

Nonplanar Push–Pull Chromophores for Opto-Electronic Applications

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Abstract: Donor-substituted cyanoethynylethenes (CEEs) are planar push–pull chromophores featuring intense intramolecular charge-transfer (CT) interactions and high third-order optical nonlinearities. Their thermal stability allows for the formation of crystalline thin films by vapor-phase deposition. On the other hand, high-quality amorphous thin films are preferred for opto-electronic applications and such films can be prepared using nonplanar push–pull chromophores with a less pronounced propensity to crystallize. By taking advantage of a versatile, atom-economic ‘click-chemistry’-type transformation, involving a formal [2 + 2] cycloaddition of tetracyanoethene (TCNE) to electron-rich alkynes, followed by cycloreversion, stable donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs) are obtained in high yield and large quantities. These nonplanar push–pull chromophores also feature intense intramolecular CT and, in many cases, high third-order optical nonlinearities. Some of these compounds form high-optical-quality amorphous thin films by vapor-phase deposition, and first applications in next-generation opto-electronic devices have already been demonstrated. Chiral derivatives display high helical twisting power and are efficient dopants to translate molecular into macroscopic chirality, by switching nematic into cholesteric liquid crystalline phases.

Keywords: Alkynes · Charge-transfer · Cycloaddition · Donor-acceptor systems · Nonlinear optics



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Introduction

Highly conjugated organic molecules, featuring tunable structural and opto-electronic properties, have been recognized as promising candidates for use in electronic and opto-electronic devices.^[1–3] Compared to their inorganic counterparts, organic materials are of particular interest due to the ease of structural variation to enhance specific properties for specialized applications and the low costs of their fabrication.^[4,5] Their highly polarizable π -conjugated structures frequently result in efficient second- and third-order nonlinear optical (NLO) responses.^[6–9]

Molecular organic donor–acceptor (D- π -A) chromophores, in particular, not only show strong second-order nonlinear optical responses but also enhanced third-order nonlinear optical polarizabilities.^[10] Most of the known D- π -A molecules are planar structures in order to ensure efficient π -conjugation between donor and acceptor. As a result of strong π - π stacking interactions and antiparallel molecular dipole alignment in the solid state, they tend to form crystalline films. For use in electronic and opto-electronic devices, however, amorphous thin films, which

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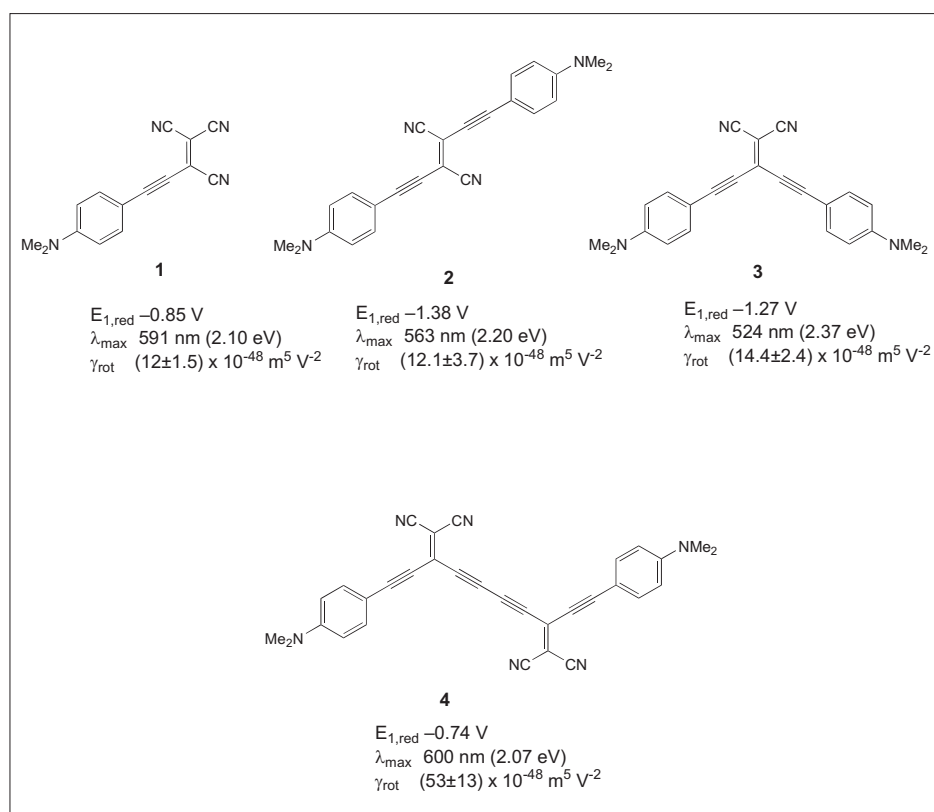


