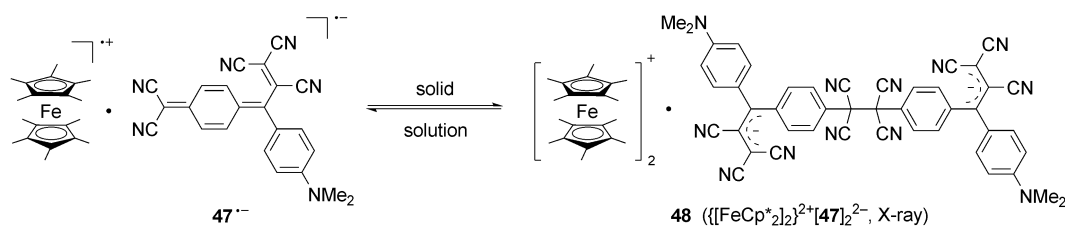


Scheme 6 Synthesis of donor-substituted PCBD **46** and expanded PCBD **47**. Given are the maxima of the longest-wavelength CT bands λ_{max} in CH_2Cl_2 at 298 K and the cyclic voltammetry data in CH_2Cl_2 + 0.1 M $n\text{Bu}_4\text{NPF}_6$ vs. Fc^+/Fc .

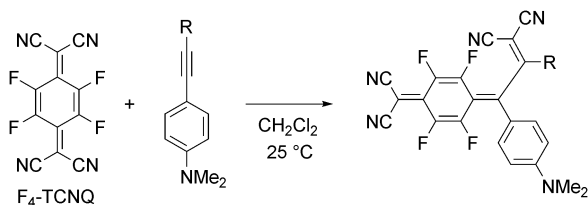
extensive study, involving the various acceptors resulting from the cycloaddition/cycloreversion sequence and potent organic and organometallic donors.

More recently, we have prepared a new family of organic “super-acceptors”, which rival the benchmark compounds TCNQ and F_4 -TCNQ in their propensity for electron uptake. We envisioned that such acceptors could be achieved by the appropriate combination of fluorinated TCNQ moieties with an increasing number of CN substituents on the final, expanded buta-1,3-diene scaffold. On the basis of this strategy, the new acceptors **49–51** were successfully synthesised (65–88%) by cycloaddition/cycloreversion of F_4 -TCNQ with “electronically confused” acetylenes, substituted with one DMA group and one CN, DCV or TCV substituent (Scheme 8).⁷¹

Electrochemical studies disclosed remarkable propensity for reversible electron uptake by the new “super-acceptors”. The first 1 e^- reduction of **49** at ± 0.00 V is greatly facilitated, compared with that of PCBD **46** (-0.30 V) and expanded PCBD **47** (-0.27 V), as a consequence of the electron-withdrawing fluorine substituents. Gradual shifts of reduction steps towards more positive potentials are expected upon increasing the number of CN groups, as indicated by the corresponding Hammett constants of σ_p of $+0.66$ ($-\text{CN}$), $+0.84$ ($-\text{CH}=\text{C}(\text{CN})_2$) and $+0.98$ ($-\text{C}(\text{CN})=\text{C}(\text{CN})_2$). Indeed, increasing the number of CN groups moving from **49** to **51** shifts the first reduction potential anodically to $+0.16$ V. Remarkably, this first reduction potential for **51** is identical to that of parent F_4 -TCNQ ($+0.16$ V), whereas the second reduction is significantly facilitated (-0.17 V (**51**) vs. -0.46 V (F_4 -TCNQ)). However, the first reduction step of **50** occurs cathodically shifted by 100 mV at -0.10 V, compared to **49**. Thus, the correlation between the observed redox potentials and the acceptor strength is not straightforward,



Scheme 7 Formation and dissociation of the solid CT salt **48** ($\{[\text{FeCp}^*_2]_2\}^{2+}[\text{47}]_2^{2-}$, X-ray).



