A novel reaction of 7,7,8,8-tetracyanoquinodimethane (TCNQ): charge-transfer chromophores by [2 + 2] cycloaddition with alkynes†

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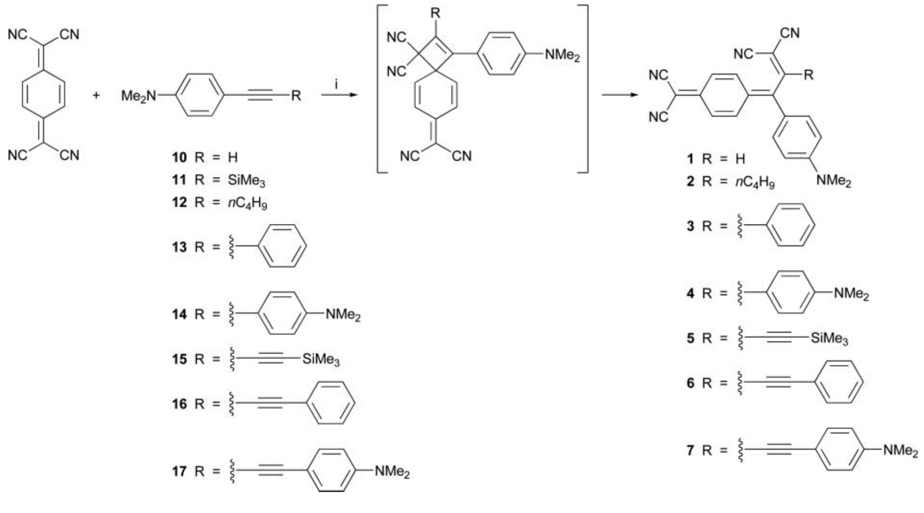
A series of donor–acceptor molecules, featuring intense low-energy intramolecular charge-transfer bands, was prepared by regioselective [2 + 2] cycloaddition between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and *N*,*N*-dialkylanilino-substituted (DAA-substituted) alkynes, followed by ring opening of the initially formed cyclobutenes.

7,7,8,8-Tetracyanoquinodimethane (TCNQ) was reported in the early 1960s,[1] and its chemical and physicochemical properties have been thoroughly investigated since then.[2,3] Due to its powerful electron-accepting properties, TCNQ forms intermolecular charge-transfer (CT) complexes with various organic and inorganic electron donors, some of them exhibiting high electric conductivity or interesting magnetic behaviour.[4,5] These properties make TCNQ still an attractive subject of contemporary advanced materials research.

However, while the reactivity of TCNQ has been explored, some of the structural features of this molecule have obviously been ignored. Namely, it possesses two types of strongly electron-deficient CC double bonds that could, in analogy to tetracyanoethylene (TCNE),[6] undergo thermal [2 + 2] cycloaddition with electron-rich alkynes. Here, we describe such a reaction between TCNQ and *N*,*N*-dialkylanilino-substituted (DAA-substituted) alkynes, giving access to a new family of non-planar CT chromophores, such as **1–9**. To the best of our knowledge, this is the very first example of a thermal [2 + 2] cycloaddition to TCNQ.

A variety of electron-rich, DAA-substituted alkynes (**10–17**) were prepared (ESI†) and subsequently subjected to the reaction with TCNQ to probe their reactivity. All acetylenic precursors reacted in a uniform manner to give products **1–7** in high to quantitative yields (except for **5**, Scheme 1).‡ Thus, terminally deprotected alkyne **10** reacted at 20 °C in CH_2Cl_2 to give adduct **1** (81%) as a black metallic solid. Chromophore **1** was also isolated in 42% yield starting from Me_3Si-protected **11**, since silyl-deprotection took place during chromatographic purification on SiO_2 (CH_2Cl_2–EtOAc 97 : 3). The use of the less labile $(i\mathrm{Pr})_3Si$ protecting group unexpectedly led to complete decomposition during attempted chromatography. Oligomeric **8** and **9** (Fig. 1) were also prepared in high yields from the corresponding alkyne precursors.[6] For example, the threefold addition of TCNQ to produce oligomeric **9** proceeded in 66% yield (that is, 87% yield for each addition step). All compounds **1–9** are dark metallic solids that are stable at ambient temperature under air.



