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Origin of Intense Intramolecular Charge-Transfer Interactions in Nonplanar Push–Pull Chromophores

Shin-ichiro Kato,[a] Milan Kivala,[a] W. Bernd Schweizer,[a] Corinne Boudon,[b] Jean-Paul Gisselbrecht,[b] and François Diederich*[a]

Planar push–pull chromophores featuring intense intramolecular charge-transfer (CT) interactions have been extensively studied in view of their potential applications in molecular electronics and optoelectronics.[1,2] In contrast, only a limited number of nonplanar low-molecular-weight donor–acceptor chromophores has been reported and the impact of nonplanarity on their π-conjugative and optoelectronic properties not been systematically investigated.[3,4] Nonplanar CT chromophores tend to feature some desirable physical properties compared to their planar counterparts: they are usually more soluble, less aggregating, and more readily sublimable, forming amorphous, rather than crystalline films for potential use in optoelectronic devices.[2a,5] We showed recently that donor-substituted alkynes undergo a formal [2+2] cycloaddition with electron-accepting olefins, such as tetracyanoethene (TCNE),[6–8] 7,7,8,8-tetracyanoquinodimethanes (TCNQs),[9–11] as well as dicyanovinyl (DCV) and tricyanovinyl derivatives,[12] followed by retroelectrocyclization, under formation of nonplanar push–pull chromophores featuring intense intramolecular CT and high third-order optical nonlinearities. Nonplanar, *N,N*-dimethylanilino (DMA) donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs), obtained by [2+2] cycloaddition of TCNE, produce high-optical quality amorphous films by vapor-phase deposition[13a] which in the meanwhile have found first application in silicon-organic-hybrid (SOH) waveguides.[13b] A key question raised was the origin of the intense intramolecular CT interactions in these push–pull chromophores, in view of their pronounced nonplanarity which is expected to lead to disruption of donor–acceptor π-conjugation and concomitant reduction in CT efficiency and optical nonlinearity. To investigate the effects of sterically enforced deconjugation on optoelectronic properties, we prepared two new series of push–pull chromophores (**1** and **2**, and **3**–**8**), by adding TCNE or TCNQ to tetrathiafulvalene (TTF)- or ferrocenyl (Fc)-substituted alkynes, respectively. These strong electron donors have found numerous applications in intermolecular[14,15] and intramolecular CT systems,[16] but have not seen much use for activating alkynes electronically for the cycloaddition of TCNE or TCNQ.[17]

TTF-appended TCBD **1** was obtained in 41 % yield as a deep blue solid by reaction of TCNE with TTF-substituted alkyne **9** in 1,2-dichloroethane at 80 °C (Scheme 1). The electronically more activated alkyne **10**, with both TTF and DMA donor groups, reacted at room temperature to give **2** in 79 % yield. The ferrocene-substituted expanded TCNQs **3**–**8** were formed as black metallic-like solids in 41–81 % yield by regioselective cycloaddition between TCNQ and the acetylenic precursors **11**–**16**. With the exception of **3** and **8**, these push–pull chromophores are thermally stable up to 300 °C, as revealed by thermal gravimetric analysis (TGA); compound **6** can actually be sublimed without decomposition at about 250 °C/1×10^{-6} Torr.

Single crystals of **1** and **3**–**5** suitable for X-ray analysis were grown from CH_2Cl_2/hexane at −15 °C (Figure 1 and Figure S1–S4 in the Supporting Information). Considerable nonplanarity is observed in the TCBD and expanded TCNQ acceptor moieties. Thus, the dihedral angle θ (C1-C2-C17-C18) between the two DCV planes in **1** (with two independent molecules) is −92.7(2)°. In the expanded TCNQ chromophores **3**–**5**, the dihedral angle θ between the DCV and the cyclohexa-2,5-diene-1,4-diylidene moiety changes from 51.9(4)° (**3**, torsional angle C1-C2-C3-C4, Figure S2) to −68.6(2)° (**5**, C5-C8-C9-C16, Figure S4), and to −94.0(2)° (**4**, C1-C12-C13-C14). Sterically enforced π-deconjugation is

