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Donor-substituted cyanoethynylethenes: powerful chromophores for opto-electronic applications†

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Donor-substituted cyanoethynylethenes (CEEs) were synthesised, structurally characterised and investigated for their electronic and two-photon absorption properties, revealing exceptionally strong intramolecular charge-transfer interactions.

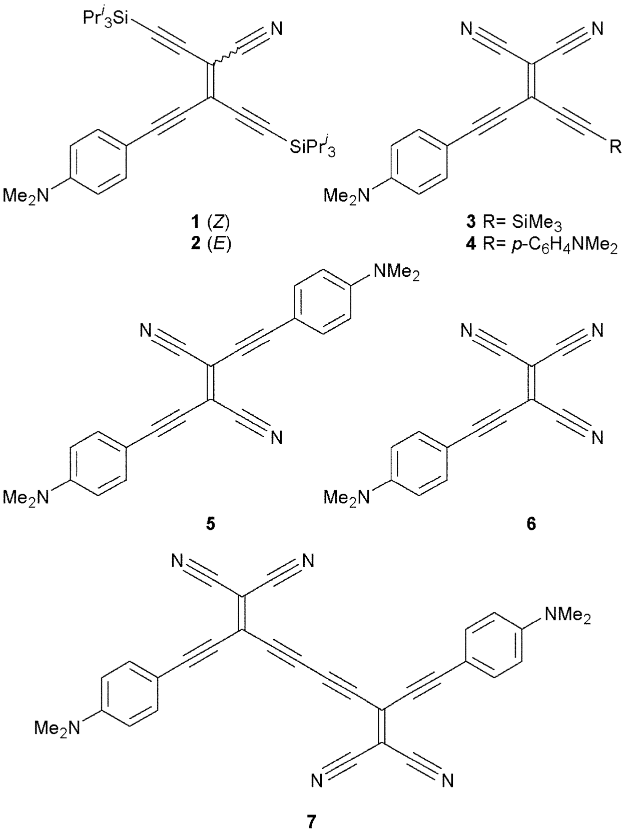

Fig. 1 New donor-substituted cyanoethynylethenes (CEEs).

Recently, we reported the extension of the family of the cyanoethynylethenes (CEEs)[1,2] and showed their powerful electron accepting properties, compared to their isoelectronic tetraethynylethene (TEE) analogues. In order to enhance their non-linear optical (NLO) and two-photon absorption (TPA) properties, we decided to introduce electron-donating groups into these systems, thereby creating strong donor–acceptor chromophores. From several structure–property relationship studies it has been concluded that donor and acceptor substitution of conjugated molecules is essential for the improvement of TPA properties.[3] A similar conclusion was reached for the enhancement of the NLO properties by a systematic study on the donor-acceptor substituted TEEs,[4] which were found to be highly active second-[5] and third-order[6] NLO chromophores. Here we present a comprehensive series of *N*,*N*-dimethylanilino- (DMA) substituted CEEs **1**–**7** (Fig. 1) and compare their electronic properties with those of donor–(DMA) acceptor-(*p*-nitrophenyl) substituted TEE analogues (for some TEE structures, see ESI†). Furthermore, a first TPA cross-section value will be reported.

Donor-substituted CEEs **1**–**4**‡ were synthesised by a Knoevenagel reaction from the corresponding ketones **8**–**10** with $\mathrm{Pr}^i_3\mathrm{SiC{\equiv}C{-}CH_2{-}CN}$ or malononitrile, respectively (Scheme 1). The *Z*- and *E*-isomers **1** and **2** were both obtained in a single reaction step and could be separated by flash chromatography (SiO_2, CH_2Cl_2–hexane 2 : 1) in the dark. Soft deprotection of **3** in a MeOH–THF solution, in the absence of base,[1] and subsequent oxidative coupling under Hay conditions (CuCl, TMEDA, O_2) resulted in dimer **7**. Compound **5** was synthesised by a Sonogashira cross-coupling of dibromofumaronitrile with $p\text{-}\mathrm{Me_2NC_6H_4C{\equiv}CH}$ in a yield of 53%.