Scheme 1 Synthesis of donor-substituted TCNQ derivatives: i, CH_2Cl_2 or toluene or 1,2-dichloroethane, 20 °C or 80 °C; 81% (**1**), 100% (**2**), 93% (**3**), 100% (**4**), 33% (**5**), 72% (**6**), 78% (**7**).

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† Electronic supplementary information (ESI) available: Syntheses and UV/Vis spectra for new compounds and crystal structures for **1** and **3**. See DOI: 10.1039/b713683h

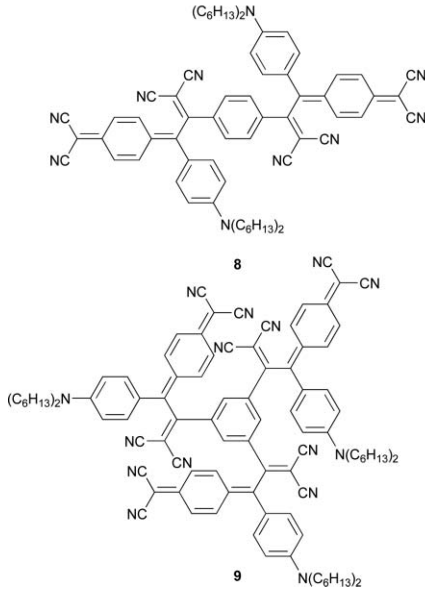

Fig. 1 Oligomeric TCNQ-based chromophores **8** and **9**.

We assume the reaction proceeds by means of thermal [2 + 2] cycloaddition between the exocyclic CC double bond of TCNQ and the triple bond of the alkyne, followed by ring opening of the intermediately formed strained cyclobutene to give the observed product. The cycloaddition step proceeds presumably *via* a zwitterionic or a biradical intermediate, as a concerted [2 + 2] mechanism involving the HOMO–LUMO interaction is symmetry forbidden.[7] The reaction is completely regioselective with respect to TCNQ and proceeds exclusively at one of the dicyanovinyl moieties and not at the endocyclic double bonds.[8]‡ No multiple additions were observed, even in the presence of an excess of alkyne at elevated temperature (up to 80 °C). The constitution of the products was unambiguously confirmed by NMR spectroscopy (HSQC and HMBC) and, as shown below, by X-ray analysis.

Single crystals of **1** and **3**, suitable for X-ray structure analysis, were grown by slow diffusion of hexane into 1,1,2,2-tetrachloroethane solutions of the compounds at 20 °C.§ The X-ray analysis (Fig. 2) nicely confirmed the regioselective addition of the alkyne at one exocyclic CC double bond of TCNQ and proved the constitution of the formed non-planar donor–acceptor chromophores (see Figs. S1 and S2 (ESI†)). In the crystal packing of **1** (Fig. 2b), two molecules related by an inversion centre show short multipolar CN···CN interactions, as already previously observed.[6] Particularly interesting are the short contacts between nitrogen atoms that are polarised in an opposite way through the intramolecular charge-transfer interactions. The negatively polarised N-atoms of a CN moiety in one molecule interact at van der Waals distance with the positively polarised N-atom of the *N*,*N*-dimethylanilino (DMA) moiety of an adjacent one. The efficiency of the CT from the donor to the acceptor moieties can be expressed as the quinoid character (δr) of the DMA ring (for its definition,[9] see caption to Fig. 2; for bond lengths, see Figs. S1 and S2 (ESI†)). In benzene, the δr value equals 0, whereas values between 0.08 and 0.10 are found in fully quinoid rings. The DMA ring in **1** exhibits a high δr value of 0.046 comparable to the highest value observed for DMA-substituted 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivatives.[6] The δr value for the DMA ring in **3** could not be estimated due to the reduced accuracy.