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[a] Dr. S.-i. Kato, Dr. M. Kivala, Dr. W. B. Schweizer,
Prof. Dr. F. Diederich
Laboratorium für Organische Chemie, ETH Zürich
Hönggerberg, HCI, 8093 Zürich (Switzerland)
Fax: (+41) 44-632-1109
E-mail: diederich@org.chem.ethz.ch

[b] Prof. Dr. C. Boudon, Dr. J.-P. Gisselbrecht
Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide
Intstitut de Chimie-UMR 7177, C.N.R.S.
Université de Strasbourg
4, rue Blaise Pascal, 67000 Strasbourg (France)

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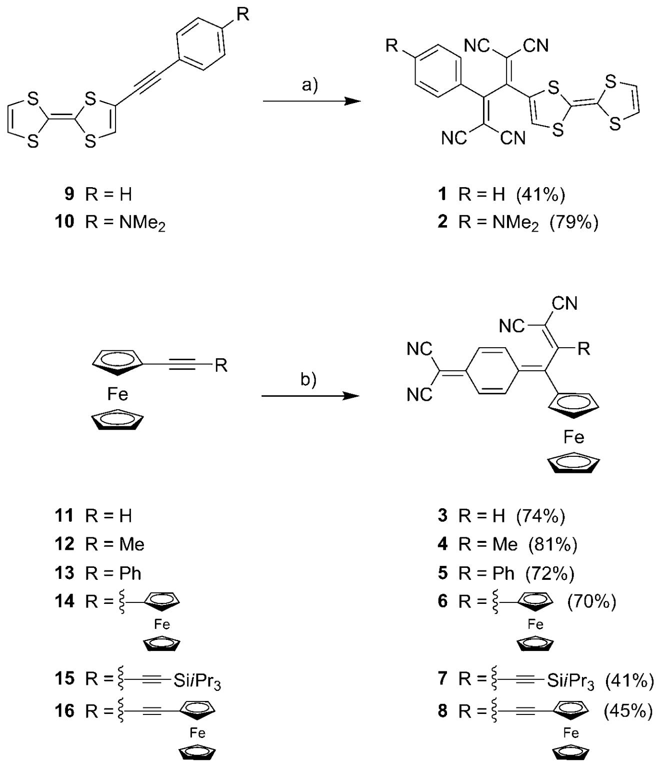

Scheme 1. Synthesis of push–pull chromophores **1**–**8**. Reagents and conditions: a) TCNE, 1,2-dichloroethane or benzene, 80 °C (**1**) or 25 °C (**2**). b) TCNQ, CH_2Cl_2 or 1,2-dichloroethane, 25 °C or 70/80 °C.

smallest in **3** with an H-substituent on the DCV moiety, and this is consistent with the UV/Vis and electrochemical data described below.

Most importantly however, the TTF and Fc donors retain nearly fully planar π-conjugation with one half of the acceptor moieties. The experimentally observed bond lengths (Figure 1, Figure S1–S4 in the Supporting Information) support a significant contribution of polar resonance structures as a result of intramolecular CT interactions in the ground state. Thus in **1**, the TTF and the neighboring DCV moiety are coplanar, with a torsional angle C1-C2-C3-S7 of 1.7(3)°. As a result of efficient intramolecular CT, the S5−C4 bond (1.694(2) Å) in the TTF moiety is significantly shorter than all other C−S bonds (between 1.733(3) and 1.7711(19) Å). Correspondingly, the C3−C4 bond (1.360(3) Å) is elongated compared to the other TTF double bond C10−C11 (1.327(4) Å). Also, the C1−C2 bond (1.372(3) Å) in the coplanar DCV is longer than the corresponding C17−C18 bond (1.352(3) Å) in the orthogonally oriented DCV. All these data support a major contribution of the charge-separated resonance structure shown in Figure 1 to the ground-state geometry of **1**.

