New strong organic acceptors by cycloaddition of TCNE and TCNQ to donor-substituted cyanoalkynes†

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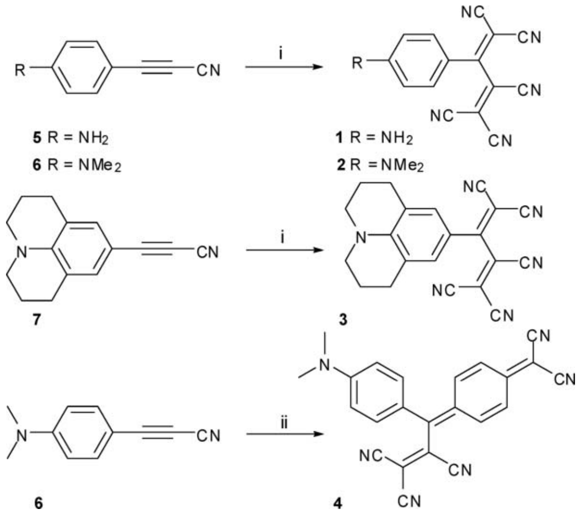
Donor-substituted 1,1,2,4,4-pentacyanobuta-1,3-dienes and a cyclohexa-2,5-diene-1,4-diylidene-expanded derivative were prepared by a [2 + 2] cycloaddition of tetracyanoethene (TCNE) or 7,7,8,8-tetracyanoquinodimethane (TCNQ) to anilino-substituted cyanoalkynes, followed by retro-electrocyclisation; they feature intense bathochromically-shifted intramolecular charge-transfer bands and undergo their first one-electron reductions at potentials similar to those reported for TCNE and TCNQ.

Stable strong electron acceptors, such as tetracyanoethene (TCNE)[1] and 7,7,8,8-tetracyanoquinodimethane (TCNQ),[2] are in high demand.[3,4] Strong acceptors are of interest as dopants in the fabrication of optical light-emitting diodes (OLEDs) and solar cells.[5] In recent years, we have introduced a series of potent acceptors, such as cyanoethynylethenes (CEEs),[6] 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs)[7] and TCNQ cycloadducts.[8] When conjugated to strong donors, the resulting push–pull chromophores undergo efficient intermolecular charge transfer (CT) interactions and feature high third-order optical non-linearities.[9] However, electrochemical measurements by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) indicated that their electron-accepting power was inferior to that of TCNE or TCNQ.[10] Here, we report the synthesis of the first 1,1,2,4,4-pentacyanobuta-1,3-dienes (PCBDs), **1–3**, and the cyclohexa-2,5-diene-1,4-diylidene-expanded derivative, **4**, potent organic acceptors that rival the benchmark compounds TCNE and TCNQ in their propensity for electron uptake.

While the [2 + 2] cycloaddition of TCNE with electron-rich metal acetylides, followed by retro-electrocyclisation to give organometallic TCDB derivatives, was described as early as 1981,[11] the corresponding reaction with electron-rich, organodonor-substituted alkynes has only been systematically explored in recent years.[7] The resulting CT chromophores displayed high third-order optical non-linearities and exceptional electron storage capacities.[12] In these studies, it was observed that TCNE reacted only with alkynes substituted with two electron-donating groups (EDG) or one EDG and one neutral substituent (such as phenyl or trialkylsilyl).[7,12] Reactions of electronically-confused alkynes substituted by one EDG and one electron-withdrawing group (EWG) have not been studied. In the present work, such a reaction is shown to be possible.

We found that the anilino donor-substituted cyanoalkynes **5–7** (see the ESI for their preparation†) reacted with TCNE at room temperature in THF to give the donor-substituted PCBDs **1–3** in good yields (Scheme 1). Under harsher conditions, by heating to 120 °C in 1,1,2,2-tetrachloroethane, TCNQ underwent a similar transformation with **6**, yielding the cyclohexa-2,5-diene-1,4-diylidene-expanded PCBD, **4**, in 27% yield.