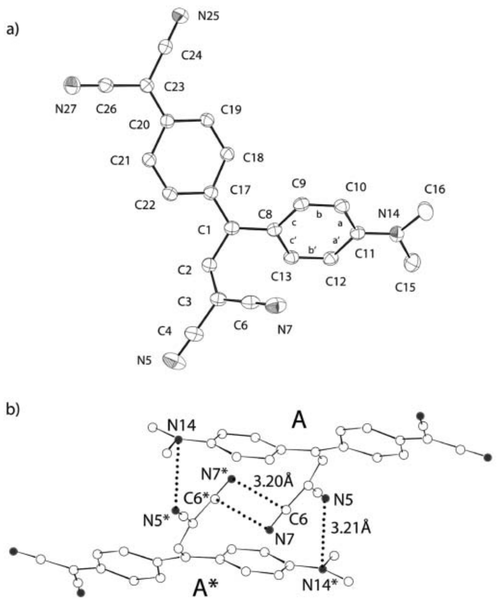

Fig. 2 (a) ORTEP plot of **1**, arbitrary numbering. Atomic displacement parameters at 220 K are drawn at the 30% probability level. (b) Arrangement of neighbouring molecules in the crystal packing of **1** showing short intermolecular contacts. Molecules A (x,y,z) and A* ($2 - x$, $-y$,$1 - z$) are related by an inversion centre. For selected bond lengths and angles, see Fig. S1 (ESI†). Quinoid character: $\delta r = (((a + a')/2 - (b + b')/2) + ((c + c')/2 - (b + b')/2))/2$.[9]

The UV/Vis spectra of chromophores **1–9** are dominated by intense, broad CT bands with end absorptions reaching into the near infrared region (Fig. 3 and Figs. S3 and S4, Table S1 (ESI†)). Upon introduction of a second DMA donor, the intensity of the CT band increases strongly (compare the spectra of **3** and **4** or **6** and **7**, Fig. 3). All molecules show a pronounced solvatochromism in CH_2Cl_2–hexane mixtures (see Table S2 (ESI†)). The largest solvent effect was observed for **2**, with the CT band shifting from λ_{max} = 559 nm (1.63 eV) in hexane to λ_{max} = 655 nm (1.89 eV) in CH_2Cl_2 (see Figs. S5 and S6, Table S2 (ESI†)).

The redox properties of **1–9** were studied by cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) in CH_2Cl_2 (+ 0.1 M

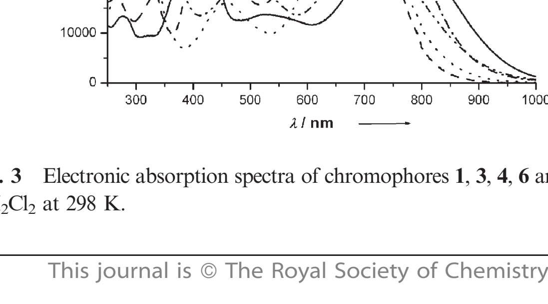

Fig. 3 Electronic absorption spectra of chromophores **1**, **3**, **4**, **6** and **7** in CH_2Cl_2 at 298 K.

$n\mathrm{Bu_4NPF_6}$) (see Table S3 (ESI†)). Each DAA moiety in chromophores **1–9** undergoes a one-electron oxidation step which is irreversible, except for **5**. While the two DMA moieties in **4** and **7** are oxidised in two separated one-electron steps, all DAA moieties in oligomeric **8** and **9** are oxidised in a single, irreversible multielectron step, denoting no electrostatic interactions between the redox centres.