The plane of the cyclopentadienyl (Cp) rings attached to the acceptor in **3**–**5** is slightly twisted against the cyclohexa-2,5-diene-1,4-diylidene plane, with torsional angles between 22.6(4)° (**3**, C4-C3-C19-C20), −20.6(3)° (**4**, C1-C12-C20-C24), and −21.6(3)° (**5**, C5-C8-C25-C29). Again the experimental bond lengths reveal efficient intramolecular CT interactions. For example, the Cp bonds C21−C22 (1.425(3) Å) and C23−C24 (1.417(3) Å) in **4** are significantly shorter than the C20−C21 and C20−C24 bonds (both 1.450(3) Å).[18] Also, the C4−C7 bond (1.387(2) Å) is much longer than the C13−C14 bond (1.347(3) Å). These data support a substantial contribution of the fulvene-type resonance structure shown in Figure 1 to the ground-state geometry.[19] Neighboring molecules in **1** and **3**–**5** interact via multiple dipolar CN···CN interactions as revealed by the crystal packings shown in the Supporting Information.[7b,10b]

Cyclic voltammetry (Table 1) and rotating-disk voltammetry (RDV, see Table S1 in the Supporting Information) in CH_2Cl_2 (+0.1 M nBu_4NPF_6, internal standard Fc^+/Fc) show that TCBDs **1** and **2** exhibit two TTF-type $1e^-$-oxidation couples at nearly same potentials (+0.24, +0.67 V for **1**). The parent TTF undergoes the oxidation steps at −0.08 and +0.40 V under the same conditions.[20] Oxidation of **1** and **2** is clearly rendered more difficult by the conjugation with the strong TCBD acceptor. The two well-resolved, reversible $1e^-$-reduction steps, centered on the TCBD acceptors, appear at −0.63 V/−0.97 V (in **1**) and at −0.83 V/−1.06 V (in **2**). The cathodic shifts observed for **2** originate from π-conjugation of the acceptor to the second donor moiety, namely DMA.

Table 1. Cyclic voltammetry (CV) data for **1** and **3**–**6** in CH_2Cl_2 (+0.1 M nBu_4NPF_6)[a] and a summary of electrochemical and optical energy gaps. The complete set of data for **1**–**8**, including those from rotating-disk voltammetry (RDV), are included in the Supporting Information.

	Cyclic voltammetry				
	$E°$ [V][b]	ΔE_p [mV][c]	E_p [V][d]	ΔE_{redox} [V][e]	ΔE_{opt} [eV][f]
1			+0.67	0.87	1.61
	+0.24	75			
	−0.63	60			
	−0.97	70			
3	+0.36	75		0.85	1.55
	−0.49	75			
	−0.75	80			
4	+0.36	85		1.17	1.66
	−0.81	120			
5	+0.34	90		1.08	1.61
	−0.74	60			
	−0.81	60			
6	+0.47	85		1.15	1.63
	+0.33	85			
	−0.82	85			
	−0.94	85			

[a] All potentials are given versus the Fc^+/Fc couple used as internal standard. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 V s^{-1}. [b] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{ox} - E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [d] E_p = Irreversible peak potential. [e] Electrochemical gap, ΔE_{redox}, is defined as the potential difference between the first oxidative and first reductive redox potentials. [f] Optical gap, ΔE_{opt}, is defined as the energy corresponding to the λ_{max} of the CT absorption.