Single crystals of **5** and **6**[1] suitable for X-ray structure analysis were grown by slow diffusion of hexane into a CH_2Cl_2 solution (Figs. 2 and 3). Both structures show a planar CEE core and, in the case of **5**, the phenyl rings are twisted out of the main plane by *ca.* 14°. The bond length alternation in the DMA rings is a good indication for the charge-transfer (CT) from the DMA donor to the CEE acceptor moiety, which can be expressed by the quinoid character (δr) of the ring defined by:[7]

$$\delta r = \frac{(a-b)+(c-b)}{2} \approx \frac{(a'-b')+(c'-b')}{2}$$

In benzene, the δr value equals 0, whereas values between 0.08 and 0.10 are found in fully quinoid rings (for the definition of bonds a,a′,b,b′,c,c′ see Fig. 2). CEE **5** exhibits a δr of 0.033 and **6** has a value of 0.037. In sharp contrast, the δr values for DMA rings in donor–acceptor substituted TEEs,[8] calculated from several X-ray structures, generally do not exceed 0.025. This clearly demonstrates the highly enhanced intramolecular CT in the CEEs, as compared to the TEEs. The δr values calculated at the B3LYP/6-31G** level of theory[9] for **5** (0.032) and **6** (0.038) are in good agreement with those determined from the X-ray crystal structure data.

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† Electronic supplementary information (ESI) available: Crystal packing of **5**, UV/Vis spectra of donor-acceptor-substituted TEEs in comparison to those of CEEs, full electrochemical data for the donor-substituted CEEs and structure of the AF-50 standard for two-photon absorption. See http://www.rsc.org/suppdata/ob/b3/b303879c/

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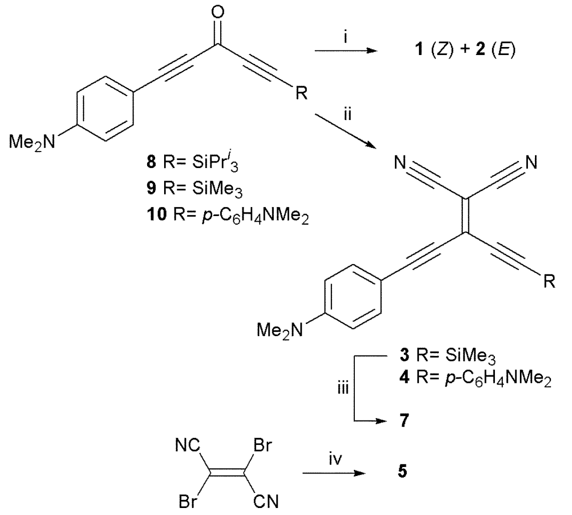
Table 1 Longest-wavelength absorption maxima from UV/Vis spectra and potential difference $E_{ox,1} - E_{red,1}$ (HOMO–LUMO gap) measured by cyclic voltammetry

	λ_{max}/nm (eV)[a]	ε/M^{-1} cm^{-1}	$E_{ox,1} - E_{red,1}$/V[b]
1	468 (2.65)	25000	2.20
2	464 (2.67)	24400	2.20
3	520 (2.38)	36700	1.91
4	524 (2.37)	47300	1.94
5	563 (2.20)	65900	1.88
6	591 (2.10)	43800	1.65
7	600 (2.07)	30700	1.43

[a] Solvent: CHCl$_3$. [b] Cyclic voltammetry data in CH$_2$Cl$_2$ (+0.1 M *n*-Bu$_4$NPF$_6$); working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl. Scan rate: 0.1 V s^{-1}. Potentials *vs.* the ferrocene–ferricenium couple.



Scheme 1 Synthesis of donor-substituted CEEs: i, Pr$^i_3$SiC≡C–CH$_2$–CN, Pr$^i_2$EtN, EtOH, 20 °C, 50% (**1**) and 30% (**2**); ii, CH$_2$(CN)$_2$, Al$_2$O$_3$ (act. II–III), CH$_2$Cl$_2$, 40 °C, 77% (**3**), 65% (**4**); iii, MeOH–THF 1 : 1, 20 °C, then CuCl, TMEDA, CH$_2$Cl$_2$, O$_2$, 20 °C, 19%; iv) Me$_2$NC$_6$H$_4$C≡CH, [PdCl$_2$(PPh$_3$)$_2$], CuI, Pr$^i_2$NH, THF, 52%.