- 49** R = CN (65%)
 λ_{max} 993 nm (1.25 eV) (ϵ 22 300 dm³ cm⁻¹ mol⁻¹)
 $E_{\text{ox},1}$ +0.61 V
 $E_{\text{red},1}$ \pm 0.00 V
- 50** R = (84%)
 λ_{max} 942 nm (1.32 eV) (ϵ 17 000 dm³ cm⁻¹ mol⁻¹)
 $E_{\text{ox},1}$ +0.59 V
 $E_{\text{red},1}$ -0.10 V
- 51** R = (88%)
 λ_{max} 1120 nm (1.11 eV) (ϵ 9 400 dm³ cm⁻¹ mol⁻¹)
 $E_{\text{ox},1}$ +0.64 V
 $E_{\text{red},1}$ +0.16 V

Scheme 8 Synthesis of fluorinated “super-acceptors”. Given are the maxima of the intramolecular CT bands λ_{max} in CH₂Cl₂ at 298 K and the cyclic voltammetry data in CH₂Cl₂ + 0.1 M *n*Bu₄NPF₆ vs. Fc⁺/Fc.

reflecting that structural congestion in these systems may impair efficient π -conjugation between the donor and acceptor moieties. Interestingly, a third reversible 1 e⁻ reduction step is observed at -1.76 and -1.19 V for **50** and **51**, respectively, again demonstrating exceptional electron uptake capacity.

The F₄-TCNQ-derived moiety in **49–51** has a significant impact on the extraordinarily small HOMO–LUMO gaps in these push–pull systems. The UV/Vis absorption spectrum of **51** features a low-energy CT band with the maximum at 1120 nm (1.11 eV, ϵ = 9400 dm³ cm⁻¹ mol⁻¹) and an end-absorption near 1600 nm (0.78 eV). This low optical gap is quite remarkable for such a small chromophore.⁷² Thus, these chromophores combine electron-accepting propensity comparable to F₄-TCNQ, amphoteric redox behaviour and small optical HOMO–LUMO gap, which makes them unique compounds for further physical studies and opto-electronic applications.

7. Non-planar push–pull chromophores with tetrathiafulvalene and ferrocene donors

In general, pronounced non-planarity in push–pull systems leads to disruption of donor–acceptor π -conjugation and concomitant reduction in CT efficiency. This is, however, apparently not the case in the non-planar push–pull chromophores obtained by cycloaddition/cycloreversion from TCNE or TCNQ and donor-substituted alkynes: they feature strong, low-energy CT maxima in the UV/Vis spectra, and efficient ground-state push–pull conjugation is indicated by a high degree of bond length alternation in the donor rings (X-ray). To gain a deeper understanding of the origin of these intense intramolecular CT interactions, we prepared two series of non-planar push–pull chromophores **52** and **53** and **54–56** with strong TTF and ferrocene donors and investigated the effects of sterically enforced deconjugation on opto-electronic properties (Fig. 5).⁷³

Extensive X-ray studies (**52** and **54–56**) revealed that the TTF and ferrocene donors retain nearly fully planar π -conjugation with one half of the acceptor moieties. The TTF and the neighbouring DCV moieties in **52** are completely coplanar with a torsional angle of only 1.7° (Fig. 6A). Also, the plane of the cyclopentadienyl ring (Cp) attached to expanded TCNQs **54–56** is only slightly twisted against the cyclohexa-2,5-diene-1,4-diylidene plane with a torsional angle of about 20°, irrespective of the substituent (H, Ph, Me) on the DCV moiety (Fig. 6B). This nearly planar π -conjugation leads to strong intermolecular CT interactions already in the ground state. A substantial contribution of the charge-separated resonance structure in the TTF and the fulvene-type resonance structure in the ferrocene chromophores is clearly supported by the significant bond length alternations found in the crystal structures. The two TTF chromophores display similar maxima of their CT bands at 767 nm (1.61 eV, ϵ = 5300 dm³ cm⁻¹ mol⁻¹) for **52** and 728 nm (1.69 eV, ϵ = 5200 dm³ cm⁻¹ mol⁻¹) for **53**. Fc-substituted expanded TCNQs show the CT absorption with maxima between 749 nm (1.66 eV, ϵ = 8000 dm³ cm⁻¹ mol⁻¹, **56**) and 801 nm (1.55 eV, ϵ = 5700 dm³ cm⁻¹ mol⁻¹, **54**). It is particularly remarkable that the observed optical HOMO–LUMO gaps in these low-molecular-weight chromophores with substantial non-planarity are comparable to the lowest values obtained for fully planar TTF- and Fc-based push–pull chromophores.^{4,5} Thus, the efficiency of donor–acceptor conjugation in these systems is equal to the best planar ones. This finding implies that the energetic effects of steric π -deconjugation between the two DCV halves are remarkably small even if the twist