In the ferrocene-substituted expanded TCNQs **3**–**8**, the first oxidation potentials, located on the ferrocene moiety,

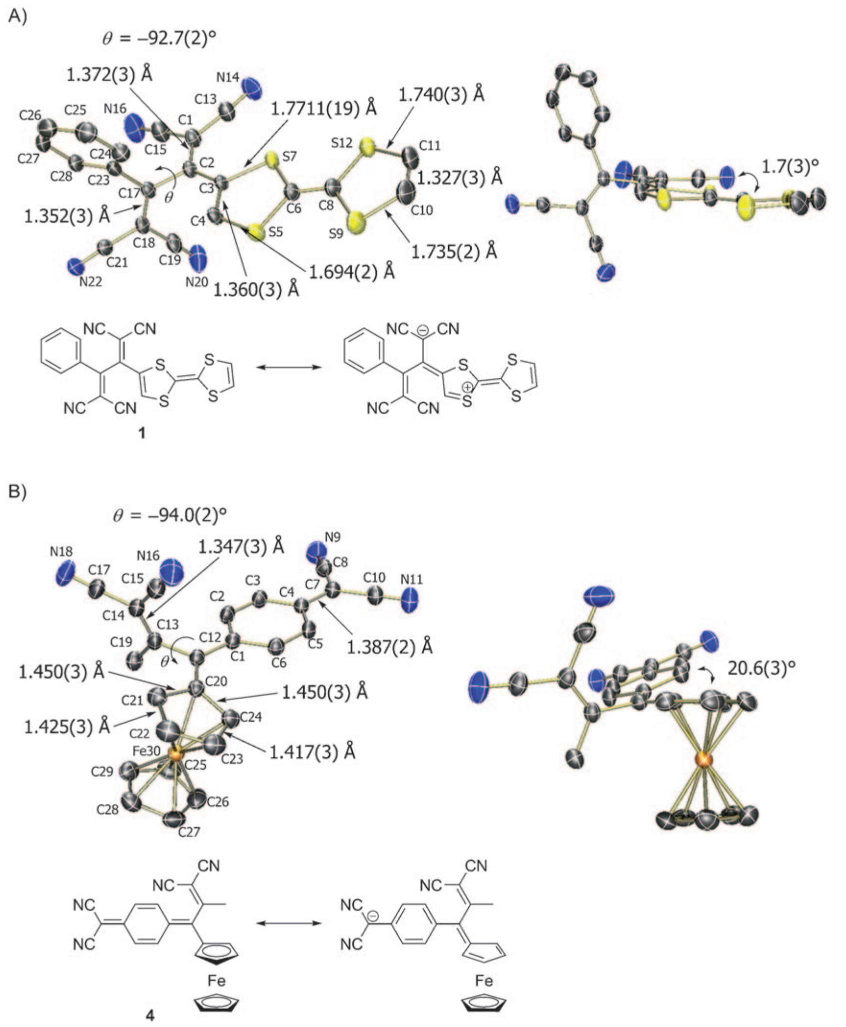

Figure 1. ORTEP plots of a) **1** and b) **4** with vibrational ellipsoids at 220 K shown at the 50 % probability level. Hydrogen atoms are omitted for clarity. Arbitrary numbering. The experimental bond lengths support a substantial contribution from polar resonance structures as a result of efficient intramolecular CT.

are nearly independent of the Fc substituent and range from +0.33 to +0.37 V. In bis-ferrocenyl derivative **6**, the two Fc moieties are in close spatial proximity and are oxidized stepwise (+0.33 and +0.47 V), while a unique two-electron oxidation is observed for **8** (+0.33 V) in which the two Fc units are located at greater distance. In **8**, the two Fc units act as independent redox centers,[21] whereas the oxidation of the second Fc unit in **6** is rendered more difficult by electrostatic repulsion. In the DCV-centered reduction processes, introduction of substituents in the series **3**–**6** results in large cathodic shifts of the first reduction potentials (−0.49 V (**3**), −0.81 V (**4**), −0.74 V (**5**), and −0.82 V (**6**)). This clearly reflects the greater twist and the resulting sterically enforced π-deconjugation between the two acceptor halves upon substitution, as evidenced by the X-ray crystal structures (Figure 1 and Figure S2–S4). The effect of steric deconjugation is equally visible in the second reduction potentials. A larger difference between the first and second reduction potentials (260 mV) is observed in unsubstituted **3**, in which the two DCV moieties are more efficiently π-conjugated. In contrast, substitution induces a large twist between the two acceptor halves in **4**–**6** (X-ray) and first and second reduction potentials, each centered on one acceptor half, differ only by 60 mV (**4**) to 120 mV (**6**). Insertion of the acetylenic spacer in **7** and **8** reduces the steric crowding and π-deconjugation, and the first reduction again becomes more favorable—by about 180 mV—as compared to **4**–**6** (Table S1).[22]