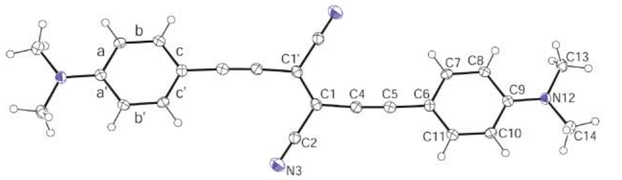


Fig. 2 ORTEP representation of **5** with vibrational ellipsoids obtained at 120 K and shown at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–C1′ 1.372(4), C1–C2 1.441(3), C2–N3 1.146(3), C1–C4 1.417(3), C4–C5 1.207(3), C6–C7 1.397(3), C6–C11 1.401(3), C7–C8 1.370(3), C8–C9 1.410(3), C9–C10 1.411(3), C9–N12 1.368(2), C10–C11 1.374(3), C2–C1–C4 118.51(18), C1–C4–C5 176.1(2), C4–C5–C6 177.6(2).

The crystal packing of **5** shows a slipped parallel stacking of the chromophores, with a DMA ring centre-to-centre distance of 3.95 Å (see ESI †), whereas **6** exhibits a favourable anti-parallel dipolar alignment in the stacks, with the DMA donor and the CEE acceptor moieties placed at a distance of 3.44 Å (Fig. 3b).

Further evidence for the pronounced CT-character of the CEEs was obtained from their UV/Vis spectra (Fig. 4, Table 1). Compared to the DMA- *p*-nitrophenyl-substituted TEEs, the maximum of the lowest-energy band λ_{max} of **4** and **5** is bathochromically shifted by 30–38 nm (0.13–0.18 eV). Furthermore, the CT-bands are much more dominant and the molar absorption coefficients higher for the CEEs then for their TEE analogues (see ESI †). Proof for the CT-character of the longest-wavelength absorption bands was obtained by the disappearance of the band upon protonation of the DMA moieties with TFA and the reappearance upon deprotonation with Et$_3$N. Increasing the number of cyano groups upon changing from **1** to **3** to **6** results in a bathochromic shift of this band. Interestingly, the CT band in the *geminally* bis-DMA-substituted **4** is hypsochromically shifted by 43 nm (0.18 eV) with respect to the corresponding absorption in the *trans* derivative **5**. A similar behaviour was observed in a series of DMA- *p*-nitrophenyl-substituted TEEs (see ESI †).[8] Extension of the conjugation from **3** to **7** results in a large red-shift of 80 nm (0.31 eV).

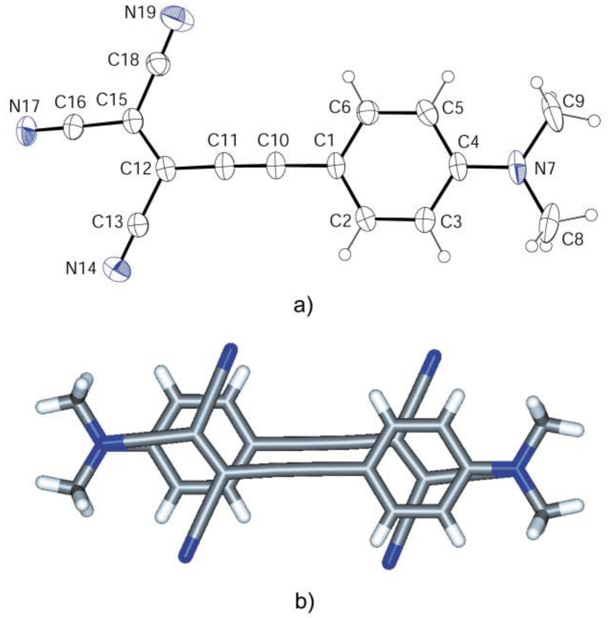


Fig. 3 a) ORTEP representation of **6** with vibrational ellipsoids obtained at 243 K and shown at the 30% probability level. Selected bond lengths (Å) and angles (°): C1–C2 1.392(2), C1–C6 1.401(2), C2–C3 1.366(2), C3–C4 1.415(2), C4–C5 1.410(3), C4–N7 1.356(2), C5–C6 1.370(2), C10–C11 1.209(2), C1–C10 1.410(2), C12–C15 1.365(3), C15–C16 1.432(2), C16–N17 1.139(2), C1–C10–C11 179.17(18), C10–C11–C12 177.93(19), C11–C12–C13 118.79(16), C16–C15–C18 119.90(16). b) Crystal packing of **6**, showing the donor–acceptor stacking of the CEE core with the DMA donor.