These PCBDs are presumed to come about by initial bond formation between the alkyne C-atom in the β-position to the anilino donor substituent and the β-C-atom of the C=C(CN)$_2$ moieties in TCNE or TCNQ, giving a resonance-stabilised zwitterionic or diradical intermediate. While these transformations involve the HOMO of the cyanoalkynes and the LUMO of the acceptors, the concerted [2 + 2] cycloaddition mechanism is symmetry-forbidden. The recombination of charges or unpaired electrons occurs to form the cyclobutene, which subsequently undergoes electrocyclic ring opening, leading to the final butadiene. The intermediate cyclobutene could be isolated in certain cases of TCNE-additions to metal-coordinated alkynes.[11b,c] The reaction of the alkyne with TCNE or TCNQ depends on the relative HOMO and LUMO energies, and on the frontier molecular orbital coefficients at the β-positions. Substitution of a



Scheme 1 Synthesis of new anilino donor-substituted acceptors. (i) 1.2 equiv. TCNE, THF, 20 °C, 12 h to 2 d, 60% (**1**), 97% (**2**), 98% (**3**); (ii) 1.0 equiv. TCNQ, 1,1,2,2-tetrachloroethane, 120 °C, 12 h, 27%.

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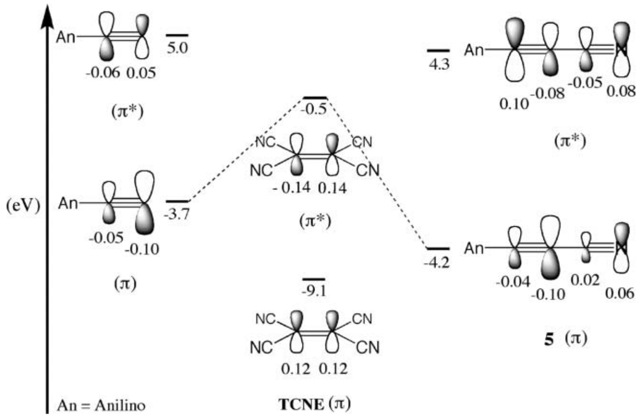
para-anilino-substituted alkyne with an EWG, such as CN, would tend to lower the HOMO energy. The new HOMO, being further in energy from the LUMO of TCNE or TCNQ, would have a diminished interaction. The presence of the cyano group may also reduce the coefficient of the HOMO orbital at the β-position to the anilino donor and negatively attenuate its reactivity with TCNE or TCNQ.[13] The ready accessibility of the PCBDs, as described in Scheme 1, is thus unexpected.

Calculations at the MP4(SDQ/6-311 + g(d,p)//B3LYP/6-311 + g(d,p) level using the Gaussian 03 program (see the ESI†) for anilinoacetylene (An–C≡CH) (An = 4-anilino), anilinocyanoacetylene (An–C≡C–C≡N) (**5**) and TCNE confirm the unexpected reactivity of **5** (Scheme 2). The HOMO energy (π) of An–C≡CH is 0.5 eV higher than that of An–C≡C–C≡N. Thus, **5** is predicted, and confirmed experimentally, to be less reactive against TCNE than the simple donor-substituted alkyne. While the reaction with the latter is nearly instantaneous at room temperature, giving quantitative yields,[7,12] the transformations of **5–7** require much longer stirring (12–48 h) at this temperature to proceed in good yield. The influence of the cyano group on the HOMO coefficient at its position of attachment, the putative initial bond-forming site, is negligible; both An–C≡CH and An–C≡C–C≡N have coefficients of −0.10. The effect on the coefficients at the adjacent alkyne carbon atoms is only minor (−0.04 (**5**) and −0.05 (An–C≡CH)).

The new push–pull systems are green (**1–3**) or black (**4**) metallic solids stable under laboratory conditions at ambient temperature for months (see ESI†). The regioselectivity observed in the addition of TCNQ to the terminal dicyanovinyl moiety is in agreement with previous findings.[8] The UV/vis spectra of the PCBDs recorded in CH_2Cl_2 display two intramolecular CT bands (Figure 1(a)): one intense and one weak one of lower energy, with their maxima shifting from λ_{max} = 406 nm (3.05 eV; ε = 21000 $dm^3\ mol^{-1}\ cm^{-1}$) and λ_{max} = 542 nm (2.28 eV; ε = 3200 $dm^3\ mol^{-1}\ cm^{-1}$) for **1**, to λ_{max} = 450 nm (2.76 eV; ε = 30000 $dm^3\ mol^{-1}\ cm^{-1}$) and λ_{max} = 643 nm (1.93 eV; ε = 3200 $dm^3\ mol^{-1}\ cm^{-1}$) for **2**, and to λ_{max} = 483 nm (2.56 eV; ε = 36000 $dm^3\ mol^{-1}\ cm^{-1}$) and λ_{max} = 731 nm (1.70 eV; ε = 3000 $dm^3\ mol^{-1}\ cm^{-1}$) for **3**. The substantial red shift of 0.35 eV upon passing from **1** to **2** reflects the increase in donor strength upon *N*-dialkylation, while the additional shift of 0.23 eV upon moving to **3** can be accounted for by the two additional σ-donating alkyl substituents and the enforced amine rigidity.[14]



Scheme 2 Representations of the relevant parts of the π and π* molecular orbitals of An–C≡CH, TCNE and An–C≡C–C≡N (**5**). MP4(SDQ/6-311 + g(d,p)//B3LYP/6-311 + g(d,p) MO coefficients are shown below the corresponding p-orbitals. The MO energy (eV) at this level (ZPE-corrected) is also given.