The UV/Vis spectra of the two series of push–pull chromophores in CH_2Cl_2 display broad CT bands with end-absorptions reaching into the near infrared (Figure 2). The two TTF chromophores exhibit similar maxima of their CT bands at $\lambda_{max} = 767$ nm (1.61 eV, **1**) and 728 nm (1.69 eV, **2**), despite the presence of the DMA donor moiety in **2** (Figure 2 A). This strongly indicates that the low-energy transitions in both molecules are predominantly TTF donor—TCBD acceptor transitions. Time-dependent density functional theory (TD-DFT) at the TD-B3LYP/cc-pVDZ//B3LYP/6-31G* level using Gaussian 03[23] reproduces well the absorption spectra of **1** and **2** and confirms that their low-energy electronic transitions occur from the TTF-located HOMO to the LUMO that is located mainly on the TCBD moiety (see the Supporting Information). The HOMO density is concentrated on the TTF moiety, irrespective of the DMA moiety in **2**. The overlap of the HOMO and LUMO in **1** and **2** is relatively small, occurring partially on the TTF moiety.

For the Fc-substituted expanded TCNQs **3**–**8**, clear steric effects on their electronic transitions are observed, in full agreement with the electrochemical properties (Figure 2 B). Thus, **3** with the H-substituent displays the lowest-energy CT band at 801 nm (1.55 eV) and an end-absorption near 1400 nm (0.89 eV). Methyl-substitution in **4** results in a hypsochromic shift to $\lambda_{max} = 749$ nm (1.66 eV), reflecting sterically enforced deconjugation between the two DCV acceptor halves. This deconjugation elevates the LUMO rather than the HOMO level, as confirmed by CV (Table 1) and theoretical calculations (see the Supporting information), thereby resulting in a larger optical gap. The CT band maxi-

