

# A new class of organic donor–acceptor molecules with large third-order optical nonlinearities†

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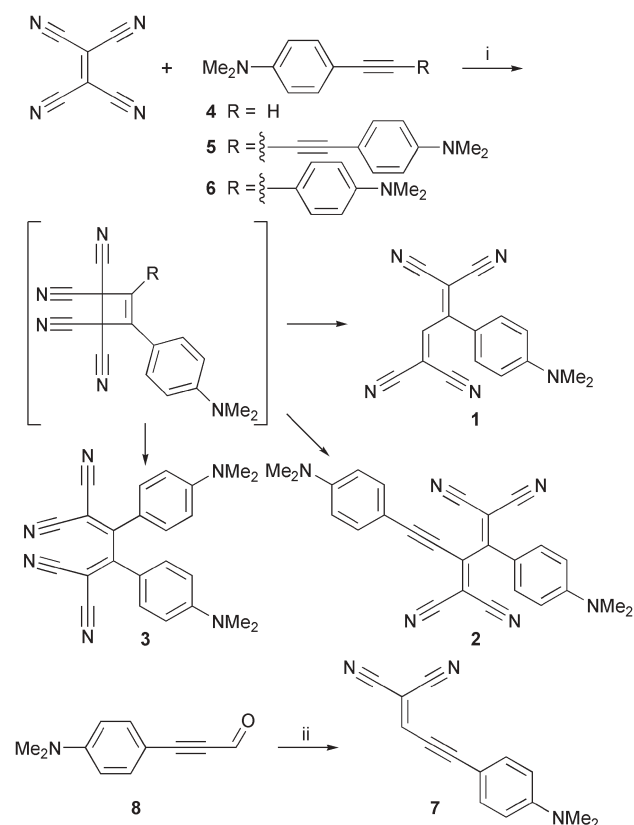
Donor–acceptor molecules with 4-(dimethylamino)phenyl donor and 1,1,4,4-tetracyanobuta-1,3-diene acceptor moieties are readily prepared by short, high-yielding routes. The quite small chromophores are characterised by X-ray crystallography and feature intense intramolecular charge-transfer bands, substantial quinoid character in the donor rings, reversible electrochemical reductions and oxidations and powerful third-order optical nonlinearities.

Organic donor–acceptor molecules are extensively studied as active nonlinear optical (NLO) materials with a wide range of potential applications such as all-optical computing and signal processing.<sup>1,2</sup> We have in the past shown that donor–acceptor substituted tetraethynylethenes (3,4-diethynylhex-3-ene-1,5-diyne, TEEs) feature high third-order optical nonlinearities, in particular in the case of low molecular symmetry,<sup>3</sup> and, more recently, provided evidence for the high potential of 4-(dimethylamino)phenyl- (“dimethylanilino”, DMA) substituted cyanoethynylethenes (CEEs) as efficient NLO chromophores.<sup>4</sup> Here we introduce a new class of low-molecular-weight chromophores featuring high third-order optical nonlinearities. They contain DMA donor and 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) acceptor moieties and are prepared by very short and high-yielding synthetic routes. TCBD-containing donor–acceptor molecules have in the past been investigated as second-order NLO materials,<sup>5</sup> but there has been, to our knowledge, no report on third-order optical nonlinearities.

The new donor-substituted TCBD derivatives **1–3** were obtained in nearly quantitative yield (96–100%) by [2 + 2] cycloaddition between tetracyanoethylene (TCNE) and DMA-substituted alkynes **4–6** (see ref. 6), followed by electrocyclic ring opening of the initially formed cyclobutenes (Scheme 1).‡ For comparison, we also prepared *gem*-dinitrile **7**, a sub-unit of **2**, by Knoevenagel condensation between **8** and malononitrile.

Single-crystals of **1–3** and **7** suitable for X-ray structure analysis were grown by slow diffusion of hexane into CH<sub>2</sub>Cl<sub>2</sub> solutions of the compounds at –15 °C (Fig. 1; for crystal packings, see Fig. 2(ESI)).§ Whereas chromophore **7** is fully planar, the TCBD moieties in **1–3** are nonplanar. However, each dicyanovinyl moiety and the directly attached DMA ring in **1–3** are nearly co-planar, which ensures efficient intramolecular charge-transfer (CT) interactions. Distortion from planarity occurs mainly by rotation around the central single bond of the TCBD moiety. The twist