Electronic transition analysis using time-dependent density functional theory at the TD-B3LYP/6-31g(d)//B3LYP/6-31g(d) level for compound **1** predicts three CT absorptions at 368, 383 and 650 nm, with oscillator strengths (*f*) of 0.43, 0.02 and 0.02, respectively (ESI†). The CT band at 368 nm refers to an excitation from the HOMO to the LUMO + 1, also with transitions from the HOMO-3, HOMO-2 and HOMO-1 to the LUMO, which are less significant. The band at 383 nm is composed of a transition from HOMO-1 to LUMO, with a minor one from HOMO to LUMO + 1. The absorption at 650 nm is predominantly a transition from HOMO to LUMO, with some HOMO to LUMO + 1. The major transitions distribute the electron density from the anilino to the pentacyanobutadienyl moiety (relevant MOs shown in ESI†).

An additional shift of the CT band to lower energy is observed in the UV/vis spectrum of TCNQ adduct **4** (Fig. 1(b)), with the maximum in CH_2Cl_2 observed at λ_{max} = 859 nm (1.44 eV; ε = 17700 $dm^3\ mol^{-1}\ cm^{-1}$). This band tails far into the near infrared, and the end-absorption is observed near 1300 nm (0.95 eV). This low optical gap is remarkable for a small chromophore, such as **4**. The CT character of the longest wavelength absorption band was confirmed in a protonation experiment. When a solution of **4** in CH_2Cl_2 was acidified by trifluoroacetic acid (TFA) (Fig. 1(b)), the band at λ_{max} = 859 nm nearly completely disappeared. However, neutralisation with K_2CO_3 did not quantitatively regenerate the original spectrum, as strongly electrophilic **4** decomposes rapidly in the presence of a base.

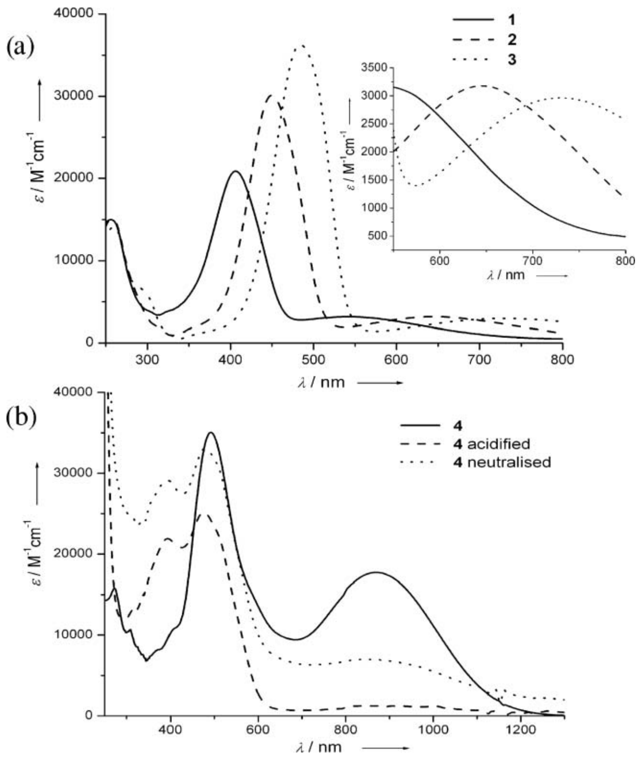
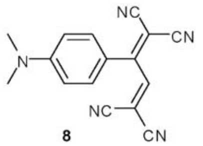


Fig. 1 (a) UV/vis spectra of **1–3** in CH_2Cl_2 at 298 K. Inset: zoom on the low energy CT bands. (b) UV/vis spectra of **4** in CH_2Cl_2 at 298 K recorded neat, after acidification with trifluoroacetic acid (TFA) and after neutralisation with K_2CO_3.