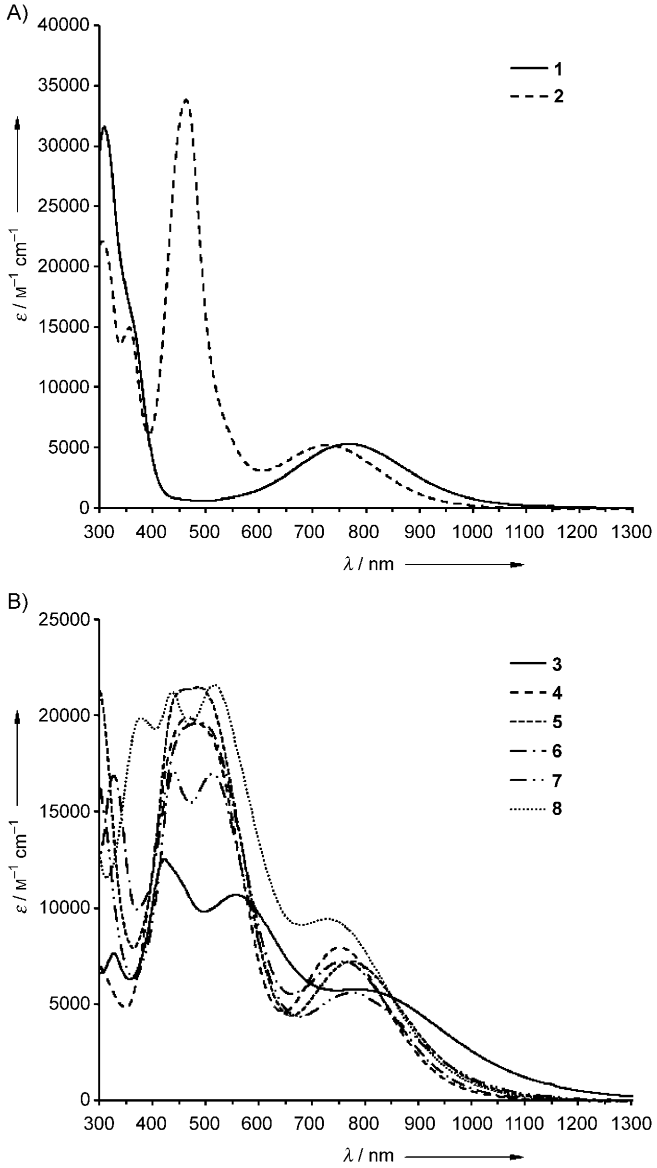

Figure 2. Electronic absorption spectra of TTF conjugates **1** and **2** (A) and Fc derivatives **3**–**8** (B) in CH_2Cl_2 at 25 °C.

mum shifts hypsochromically (801 nm (**3**), 772 nm (**5**), 749 nm (**4**)) as the twist in the acceptor increases (see above). The introduction of the substituent groups on the acceptor moiety affords an enhancement of the molar extinction coefficient ε in the shorter-wavelength region around 400–550 nm, which would be assignable to π-π* transitions,[17b] relative to the intensity of the CT band around 650–1000 nm. There exists a good linear correlation between the electrochemical gap (ΔE_{redox}) and the optical gap (ΔE_{opt}; energy of the longest-wavelength maximum), except for **8** (see the Supporting Information). A large solvatochromism is observed: the CT band of **7** shifts from $\lambda_{max} = 778$ nm (1.59 eV) in pure CH_2Cl_2 to 729 nm (1.70 eV) in CH_2Cl_2/*n*-hexane 1:19 (see the Supporting Information).

Based on this study, a clearer picture of the optoelectronic properties of the nonplanar push–pull chromophores obtained by cycloaddition of strong acceptors (TCNE, TCNQ) to donor-substituted alkynes emerges. While the resulting TCBD and expanded TCNQ acceptor moieties are highly nonplanar and the twist between the planes of the two DCV acceptor halves can be further increased by substitution, one DCV moiety in **1** and **2** as well as the cyclohexa-2,5-diene-1,4-diylidene-spaced DCV moiety in **3**–**8** remain in nearly planar π-conjugation with the donor, as evidenced by the X-ray crystal structures. The intramolecular CT mainly involves this part of the molecule. The second DCV moiety however, even if twisted out of this plane up to near orthogonality, also contributes to the acceptor potency by its strong electron-accepting σ-induction. This picture explains that the energetic effects of steric π-deconjugation in the acceptor are remarkably small, with $\lambda_{max} = 801$ (1.55 eV) in H-substituted **3** (twist angle between the two acceptor halves of 51.9(4)°) and 749 (1.66 eV) in Me-substituted **4** (twist angle: −94.0(2)°). Thus, the energy of the CT bands and the electrochemical HOMO–LUMO gaps of these nonplanar push–pull systems are comparable to the lowest values obtained for fully planar TTF- and ferrocene-based push–pull chromophores.[16] On the other hand, the nonplanar chromophores add distinct advantages in physical properties, favoring their use in optoelectronic devices.[13] These include higher solubility, less propensity to undergo aggregation which affects the optical properties, and frequently sublimability without decomposition, allowing amorphous high-quality optical film formation by vapor-phase deposition. Another specific advantage of the reported class of nonplanar push–pull chromophores remains undoubtedly their short and efficient one-step synthesis, which allows rapid establishment of comprehensive structure–property relationships in the development of advanced functional materials.

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