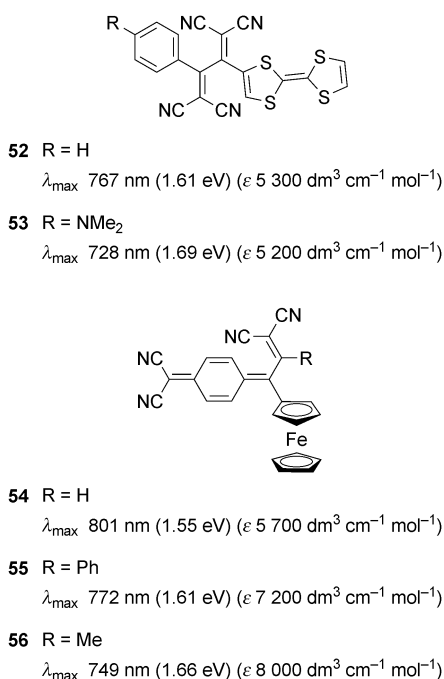


Fig. 5 TTF-appended TCBDs and ferrocene-substituted expanded TCNQs. Given are the maxima of the intramolecular CT bands λ_{max} in CH₂Cl₂ at 298 K.

between the two DCV acceptor halves is enhanced upon further substitution as evidenced by X-ray (twist angle between two acceptor halves of 51.9° in H-substituted **54** and -94.0° in Me-substituted **56**). Thus, it can be concluded that intense intramolecular CT interactions in the non-planar push-pull chromophores mainly originate from nearly planar π -conjugation between the donor and one half of the acceptor moiety. The second DCV moiety, even if twisted out of the plane up to near orthogonality, significantly contributes to the acceptor potency by its strong electron-accepting σ -inductive effect.

Conclusions

The non-planar push-pull chromophores resulting from [2 + 2] cycloadditions of electron-withdrawing cyanoolefins, such as TCNE, DCVs, TCVs, TCNQ and F₄-TCNQ, to electron-rich alkynes exhibit diverse interesting properties, such as intense intramolecular CT interactions, amphoteric electrochemical behaviour, electron-accepting propensity comparable to benchmark acceptors and versatile functionalisation. The non-planarity profoundly enhances the physical properties, such as high solubility and thermal stability. More importantly, the low-molecular-weight non-planar chromophores are less aggregating in the solid state. This adds frequently sublimability without decomposition, thereby allowing formation of high-optical-quality amorphous films rather than crystalline thin films by vapour deposition as demonstrated in opto-electronic applications with **5**. These physical advantages clearly favour their use in opto-electronic devices over planar push-pull chromophores. Multiple TCNE cycloaddition/retro-electrocyclisations to the corresponding oligo(butadiyne) precursors provide a facile synthesis of