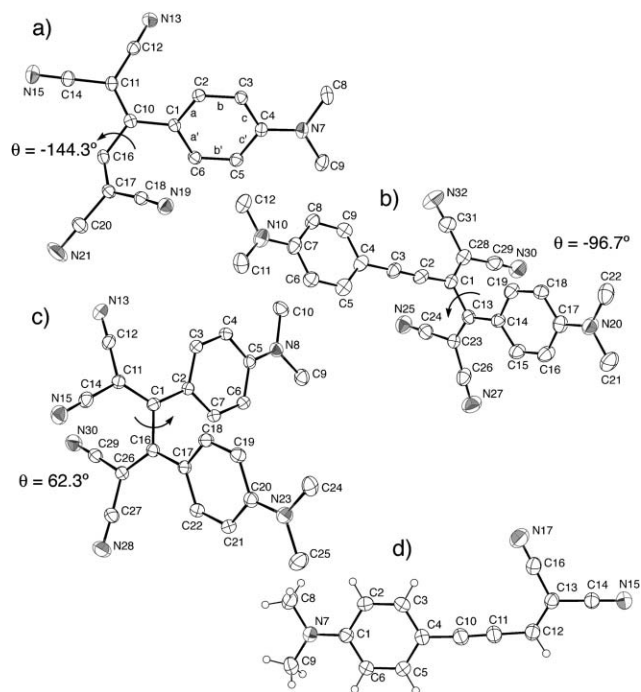
between the two dicyanovinyl planes in **1** (with two independent molecules) is expressed by the torsion angles  $\theta$  (C(11)–C(10)–C(16)–C(17)) = –144.3° and  $\theta$  (C(11′)–C(10′)–C(16′)–C(17′)) = 146.5°. The corresponding  $\theta$  values obtained for **2** (C(28)–C(1)–C(13)–C(23)) and **3** (C(11)–C(1)–C(16)–C(26)) are –96.7° and 62.3°, respectively (for atom numbering, see Fig. 1). Note that the TCBD moiety of **3** has *s-cis* configuration. Clearly, sterically enforced deconjugation of the two dicyanovinyl moieties is the least pronounced in **1** and this is consistent with the UV/Vis and electrochemical data described below. Bond length alternation in the DMA rings is a good indication for the efficiency of the charge-transfer from the donor to the acceptor moieties, which can be expressed by the quinoid character ( $\delta r$ ) of the ring (for a definition,<sup>7</sup> see caption to Fig. 1, for bond lengths, see



**Scheme 1** Synthesis of donor-substituted TCBD derivatives: i, C<sub>6</sub>H<sub>6</sub> or THF, 20 °C; 97% (**1**), 96% (**2**), 100% (**3**); ii, CH<sub>2</sub>(CN)<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> (act. II-III), CH<sub>2</sub>Cl<sub>2</sub>, 40 °C; 87%.

† Electronic Supplementary Information (ESI) available: Syntheses, crystal structures and electrochemical data for **1–3** and **7**. See <http://www.rsc.org/suppdata/cc/b417393g/>

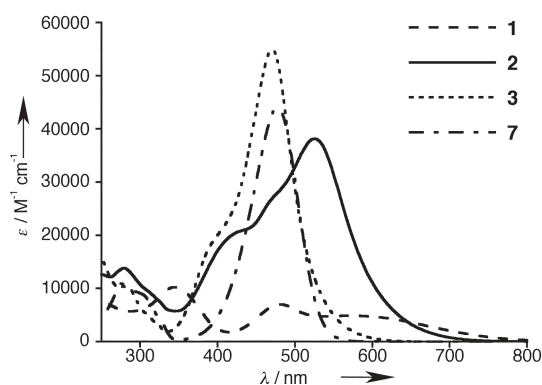
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**Fig. 1** ORTEP plots of **1** (a), **2** (b), **3** (c) and **7** (d) with vibrational ellipsoids shown at the 30% probability level. For selected bond lengths (Å) and angles (°), see Fig. 1(ESI).† Quinoid character:  $\delta r = (((a + a')/2 - (b + b')/2) + ((c + c')/2 - (b + b')/2))/2$ .<sup>7</sup>

Fig. 1(ESI)†. In benzene, the  $\delta r$  value equals 0, whereas values between 0.08 and 0.10 are found in fully quinoid rings. For the DMA rings in the two different molecules in the unit cell of **1**,  $\delta r$  averages to 0.036. The DMA rings in **3** exhibit a very high  $\delta r$  value of 0.050, which is unprecedented for molecules with anilino donor and cyano acceptor groups (see Table 1(ESI)).<sup>8</sup> The quinoid character of **2** shows the same trend, but because of the reduced accuracy the results are less reliable.