Fig. 1. Examples of donor-substituted cyanoethynylethenes (CEEs) **1–4**. Given are the reversible first one-electron reduction potentials $E_{1,\text{red}}$ (V) in CH_2Cl_2 (+0.1 M $n\text{Bu}_4\text{NPF}_6$, vs. Fc^+/Fc), the maxima of the intramolecular CT bands λ_{max} (nm and eV) in CH_2Cl_2 at 298 K, and the third-order polarizability γ_{rot} measured by degenerate four-wave mixing (DFWM) experiments in CH_2Cl_2 .

can achieve high homogeneity and a high optical quality over large areas, are preferred. Thus, a key issue in our research has become molecular design to control the morphology of thin films. We found that nonplanar D- π -A push-pull chromophores have certain advantages in terms of solubility, aggregation, and sublimability over their planar counterparts, thereby enabling the formation by vapor-phase deposition of high-optical-quality amorphous thin films for use in opto-electronic devices.^[11–13] These recent developments in our laboratories are summarized in this article.

Cyanoethynylethenes

In the early 2000s, the Diederich group introduced a new class of planar CT chromophores, the donor-substituted cyanoethynylethenes (CEE), such as **1–4**,^[14–17] and demonstrated their outstanding opto-electronic properties which include intense low-energy CT bands and facile electron uptake capability (Fig. 1). The third-order NLO properties were investigated by degenerate four-wave mixing (DFWM), resulting in extraordinarily large third-order optical nonlinearities, relative to the small molecular mass of the chromophores.^[18]

All of the CT chromophores are thermally stable up to 250 °C. Most of them can be sublimed without decomposition, thus allowing thin film formation by vapor-phase deposition. In this way, donor-substituted CEE **1** yielded a high-quality crystalline thin film (20 nm thickness) on highly orientated pyrolytic graphite (HOPG).^[19] Nanoscale data recording into the crystalline film by scanning tunneling microscopy (STM) yielded dots featuring an average diameter of approximately 2.1 nm, which corresponds to a possible storage density of 10^{13} bits cm^{-2} . The chemistry of acetylene-based, planar push-pull chromophores, such as donor-substituted CEEs and donor-acceptor-substituted tetraethynylethenes (TEEs), has recently been reviewed.^[20]

Donor-substituted 1,1,4,4-Tetracyanobuta-1,3-dienes

Bruce and coworkers reported in 1981 the first example of a [2+2] cycloaddition of tetracyanoethene (TCNE) with electron-rich ruthenium acetylides, which was followed by a cycloreversion to give organometallic 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs).^[21] While a variety of other cycloadditions to metal acetylides were de-