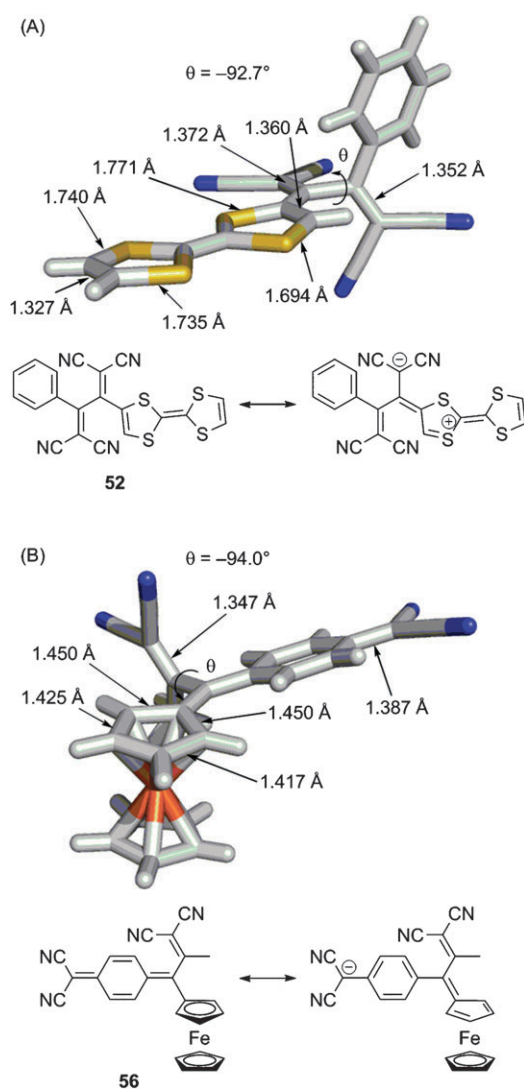


Fig. 6 X-Ray crystal structures of TTF-appended TCBD **52** (A) and Fc-substituted expanded TCNQ **56** (B). A substantial contribution from polar resonance structures as a result of efficient intramolecular CT is supported by experimental bond lengths.

dendritic push-pull systems which act as “molecular batteries”. One-pot domino-reactions, consisting of electronically controlled, sequential cycloadditions/cycloreversions of TCNE and TTF with polyyne oligomers, allow easy preparation of multivalent push-pull chromophores with a unique dendralene-type backbone, as demonstrated in the synthesis of **41**. The first isolation of an intermolecular charge-transfer salt formed by **47** should open up new research field in the future to develop conductive or magnetic charge-transfer salts between potent “super-acceptors” resulting from the formal [2 + 2] cycloaddition/cycloreversion sequence and various organic and organometallic donors. The specific advantage of the reported class of non-planar push-pull chromophores remains undoubtedly their efficient one-step synthesis, amenable to a large scale. This ready accessibility enables rapid establishment of comprehensive structure-property relationships and will increase their use in future practical applications.