Dicyanovinyl derivative **7** displays a single CT band at  $\lambda_{\max} = 477$  nm (2.60 eV), whereas the TCBD derivatives show multiple transitions (Fig. 2), resulting from different donor–acceptor pathways. One of these transitions is always close in energy to the CT band in **7**. For example, the spectrum of **1** exhibits two rather weak CT bands at 481 and 570 nm (2.58 and 2.18 eV, respectively) with the end absorption reaching into the near infrared (960 nm, 1.29 eV). Upon introduction of a second



**Fig. 2** Electronic absorption spectra of **1**, **2**, **3** and **7** in  $\text{CH}_2\text{Cl}_2$ .

DMA donor group, the intensity of the CT band increases dramatically. All molecules show a distinct solvatochromism in hexane– $\text{CHCl}_3$  mixtures. The largest solvent effect is observed for **2**, with the CT absorption shifting from 477 nm (2.60 eV) in hexane to 526 nm (2.36 eV) in  $\text{CHCl}_3$ .

Compounds **1–3** and **7** all displayed reversible first oxidation and reduction steps (except for the irreversible reduction of **7**) in the cyclic voltammograms (CVs) recorded in  $\text{CH}_2\text{Cl}_2$  (+0.1M  $\text{Bu}_4\text{NPF}_6$ ) at room temperature (see Table 2(ESI)). Thus, **1** gave two well-resolved, reversible, TCBD-centered reduction steps at  $-0.69$  and  $-1.26$  V (vs.  $\text{Fc}^+/\text{Fc}$ ). The first of the two reversible  $1e^-$ -reductions in **2** and **3** are more cathodically shifted ( $-0.89$  in **2** and  $-1.06$  in **3**), which reflects the presence of two DMA donor groups. With a first DMA-centered oxidation potential of 0.86 V, the electrochemical HOMO–LUMO gap for **1** was estimated as 1.55 V; it is the lowest in the series. The two DMA groups in **2** are oxidized at separate potentials (0.72 and 0.90 V; HOMO–LUMO gap: 1.61 V), while **3** shows a single oxidation peak for a  $2e^-$ -transfer at ca. 0.90 V (HOMO–LUMO gap: 1.92 V). In comparison, oxidation of the DMA moiety in **7** takes place at 0.66 V.

In investigations of the third-order nonlinear optical properties, the rotational average of the second hyperpolarisability  $\gamma$  was measured in the zero-frequency limit by degenerate four-wave mixing in  $\text{CH}_2\text{Cl}_2$  at a wavelength of 1.5  $\mu\text{m}$ , using fused silica, with a third-order susceptibility  $\chi^{(3)} = 1.9 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  at 1.5  $\mu\text{m}$ , as a reference. Whereas compound **1** showed a  $\gamma$ -value of the order of  $4 \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$ , the more extended chromophore **2** with its two, nearly orthogonal, donor–acceptor pathways, gave  $\gamma = (12 \pm 2) \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$ . This value is comparable to the highest values obtained for donor–acceptor substituted TEEs and other potent NLO chromophores<sup>1c</sup> and quite significant considering the small number of delocalised  $\pi$ -electrons in **2**.

In conclusion, we have prepared, by elegant one- or two-step protocols shown in Scheme 1, a series of new chromophores in which DMA donors undergo efficient intramolecular CT interactions with TCBD acceptors. The low energy of the CT bands and the low electrochemical HOMO–LUMO gaps, in particular of **1** and **2**, demonstrate substantial  $\pi$ -conjugative effects (beside  $\sigma$ -effects) despite the twist of the planes of the two dicyanovinyl moieties as observed by X-ray analysis. The compounds are thermally stable up to the melting points (**1**: 144–145 °C; **2**: 191–193 °C; **3**: 273.5–274.6 °C) and can be sublimed without decomposition, which opens perspectives for device construction by vapor phase deposition techniques that are currently pursued.

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## Notes and references

† All new molecules were fully characterised by IR, UV/Vis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass spectrometry and elemental analysis.