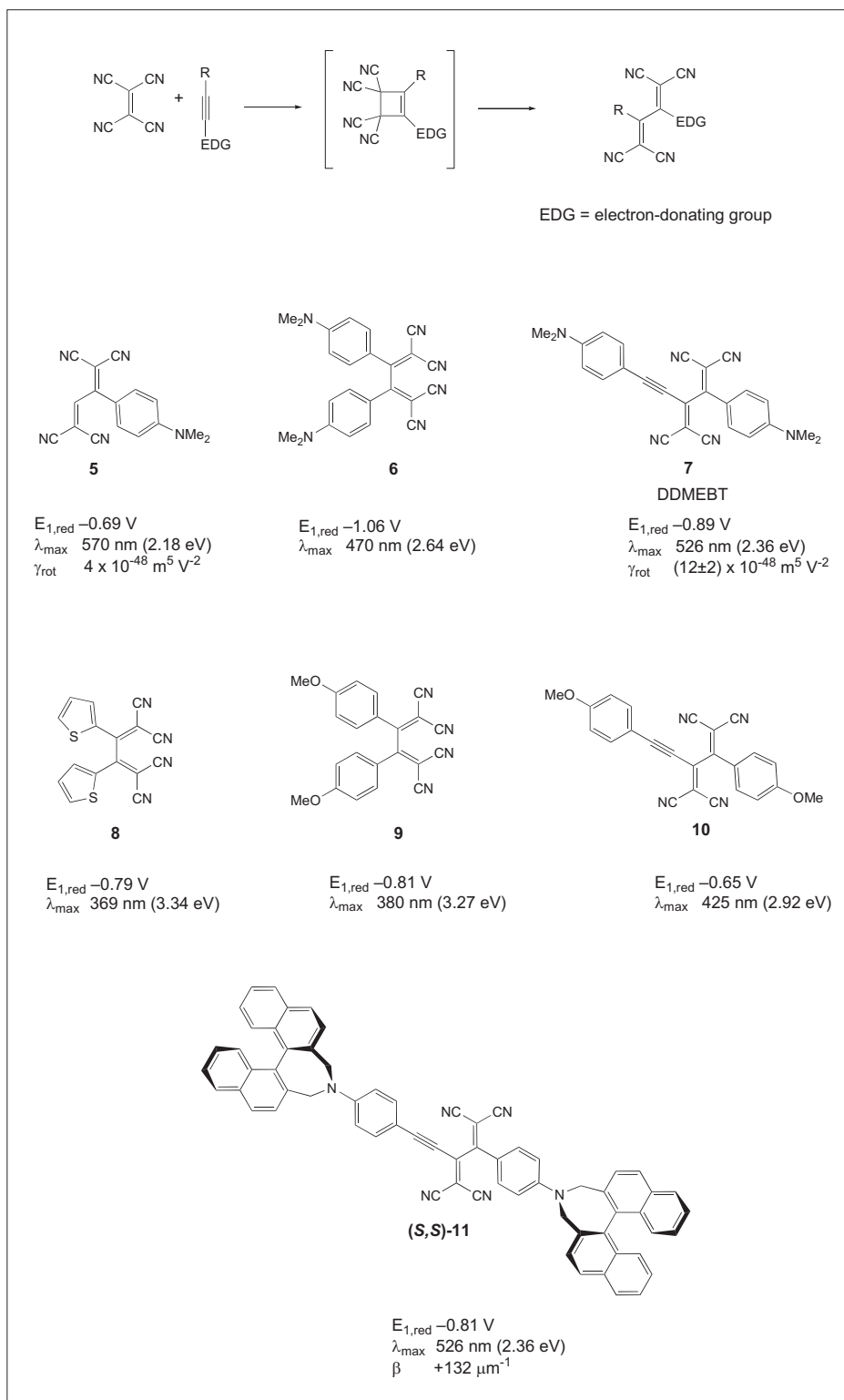
scribed in the following years, only a few examples of TCNE additions to organo-donor-substituted alkynes had been investigated.^[22,23]

In systematic and comprehensive studies since 2005, we showed that alkynes, substituted by a variety of organic donors, generally undergo facile, high-yielding [2+2] cycloaddition with TCNE, followed by cycloreversion of the initially formed cyclobutenes, to give nonplanar donor-substituted TCBDs, such as **5–11**.^[22,24–28] (Scheme 1). Some of these atom-economic conversions, with the character of ‘click’-reactions, even proceed quantitatively in the absence of solvent, in a ballmill or using mortar and pestle. Despite their pronounced nonplanarity, the resulting push-pull chromophores feature intense intramolecular charge-transfer interactions.