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References

- R. Gompper and H.-U. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1437–1455.
- (a) Special issue on organic electronics: *J. Mater. Res.*, ed. F. Faupel, C. Dimitrakopoulos, A. Kahn and C. Wöll, 2004, **19**, pp. 1887–2203; (b) Special issue on organic electronics and opto-electronics: *Chem. Rev.*, ed. S. R. Forrest and M. E. Thompson, 2007, vol. 107, pp. 923–1386.
- S. Barlow and S. R. Marder, *Functional Organic Materials*, ed. T. J. J. Müller and U. H. F. Bunz, Wiley-VCH, Weinheim, 2007, pp. 393–437.
- S. Barlow and S. R. Marder, *Chem. Commun.*, 2000, 1555–1562.
- J. L. Segura and N. Martín, *Angew. Chem., Int. Ed.*, 2001, **40**, 1372–1409.
- M. Szablewski, P. R. Thomas, A. Thornton, D. Bloor, G. H. Cross, J. M. Cole, J. A. K. Howard, M. Malagoli, F. Meyers, J.-L. Brédas, W. Wenseleers and E. Goovaerts, *J. Am. Chem. Soc.*, 1997, **119**, 3144–3154.
- R. R. Tykwinski, U. Gubler, R. E. Martin, F. Diederich, C. Bosshard and P. Günter, *J. Phys. Chem. B*, 1998, **102**, 4451–4465.
- (a) Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1–25; (b) Y. Shirota, *J. Mater. Chem.*, 2005, **15**, 75–93.
- P. Stroehriegel and J. V. Grazulevicius, *Adv. Mater.*, 2002, **14**, 1439–1452.
- J. Roncali, P. Leriche and A. Cravino, *Adv. Mater.*, 2007, **19**, 2045–2060.
- (a) N. N. P. Moonen, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross and F. Diederich, *Angew. Chem., Int. Ed.*, 2002, **41**, 3044–3047; (b) N. N. P. Moonen, R. Gist, C. Boudon, J.-P. Gisselbrecht, P. Seiler, T. Kawai, A. Kishioka, M. Gross, M. Irie and F. Diederich, *Org. Biomol. Chem.*, 2003, **1**, 2032–2034; (c) N. N. P. Moonen and F. Diederich, *Org. Biomol. Chem.*, 2004, **2**, 2263–2266; (d) N. N. P. Moonen, W. C. Pomerantz, R. Gist, C. Boudon, J.-P. Gisselbrecht, T. Kawai, A. Kishioka, M. Gross, M. Irie and F. Diederich, *Chem.–Eur. J.*, 2005, **11**, 3325–3341.
- (a) F. Bureš, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, M. Gross and F. Diederich, *Eur. J. Org. Chem.*, 2008, 994–1004; (b) F. Bureš, O. Pytela and F. Diederich, *J. Phys. Org. Chem.*, 2009, **22**, 155–162.
- For earlier examples of CEEs, see: (a) T. Metler, A. Uchida and S. I. Miller, *Tetrahedron*, 1968, **24**, 4285–4297; (b) L. Y. Ukhin, A. M. Sladkov and Z. I. Orlova, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1969, **18**, 637–638; (c) H. Hopf and M. Kreutzer, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 393–395; (d) L. Dulog, B. Körner, J. Heinze and J. Yang, *Liebigs Ann.*, 1995, 1663–1671.
- (a) J. C. May, J. H. Lim, I. Biaggio, N. N. P. Moonen, T. Michinobu and F. Diederich, *Opt. Lett.*, 2005, **30**, 3057–3059; (b) J. C. May, I. Biaggio, F. Bureš and F. Diederich, *Appl. Phys. Lett.*, 2007, **90**, 251106/1–251106/3.
- U. Gubler, Ch. Bosshard, P. Günter, M. Y. Balakina, J. Cornil, J. L. Brédas, R. E. Martin and F. Diederich, *Opt. Lett.*, 1999, **24**, 1599–1601.
- G. Jiang, T. Michinobu, W. Yuan, M. Feng, Y. Wen, S. Du, H. Gao, L. Jiang, Y. Song, F. Diederich and D. Zhu, *Adv. Mater.*, 2005, **17**, 2170–2173.
- M. Kivala and F. Diederich, *Acc. Chem. Res.*, 2009, **42**, 235–248.
- H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.
- (a) M. C. Diaz, B. M. Illescas, C. Seoane and N. Martín, *J. Org. Chem.*, 2004, **69**, 4492–4499; (b) B. Insuasty, C. Atienza, C. Seoane, N. Martín, J. Garin, J. Orduna, R. Alcalá and B. Villacampa, *J. Org. Chem.*, 2004, **69**, 6986–6995.
- R. Gómez, C. Seoane and J. L. Segura, *Chem. Soc. Rev.*, 2007, **36**, 1305–1322.