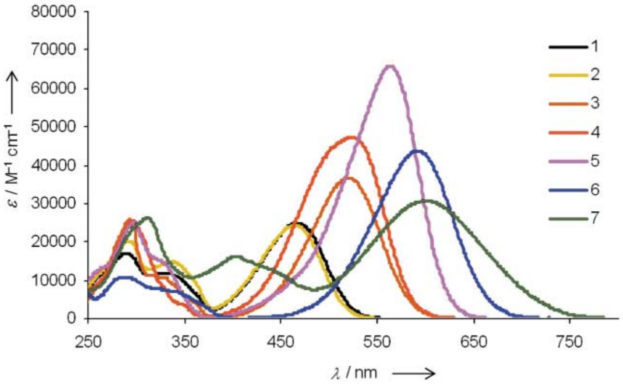


Fig. 4 UV/Vis spectra of **1**–**7** in CHCl$_3$.

Interestingly, the DMA–CEE conjugates **3**,**4**,**6** and **7** are not or only very weakly fluorescent, whereas **5** is highly fluorescent with a quantum yield of 0.58 in hexane–CHCl$_3$ 95 : 5 (but not in pure CHCl$_3$ or CH$_2$Cl$_2$). The fluorescence quantum yields of **1** and **2** could not be accurately determined due to fast *cis*–*trans* isomerisation of these compounds in hexane.

The difference between first oxidation potential and first reduction potential, $E_{ox,1} - E_{red,1}$, determined by cyclic voltammetry (Table 1) can be regarded as a measure for the HOMO–LUMO gap. There exists a strong linear correlation

($R = 0.97$) between the $E_{\mathrm{ox},1} - E_{\mathrm{red},1}$ (V) and $\lambda_{\max}$ values (in eV) of **1**–**6**, indicating that both quantities represent the same physical effect.

In order to obtain a first impression of the two-photon absorption (TPA) properties of the new chromophores, the TPA cross-section of CEE **4** was measured. A value of 8.8×10^{-49} cm^4 s photon^{-1} at 900 nm in 1,1,2,2-tetrachloroethane was found, which is about three times higher than the value for the AF-50 standard (3.0×10^{-49} cm^4 s photon^{-1} at 796 nm in benzene, see ESI †),[10] indicating the enormous potential of the small CEE molecules for opto-electronic applications. In this context of potential technological applications, it should be noted that the new chromophores **5** and **6** can be sublimed without decomposition under laboratory conditions (100–160 °C, 0.1 Torr), which is not possible with the corresponding TEEs and could pave the way for the preparation of ultra-thin films by vapor deposition.

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Notes and references

‡ All new compounds were characterised by IR, UV/Vis, ^{1}H and ^{13}C NMR, elemental analysis or HR-MS. Crystal data of **5** at 120 K: $C_{24}H_{20}N_4$, [M_r = 364.44]: monoclinic, space group $P2_1/n$ (no. 14), $D_c = 1.237$ g cm^{-3}, $Z = 2$, $a = 3.9477(2)$, $b = 11.1064(4)$, $c = 22.3725(9)$ Å, $\beta = 93.769(2)°$, $V = 978.79(7)$ Å^3. Bruker-Nonius Kappa-CCD, MoK$_\alpha$ radiation, $\lambda = 0.7107$ Å. Final $R(F) = 0.053$, $wR(F^2) = 0.108$ for 128 parameters and 2232 reflections with $I > 2\sigma(I)$ and $2.05 < \theta < 27.52°$ (corresponding R-values based on all 4186 reflections are 0.108 and 0.158, respectively). Crystal data of **6** at 243 K ($C_{15}H_{10}N_4$, $M_r = 246.27$): triclinic, space group $P\bar{1}$, $D_c = 1.220$ g cm^{-3}, $Z = 2$, $a = 7.014(1)$, $b = 7.085(1)$, $c = 14.149(2)$ Å, $\alpha = 77.79\ (2)°$, $\beta = 89.21(1)°$, $\gamma = 77.40(2)°$, $V = 670.28(16)$ Å^3. Nonius CAD4 diffractometer, CuK$_\alpha$ radiation, $\lambda = 1.5418$ Å. Final $R(F) = 0.058$, $wR(F^2) = 0.172$ for 183 parameters and 2631 reflections with $I > 2\sigma(I)$ and $3.20 < \theta < 74.87°$ (corresponding R-values based on all 2922 reflections are 0.064 and 0.179, respectively). CCDC reference numbers 207516 and 207517. See http://www.rsc.org/suppdata/ob/b3/b303879c/ for crystallographic data in .cif or other electronic format.

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