Table 1 Electrochemical data (CV) in CH_2Cl_2 (+0.1 M n-Bu_4NPF_6) *vs.* Fc^+/Fc (scan rate v = 0.1 V s^{-1})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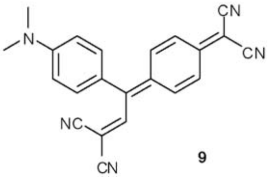
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	$E°/V^a$	$\Delta E_p/mV^b$	E_p/V^c		$E°/V^a$	$\Delta E_p/mV^b$	E_p/V^c
1			+1.14	**TCNE**	−0.32[d]		
	−0.27	100			−1.35[d]		
	−0.86	100					
2	+1.00	90		**TCNQ**	−0.25[d]		
	−0.30	90			−0.81[d]		
	−0.85	100					
3	+0.74	75		**8**	+0.86[e]	80	
	−0.32	60			−0.69[e]	80	
	−0.81	75			−1.26[e]	90	
4			+0.52	**9**			+0.42[f]
	−0.27	80			−0.50[f]	80	
	−0.53	85			−0.76[f]	80	

[a] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{ox} - E_{red}$, where subscripts 'ox' and 'red' refer to the conjugated oxidation and reduction steps, respectively. [c] E_p = Irreversible peak potential at sweep rate v = 0.1 V s^{-1}. [d] Taken from ref. 15. [e] Taken from ref. 7*b*. [f] Taken from ref. 8.

The electrochemical properties of the new chromophores were recorded by CV and RDV (see ESI†), and compared to those of TCNE,[15] TCNQ,[15] anilino-substituted TCBD **8**[7b] and TCNQ adduct **9** (Table 1).[8] All three PCBDs, **1–3**, give two well-defined reversible one-electron reduction steps, with the first electron transfer occurring at −0.27 to −0.32 V and the second at −0.81 to −0.86 V. The electron uptakes occur on the PCBD moieties, as suggested by molecular orbital analysis (see ESI†). The observed one-electron oxidation step occurs on the anilino donor moiety and becomes facilitated upon moving from **1** (irreversible oxidation with E_p = +1.14 V) to **2** ($E°_{ox}$ = +1.00 V) and on to **3** ($E°_{ox}$ = +0.74 V). A good correlation exists between the optical spectroscopic and the electrochemical data: both the optical and electrochemical gap are reduced upon moving from **1** to **2** and on to **3** (see ESI†). The introduction of the extra CN group upon moving from TCBD **8**[7b] to PCBD **2** has a dramatic effect on the redox properties. The CT interaction is much more efficient due to the increased acceptor strength, and this is reflected in the oxidation potential, which shifts from +0.86 V (**8**) to +1.00 V (**2**). More importantly, the two first electron uptakes become considerably more favoured as a result of the extra CN group in the acceptor; TCBD **8** is reduced at −0.69 and −1.26 V, whereas the two electron transfers in PCBD **2** occur at −0.30 and −0.85 V, respectively. Thus, both reduction steps in **2** are greatly, and nearly equally, facilitated, occurring at a *ca.* 400 mV less negative potential.[16] Gratifyingly, despite substitution with potent anilino donors, the first reduction of **1–3** (−0.27 to −0.32 V) occurs at very similar potentials to that of TCNE (−0.32 V), whereas the second electron uptake is even more greatly facilitated (**1–3**: −0.81 to −0.86 V; TCNE: −1.35 V). Both the first and second reduction potentials of **1–3** approach those of TCNQ (−0.25 and −0.81 V). It can be expected that, upon attenuation of the donor moiety, the reduction steps become further facilitated.

TCNQ adduct **4** undergoes two one-electron reductions at −0.27 and −0.53 V, as well as an irreversible one-electron oxidation at +0.52 V (Table 1). Again, a large influence on the redox properties are observed, compared to **9** (−0.50 and −0.76 V), as a result of the additional CN group; both reduction steps occur anodically-shifted by 230 mV. While the first reduction is similar to that in TCNQ (−0.25 *vs.* −0.27 V (**4**)), the second is greatly facilitated (−0.53 (**4**) *vs.* −0.81 V (TCNQ)), which can be explained by the larger distance between the charge-hosting dicyanovinyl and tricyanovinyl moieties in **4** and the concomitant reduction of electrostatic repulsion. Ground state CT interactions are much less effective in **4** than in **1–3**; the anilino donor is much more readily oxidised (E_p = +0.52 V), which means that it transfers less electron density into the acceptor chromophore.

The full scope of the reaction between TCNE or TCNQ and electronically confused alkynes and the optoelectronic applications of these new advanced materials are now being investigated.

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