Donor-substituted TCBDs are thermally stable up to 300 °C, as determined by thermogravimetric analysis (TGA), and can be sublimed without decomposition. DDMEBT (**7**, 2-[4-(dimethylamino)phenyl]-3-([4-(dimethylamino)phenyl]-ethynyl)buta-1,3-diene-1,1,4,4-tetracyanonitrile) shows a large third-order nonlinear optical response with $\gamma_{\text{rot}} = 12 \pm 2 \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$.^[24] This value is comparable to the highest values obtained for planar, donor-acceptor substituted tetraethynylethenes (TEEs) and other potent NLO chromophores and is quite significant, considering the small number of delocalized π -electrons in the nonplanar chromophore.

Both high stability and easy accessibility of larger compound quantities make donor-substituted TCBDs attractive chromophores for the fabrication of opto-electronic devices. DDMEBT is especially important in this context because it does not form crystalline films by vapor-phase deposition, but rather produces high-optical-quality amorphous thin films (Fig. 2).^[11] This desirable film-forming behavior is a direct consequence of the nonplanarity of the push-pull chromophore and the resulting reduced tendency for crystalline self-association in the solid state.

Degenerate four-wave mixing measurements on thin films of DDMEBT revealed an exceptionally high isotropic third-order susceptibility with the $\chi_{1111}^{(3)}$ value of $2 \pm 1 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$ at the off-resonant wavelength of 1.5 μm . This value is $\sim 10^3$ times larger than the value for fused silica ($1.9 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$).^[11] A transmission spectrum taken at normal incidence for an amorphous DDMEBT film is shown in Fig. 3 together with the extinction coefficient of the same molecule in solution. The films have a wide transparency range starting at wavelengths above 700 nm, with a modulation in the transmission at longer wavelengths as a result of multiple reflection. Such a clear transmission modulation



Scheme 1. Top: Reaction between TCNE and an alkyne, substituted with an electron-donating group (EDG). Bottom: Examples of donor-substituted TCBDs **5–11**. Given are the reversible first one-electron reduction potentials $E_{1,\text{red}}$ (V) in CH_2Cl_2 (+0.1 M $n\text{Bu}_4\text{NPF}_6$, vs. Fc^+/Fc), the maxima of the intramolecular CT bands λ_{max} (nm and eV) in CH_2Cl_2 at 298 K, the third-order polarizability γ_{rot} measured by degenerate four-wave mixing (DFWM) experiments in CH_2Cl_2 for DMA-substituted TCBDs, and the helical twisting power β for N-phenyl-dinaphthazepine-appended TCBD (S,S)-**11**.

with wavelength indicates the high quality of the film with respect to small absorption and scattering losses.

Atomic force microscopy (AFM) confirms that the vapor-phase deposited films of **7** are homogenous with surface height

variations of less than 5 nm over distances of 0.5 μm in films with a thickness of 1 μm (Fig. 4).^[11] Many square centimeters of any substrate can easily be covered with such high-quality nonlinear optical film, which makes this an almost ideal material

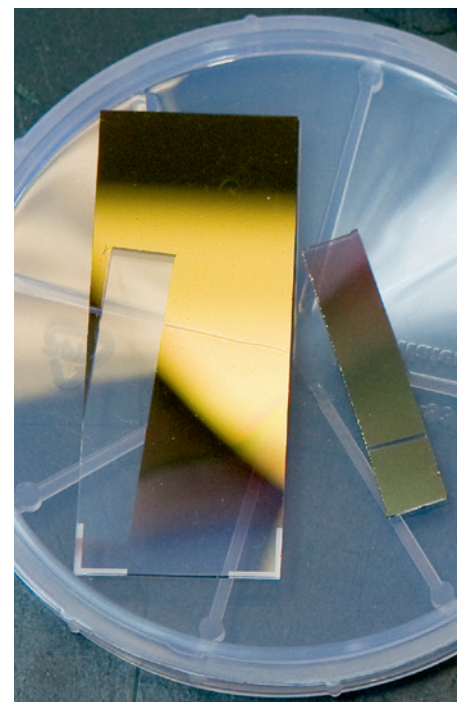


Fig. 2. Photograph of a high-optical-quality amorphous DDMEBT thin film on glass obtained by vapor-phase deposition.

for integration with existing guided-wave photonic technology, and for the development of new hybrid optical devices.