§ Crystal data of **1** at 173 K: C<sub>16</sub>H<sub>11</sub>N<sub>5</sub>, [*M<sub>r</sub>* = 273.30]: triclinic, space group *P* $\bar{1}$  (no. 2), *D<sub>c</sub>* = 1.236 g cm<sup>-3</sup>, *Z* = 4,  $\mu$  = 0.079, *a* = 10.7459(2), *b* = 11.0754(3), *c* = 15.1601(5) Å,  $\alpha$  = 70.935(1),  $\beta$  = 71.461(1),  $\gamma$  = 61.437(2)°, *V* = 1469.05(7) Å<sup>3</sup>. Bruker-Nonius Kappa-CCD diffractometer, Mo-K $\alpha$  radiation,  $\lambda$  = 0.7107 Å. Number of reflections measured = 11122, number of independent reflections = 6573, *R<sub>int</sub>* = 0.03, final *R(F)* = 0.046, *wR(F<sup>2</sup>)* = 0.096 for 394 parameters and 5258 reflections with *I* > 2σ(*I*) and 3.68 <  $\theta$  < 27.45° (corresponding *R*-values based on all 6573 reflections are 0.061 and 0.105, respectively). Crystal data of **2** at 263 K: C<sub>26</sub>H<sub>20</sub>N<sub>6</sub>, 2(CH<sub>2</sub>Cl<sub>2</sub>)[*M<sub>r</sub>* = 586.33]: triclinic, space group *P* $\bar{1}$  (no. 2), *D<sub>c</sub>* = 1.332 g cm<sup>-3</sup>, *Z* = 2,  $\mu$  = 0.433, *a* = 7.3661(1), *b* = 9.5653(2), *c* = 20.8690(4) Å,  $\alpha$  = 91.580(8),  $\beta$  = 95.014(7),  $\gamma$  = 92.986(9)°, *V* = 1462.03(5) Å<sup>3</sup>. Bruker-Nonius Kappa-CCD diffractometer, Mo-K $\alpha$  radiation,  $\lambda$  = 0.7107 Å. Number of reflections measured = 3850, number of independent reflections = 2595, *R<sub>int</sub>* = 0.03, final *R(F)* = 0.100, *wR(F<sup>2</sup>)* = 0.235 for 348 parameters and 2223 reflections with *I* > 2σ(*I*) and 2.38 <  $\theta$  < 20.81° (corresponding *R*-values based on all 2595 reflections are 0.114 and 0.245, respectively). Crystal data of **3** at 220 K: C<sub>24</sub>H<sub>20</sub>N<sub>6</sub>, [*M<sub>r</sub>* = 392.46]: orthorhombic, space group *P bca* (no. 61), *D<sub>c</sub>* = 1.270 g cm<sup>-3</sup>, *Z* = 8,  $\mu$  = 0.079, *a* = 15.0448(7), *b* = 15.9323(8), *c* = 17.1300(8) Å, *V* = 4106.0(3) Å<sup>3</sup>. Bruker-Nonius Kappa-CCD diffractometer, Mo-K $\alpha$  radiation,  $\lambda$  = 0.7107 Å. Number of reflections measured = 7171, number of independent reflections = 3962, *R<sub>int</sub>* = 0.05, final *R(F)* = 0.050, *wR(F<sup>2</sup>)* = 0.107 for 296 parameters and 2861 reflections with *I* > 2σ(*I*) and 3.02 <  $\theta$  < 26.01° (corresponding *R*-values based on all 3962 reflections are 0.079 and 0.119, respectively). Crystal data of **7** at 273 K: C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>, [*M<sub>r</sub>* = 221.26]: monoclinic, space group *P* 2<sub>1</sub>/*n* (no. 14), *D<sub>c</sub>* = 1.200 g cm<sup>-3</sup>, *Z* = 4,  $\mu$  = 0.074, *a* = 4.0006(3), *b* = 17.9661(10), *c* = 17.145(20) Å,  $\beta$  = 96.308(3), *V* = 1224.85(9) Å<sup>3</sup>. Bruker-Nonius Kappa-CCD diffractometer, Mo-K $\alpha$  radiation,  $\lambda$  = 0.7107 Å. Number of reflections measured = 2749, number of independent reflections = 1465, *R<sub>int</sub>* = 0.03, final *R(F)* = 0.044, *wR(F<sup>2</sup>)* = 0.120 for 167 parameters and 1176 reflections with *I* > 2σ(*I*) and 2.27 <  $\theta$  < 21.98° (corresponding *R*-values based on all 1465 reflections are 0.057 and 0.128, respectively). CCDC 256337–256340. See <http://www.rsc.org/suppdata/cc/b4/b417393g/> for crystallographic data in .cif format.

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