Monomeric chromophores **1–7** remain potent electron-acceptors, and display two reversible one-electron reduction steps, centred on the two dicyanovinyl moieties. Except for **1**, the observed potential difference is rather small (ranging from 90 mV for **4** to 150 mV for **5** and **6**). The difference is indeed much smaller than previously observed for DAA-substituted TCBD derivatives (230–570 mV).[6] This is readily explained by the larger distance between the two dicyanovinyl groups in **2–7** as a result of insertion of the cyclohexa-2,5-diene-1,4-diylidene moiety. However, in the case of **1**, the potential difference is somewhat larger (260 mV). With its small H-atom substituent, **1** may adopt a more planar structure in solution, thereby making the conjugation between the dicyanovinyl moieties and the DAA donor more efficient than in the other cases. As a result of higher planarity, the electrostatic repulsion for the electrogenerated dianion is stronger in **1**. The stepwise reduction of **8** and **9**, with the latter undergoing six reversible one-electron reductions in the narrow potential range between −0.51 and −1.14 V, is a good indication that the dicyanovinyl moieties in these chromophores are not independent redox-active centres, as observed previously.[10]

In summary, we have described a novel, completely regioselective [2 + 2] cycloaddition of TCNQ with DAA-substituted alkynes, followed by ring opening of the initially formed cyclobutene derivative to yield new CT chromophores with appealing optoelectronic and redox properties. The generality of this generally high-yielding, atom-economic transformation was demonstrated by running the reaction with a series of acetylenic substrates. The exploration of the optical nonlinearities of these new TCNQ derivatives and their application to the preparation of organic-based magnets and conductive materials are currently under investigation.

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Notes and references

‡ All new compounds were fully characterised by IR, UV/Vis, ^{1}H and ^{13}C NMR, mass spectrometry and/or elemental analysis. The regioselectivity with respect to alkyne addition is unambiguous for **1–6**, **8** and **9**. Spectral similarity suggests for **7** the constitution shown in Scheme 1.

§ Crystal data of **1** at 220(2) K: $C_{22}H_{15}N_5$, $M_r = 349.39$: triclinic, space group $P\bar{1}$ (no. 2), $D_c = 1.241$ g cm^{-3}, $Z = 2$, $a = 8.8680(13)$, $b = 9.2552(14)$, $c = 11.7022(14)$ Å, $\alpha = 101.406(2)$, $\beta = 93.315(12)$, $\gamma = 94.983(2)°$, $V = 935.2(2)$ Å^3. Bruker-Nonius Kappa-CCD diffractometer, MoK_α radiation, $\lambda = 0.7107$ Å, $\mu = 0.077$ mm^{-1}. Crystal dimensions *ca.* 0.25 × 0.23 × 0.20 mm. The numbers of measured and unique reflections are 6407 and 3755, respectively. ($R_{int} = 0.035$). Final $R(F) = 0.045$, $wR(F^2) = 0.119$ for 247 parameters and 3099 reflections with $I > 2\sigma(I)$ and $3.03 < \theta < 26.32°$ (corresponding R-values based on all 3755 reflections are 0.057 and 0.128, respectively). Crystal data of **3** at 173(2) K: $3(C_{28}H_{19}N_5)$, $1.5(C_2H_2Cl_4)$, $M_r = 1528.20$: triclinic, space group $P\bar{1}$ (no. 2), $D_c = 1.283$ g cm^{-3}, $Z = 2$, $a = 11.1429(14)$, $b = 16.3191(15)$, $c = 22.2110(17)$ Å, $\alpha = 82.970(11)$, $\beta = 85.747(12)$, $\gamma = 81.416(11)°$, $V = 3957.2(7)$ Å^3. Bruker-Nonius Kappa-CCD diffractometer, MoK_α radiation, $\lambda = 0.7107$ Å, $\mu = 0.273$ mm^{-1}. Crystal dimensions *ca.* 0.11 × 0.10 × 0.09 mm. The numbers of measured and unique reflections are 18424 and 10703, respectively. ($R_{int} = 0.054$). Final $R(F) = 0.111$, $wR(F^2) = 0.288$ for 980 parameters and 7198 reflections with $I > 2\sigma(I)$ and $2.95 < \theta < 22.92°$ (corresponding R-values based on all 10703 reflections are 0.151 and 0.326, respectively). CCDC 658467–658468. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713683h. As a note of caution, exposure to 1,1,2,2-tetrachloroethane should be avoided due to its high toxicity.

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