Amorphous films of DDMEBT, obtained by vapor-phase deposition, have been introduced in a multidisciplinary collaboration into highly nonlinear silicon-organic hybrid slot waveguides for all-optical high-speed processing with excellent performance.^[11,12] In these hybrid silicon-on-insulator waveguides, the organic material provides the nonlinearity while silicon takes the role of the passive material that provides for waveguiding. In particular, and almost importantly, the vapor deposition process was able to homogeneously and completely fill a 160 nm wide and 220 nm tall trench between two silicon waveguides (Fig. 5).^[11,29] The resulting hybrid waveguide had a record nonlinearity coefficient of $\gamma \approx 1 \times 10^5 \text{ W}^{-1} \text{ km}^{-1}$ and was the first silicon-organic-hybrid implementation to perform all-optical demultiplexing of a 170.8 Gb s^{-1} .^[12]

For some time we have also been interested in translating molecular into macroscopic chirality, by developing potent dopants with a high helical twisting power (HTP) to switch nematic into cholesteric liquid crystalline phases.^[30,31] For this purpose, we recently prepared the axially chiral, nonplanar push-pull chromophore TCBD (S,S)-**11** by addition of TCNE to a buta-1,3-diene activated by two *N*-arylated 3,5-dihydro-4*H*-dinaphtho[2,1-*c*:1',2'-*e*]azepines (*N*-arylated dinaphthazepines). Comparative analysis of bond-length al-

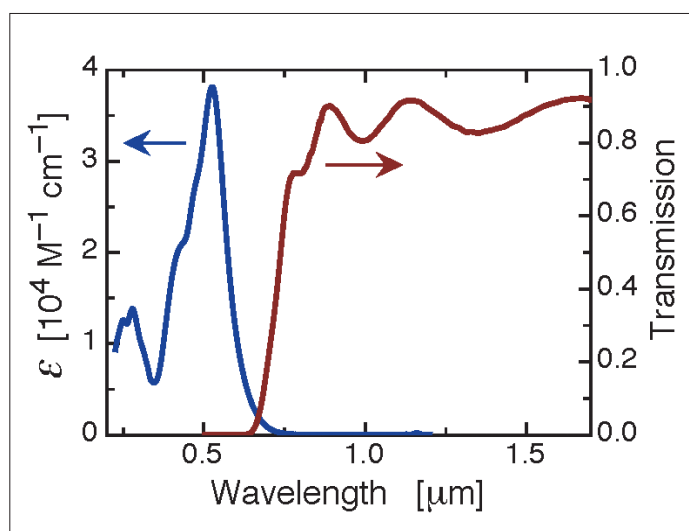


Fig. 3. Molar extinction coefficient of DDMEBT in a CH_2Cl_2 solution and transmission spectrum of a 950 nm thick DDMEBT film deposited on glass. The transmission modulation in the infrared is caused by multiple reflections at the film surfaces.