- A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4273–4276.
- A. Ortiz, B. Insuasty, M. R. Torres, M. Á. Herranz, N. Martín, R. Viruela and E. Ortí, *Eur. J. Org. Chem.*, 2008, 99–108.
- (a) M. I. Bruce, J. R. Rodgers, M. R. Snow and A. G. Swincer, *J. Chem. Soc., Chem. Commun.*, 1981, 271–272; (b) M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *Organometallics*, 1985, **4**, 494–500; (c) M. I. Bruce, T. W. Hambley, M. R. Snow and A. G. Swincer, *Organometallics*, 1985, **4**, 501–508; (d) M. I. Bruce, M. P. Cifuentes, M. R. Snow and E. R. T. Tiekink, *J. Organomet. Chem.*, 1989, **359**, 379–399; (e) M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 3719–3728; (f) M. I. Bruce, P. J. Low, M. Ke, B. D. Kelly, B. W. Skelton, M. E. Smith, A. H. White and N. B. Witton, *Aust. J. Chem.*, 2001, **54**, 453–460; (g) M. I. Bruce, M. E. Smith, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 2001, **637–639**, 484–499; (h) M. I. Bruce, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Organomet. Chem.*, 2002, **650**, 141–150; (i) M. I. Bruce, F. de Montigny, M. Jevric, C. Lapinte, B. W. Skelton, M. E. Smith and A. H. White, *J. Organomet. Chem.*, 2004, **689**, 2860–2871; (j) M. I. Bruce, P. J. Low, F. Hartl, P. A. Humphrey, F. de Montigny, M. Jevric, C. Lapinte, G. J. Perkins, R. L. Roberts, B. W. Skelton and A. H. White, *Organometallics*, 2005, **24**, 5241–5255; (k) M. I. Bruce, P. A. Humphrey, M. Jevric, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 2007, **692**, 2564–2574; (l) M. I. Bruce, M. Jevric, C. R. Parker, W. Patalinghug, B. W. Skelton, A. H. White and N. N. Zaitseva, *J. Organomet. Chem.*, 2008, **693**, 2915–2920; (m) M. I. Bruce, A. Burgun, K. A. Kramarczuk, B. K. Nicholson, C. R. Parker, B. W. Skelton, A. H. White and N. N. Zaitseva, *Dalton Trans.*, 2009, 33–36.
- (a) K. Onitsuka and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1995, 2095–2096; (b) K. Onitsuka, N. Ose, F. Ozawa and S. Takahashi, *J. Organomet. Chem.*, 1999, **578**, 169–177.
- Y. Yamamoto, R. Satoh and T. Tanase, *J. Chem. Soc., Dalton Trans.*, 1995, 307–311.
- T. Mochida and S. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 2002, 3559–3564.
- R. L. Cordiner, M. E. Smith, A. S. Batsanov, D. Albesa-Jové, F. Hartl, J. A. K. Howard and P. J. Low, *Inorg. Chim. Acta*, 2006, **359**, 946–961.
- M. Hussain, D. Albert, R. Wartchow and H. Butenschön, *Chem.–Asian J.*, 2007, **2**, 782–793.
- X. Wu, J. Wu, Y. Liu and A. K.-Y. Jen, *J. Am. Chem. Soc.*, 1999, **121**, 472–473.
- C. Cai, I. Liakatas, M.-S. Wong, M. Bösch, C. Bosshard, P. Günter, S. Concilio, N. Tirelli and U. W. Suter, *Org. Lett.*, 1999, **1**, 1847–1849.
- Y. Morioka, N. Yoshizawa, J. Nishida and Y. Yamashita, *Chem. Lett.*, 2004, **33**, 1190–1191.
- J. Xu, X. Liu, J. Lv, M. Zhu, C. Huang, W. Zhou, X. Yin, H. Liu, Y. Li and J. Ye, *Langmuir*, 2008, **24**, 4231–4237.
- T. Michinobu, *J. Am. Chem. Soc.*, 2008, **130**, 14074–14075.
- T. Shoji, S. Ito, K. Toyota, M. Yasunami and N. Morita, *Chem.–Eur. J.*, 2008, **14**, 8398–8408.
- W. Zhou, J. Xu, H. Zheng, X. Yin, Z. Zuo, H. Liu and Y. Li, *Adv. Funct. Mater.*, 2009, **19**, 141–149.
- T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio and F. Diederich, *Chem. Commun.*, 2005, 737–739.
- T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross and F. Diederich, *Chem.–Eur. J.*, 2006, **12**, 1889–1905.
- B. Strehmel, A. M. Sarker and H. Detert, *ChemPhysChem*, 2003, **4**, 249–259.
- B. Emsbeson, M. L. Scimeca, T. Michinobu, F. Diederich and I. Biaggio, *Adv. Mater.*, 2008, **20**, 4584–4587.