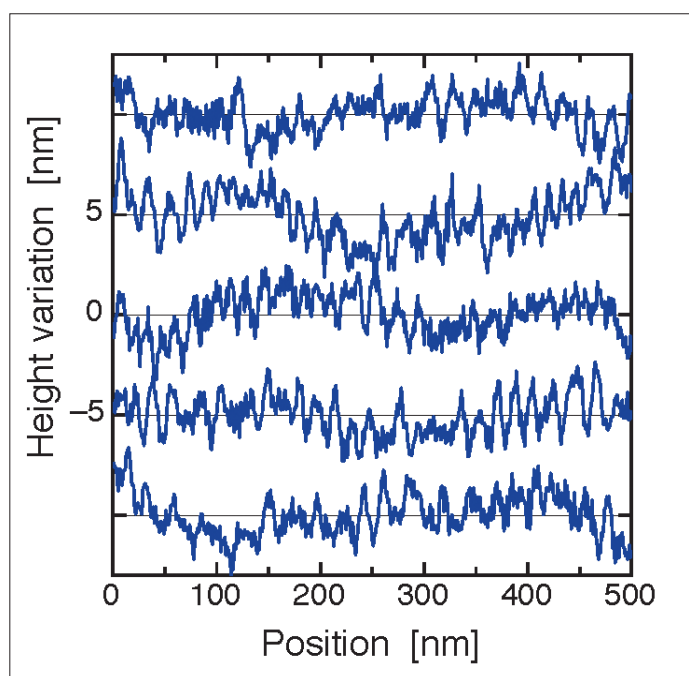


Fig. 4. Atomic force microscope scans showing height variations in a 950 nm thick DDMEBT film over an area of 500 nm \times 500 nm. Shown are five line scans taken every 100 nm, with the data displaced vertically by 5 nm for clarity.

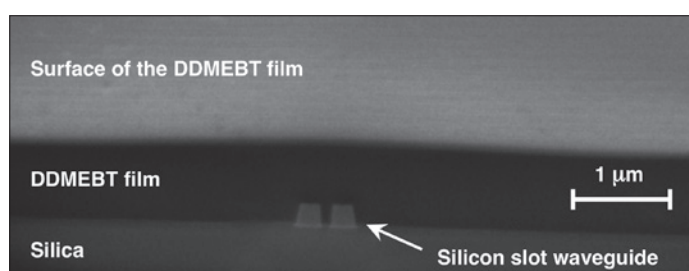


Fig. 5.

ternation in X-ray diffraction analyses and electrochemical and UV/Vis measurements confirmed that chiral *N*-arylated dinaphthazepine are similarly potent to achiral *N,N*-dimethylanilino (DMA) moieties in terms of electron donor strength and their capacity to engage in strong intramolecular CT interactions. Additionally as a result of their chirality, they feature high chiroptical responses and are potent cholesteric inducers. Electronic circular

dichroism (ECD) spectra of their push-pull chromophores, obtained in the 'click'-reaction with TCNE, feature Cotton effects of exceptional intensity with molar circular dichroisms $\Delta\epsilon$ reaching values above 1000 $\text{M}^{-1} \text{cm}^{-1}$. With their elongated shape and the rigidity of the chiral *N*-dinaphthazepine donors, push-pull chromophores such as (*S,S*)-**11** are also effective inducers of cholesteric supramolecular assemblies in nematic liquid crystals (LCs).^[26] Collab-

orative efforts revealed for (*S,S*)-**11** a high value of the helical twisting power β (+132 μm^{-1}), that describes the ability of a chiral dopant to twist a nematic phase. Only few examples of dopants have been reported with β values of the order of hundreds of μm^{-1} .^[31]

In summary, the examples from our recent research reviewed in this article demonstrate the power of a synthesis-driven approach towards new, acetylene-based CT materials. The 'click'-reaction of TCNE and other strong acceptors to electron-donor-activated alkynes enables versatile access to a broad range of highly stable, non-planar, and sublimable push-pull chromophores and organic super-acceptors (currently with potentials for first reversible one electron-uptake up to $E_{1,red} = +0.16$ vs. Fc^+/Fc in CH_2Cl_2 (+0.1 M *n*-Bu₄NPF₆),^[32] and the investigations of their technological potential in fertile collaborative efforts is just at the beginning.

Acknowledgment

This work was supported by the ETH Research Council and the NCCR 'Nanoscale Science', Basel. B. B. is grateful for a Kekulé Fellowship of the German Fonds der Chemischen Industrie.

Received: April 20, 2010

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