- 40 (a) C. Koos, P. Vorreau, T. Vallaitis, P. Dumon, W. Bogaerts, R. Baets, B. Esembeson, I. Biaggio, T. Michinobu, F. Diederich, W. Freude and J. Leuthold, *Nat. Photonics*, 2009, **3**, 216–219; (b) J. Leuthold, W. Freude, J.-M. Brosi, R. Baets, P. Dumon, I. Biaggio, M. L. Scimeca, F. Diederich, B. Frank and C. Koos, *Proc. IEEE*, 2009, **97**, 1304–1316; (c) T. Vallaitis, S. Bogatscher, L. Alloatti, P. Dumon, R. Baets, M. L. Scimeca, I. Biaggio, F. Diederich, C. Koos, W. Freude and J. Leuthold, *Opt. Express*, 2009, **17**, 17357–17368.
- 41 B. Frank, B. C. Blanco, S. Jakob, F. Ferroni, S. Pieraccini, A. Ferrarini, C. Boudon, J.-P. Gisselbrecht, P. Seiler, G. P. Spada and F. Diederich, *Chem.–Eur. J.*, 2009, **15**, 9005–9016.
- 42 R. Eelkema and B. L. Feringa, *Org. Biomol. Chem.*, 2006, **4**, 3729–3745.
- 43 P. D. Jarowski, Y.-L. Wu, W. B. Schweizer and F. Diederich, *Org. Lett.*, 2008, **10**, 3347–3350.
- 44 P. D. Jarowski, Y.-L. Wu, C. Boudon, J.-P. Gisselbrecht, M. Gross, W. B. Schweizer and F. Diederich, *Org. Biomol. Chem.*, 2009, **7**, 1312–1322.
- 45 (a) J. Cornil, J.-L. Brédas, J. Zaumseil and H. Sirringhaus, *Adv. Mater.*, 2007, **19**, 1791–1799; (b) M. Mas-Torrent and C. Rovira, *Chem. Soc. Rev.*, 2008, **37**, 827–838.
- 46 Q. Xie, E. Pérez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978–3980.
- 47 M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross and F. Diederich, *Angew. Chem., Int. Ed.*, 2007, **46**, 6357–6360.
- 48 (a) J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248–4253; (b) M.-C. Daniel, J. Ruiz, J.-C. Blais, N. Daro and D. Astruc, *Chem.–Eur. J.*, 2003, **9**, 4371–4379; (c) V. J. Chebny, D. Dhar, S. V. Lindeman and R. Rathore, *Org. Lett.*, 2006, **8**, 5041–5044; (d) K. Hosomizu, H. Imahori, U. Hahn, J.-F. Nierengarten, A. Listorti, N. Armaroli, T. Nemoto and S. Isoda, *J. Phys. Chem. C*, 2007, **111**, 2777–2786.
- 49 D. Astruc, C. Ornelas and J. Ruiz, *Chem.–Eur. J.*, 2009, **15**, 8936–8944.
- 50 M. Kivala, T. Stanoeva, T. Michinobu, B. Frank, G. Gescheidt and F. Diederich, *Chem.–Eur. J.*, 2008, **14**, 7638–7647.
- 51 H. Hopf, M. Kreutzer and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1127–1128.
- 52 G. Schermann, O. Vostrowsky and A. Hirsch, *Eur. J. Org. Chem.*, 1999, 2491–2500.
- 53 (a) H. Hopf, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 948–959; (b) H. Hopf, *Angew. Chem., Int. Ed.*, 2001, **40**, 705–707.
- 54 A. D. Payne, G. Bojase, M. N. Paddon-Row and M. S. Sherburn, *Angew. Chem., Int. Ed.*, 2009, **48**, 4836–4839.
- 55 (a) Special issue on molecular conductors; *Chem. Rev.*, ed. P. Batail, 2004, vol. 104, pp. 4887–5782; (b) G. Saito and Y. Yoshida, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 1–137.
- 56 (a) J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385–415; (b) J. S. Miller, *Inorg. Chem.*, 2000, **39**, 4392–4408.
- 57 K. Walzer, B. Maennig, M. Pfeiffer and K. Leo, *Chem. Rev.*, 2007, **107**, 1233–1271.
- 58 S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*, 2003, **246**, 103–130.
- 59 H. Masai, K. Sonogashira and N. Hagihara, *J. Organomet. Chem.*, 1972, **34**, 397–404.
- 60 K.-i. Onuma, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1696–1700.
- 61 (a) B. P. Bespalov and V. V. Titov, *Russ. Chem. Rev.*, 1975, **44**, 1091–1108; (b) W. Kaim and M. Moscherosch, *Coord. Chem. Rev.*, 1994, **129**, 157–193.
- 62 M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross and F. Diederich, *Chem. Commun.*, 2007, 4731–4733.
- 63 K. Tahara, T. Fujita, M. Sonoda, M. Shiro and Y. Tobe, *J. Am. Chem. Soc.*, 2008, **130**, 14339–14345.
- 64 (a) W. Zhou, J. Xu, H. Zheng, H. Liu, Y. Li and D. Zhu, *J. Org. Chem.*, 2008, **73**, 7702–7709; (b) W. Zhou, S. Zhang, G. Li, Y. Zhao, Z. Shi, H. Liu and Y. Li, *ChemPhysChem*, 2009, **10**, 2066–2072.
- 65 T. Shoji, S. Ito, K. Toyota, T. Iwamoto, M. Yasunami and N. Morita, *Eur. J. Org. Chem.*, 2009, 4316–4324.
- 66 M. I. Bruce, M. L. Cole, C. R. Parker, B. W. Skelton and A. H. White, *Organometallics*, 2008, **27**, 3352–3367.
- 67 P. Butler, A. R. Manning, C. J. McAdam and J. Simpson, *J. Organomet. Chem.*, 2008, **693**, 381–392.
- 68 Q.-Y. Lv, S.-D. Tang, X.-W. Tan, W.-J. Lei, Y. Wang, H.-K. Lin, Z.-Q. Wu and S.-Z. Zhan, *J. Organomet. Chem.*, 2009, **694**, 3242–3246.
- 69 N. Martín and M. Hanack, *J. Chem. Soc., Chem. Commun.*, 1988, 1522–1524.
- 70 P. Reutenauer, M. Kivala, P. D. Jarowski, C. Boudon, J.-P. Gisselbrecht, M. Gross and F. Diederich, *Chem. Commun.*, 2007, 4898–4900.
- 71 M. Kivala, C. Boudon, J.-P. Gisselbrecht, B. Enko, P. Seiler, I. B. Müller, N. Langer, P. D. Jarowski, G. Gescheidt and F. Diederich, *Chem.–Eur. J.*, 2009, **15**, 4111–4123.
- 72 D. F. Perepichka and M. R. Bryce, *Angew. Chem., Int. Ed.*, 2005, **44**, 5370–5373.
- 73 S.-i. Kato, M. Kivala, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht and F. Diederich, *Chem.–Eur. J.*, 2009, **15**, 8687–8691.