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Metal-acetylide addition to tetracyanoethylene

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ABSTRACT

Two push-pull chromophores that have shown utility in the field of molecular electronics and non-linear optics are DDMEBT (1, 2-(4-dimethylamino)phenyl)-3-((4-(dimethylamino)phenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile) and TDMEE (2, 4-(4-dimethylamino)phenyl)but-1-en-3-yne-1,1,2-tricarbonitrile). Unfortunately, the methods reported for their synthesis give variable yields, use toxic solvents, and only provide small amounts of material. We report improved synthetic protocols, providing access to larger quantities of material. By investigating multiple metal-acetylides of 4-ethynyl-N,N-dimethylaniline and their subsequent addition to TCNE, we obtained various products depending on the identity of the metal ion. This led to the simple synthesis of push-pull chromophoric compounds.

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Organic donor–acceptor chromophores are valuable systems for nonlinear optical (NLO) materials applications, such as alloptical computing and signal processing.¹ Organic NLO materials hold promise for the transmission of data at higher speed while in turn reducing the size of devices required.²

We have previously shown the high potential of 4-(dimethylamino)phenyl-(*N*,*N*-dimethylanilino, DMA) substituted cyanoethenes, such as 1-3 (Fig. 1), as efficient NLO chromophores.³ Compounds 1 (DDMEBT) and 3 are both obtained through the cycloaddition-retroelectrocyclization (CA-RE) reaction with tetracyanoethene (TCNE),^{3b,4} whereas compound 2 (TDMEE) can be prepared by cyano-substitution of TCNE.^{3a} DDMEBT and TDMEE have shown excellent twophoton absorption, by an order of magnitude larger than regularly used reference molecules.⁵ DDMEBT has been applied to the formation of high-optical-quality amorphous thin films for use in ultrafast, all-optical switching devices.⁶ Significant quantities of these materials to further investigate their properties were needed which required a reexamination of their preparation methods.

The reported synthesis of **1** was conducted on a milligram scale and used benzene as the solvent to effect the CA–RE reaction.^{3b} We aimed for conditions that would be successful on the gram scale and avoid the use of benzene as solvent. The reported synthesis of **2** involves the formation of the Cu(I)-acetylide of *N*,*N*-dimethylanilino-acetylene (DMAA) (**4**) and its subsequent addition to TCNE. The yields are variable and low, less than 30%, ^{3a} and the protocol not amenable to scale up, mostly due to a competing CA–RE reaction between the alkyne

and TCNE, affording **3** as the major product. The Cu(I)-acetylide can undergo the CA–RE reaction followed by protodemetallation, or it may be that not all of the acetylene is converted to the required metal species. In both cases, the product expected to be formed would be **3**. The Cu(I) source is also reported as copper(I) acetate, which is highly reactive and undergoes rapid air oxidation to Cu(II).



Figure 1. Previously synthesized organic donor-acceptor molecules.

The improved synthesis of compound 1 on multigram scale could be easily achieved through a dimerization of compound 4 using Hay catalyst to afford compound 5 (Scheme 1). Subjecting 5 to the CA-RE reaction with tetracyanoethylene (TCNE) in acetonitrile, rather than benzene, cleanly afforded high purity compound following a short silica column. The combined yield for these two steps affording more than 6 g of compound 1 was 95%.

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Scheme 1. Revised synthesis of compound 1. Reagents and conditions: a) CuCl (10 mol%), tetramethylenediamine (TMEDA, 20 mol%), 4 Å molecular sieves, CH_2Cl_2 , 20 °C, 1.5 h; b) TCNE (1.0 equiv), MeCN, 20 °C, 1 h.

Greater issues existed around improving the synthesis of TDMEE (2), and we aimed at improving the yields and operating procedure. Instead of examining different variations of Cu(I), we turned our attention to other metal- and metalloid-acetylides (Scheme 2). When using CuOAc, it was difficult to determine if all acetylene had been converted to the corresponding Cu(I) species, so we first investigated the organostannane, which would allow isolation. Stannylation was easily achieved through deprotonation of DMAA (4) with *n*-BuLi, followed by reaction with Me₃SnCl. In this way, compound 6 could be obtained in 66% yield. Interestingly however, 6 undergoes a complete dimerization process at ambient conditions overnight to give the dialkyne 5. Confirmation of this process was obtained by reacting the dimer with TCNE to give 1. Keeping compound 6 in CH₂Cl₂ solution at -20 °C prolonged the half-life to months.

When the Sn-acetylide **6** was freshly prepared and then reacted with TCNE, a facile transformation occurred to give **2** in 63% yield (ca <30\% reported previously from CuOAc).^{3a} Despite meeting our target, we hoped to eliminate the need for toxic tin reagents and therefore investigated other metal-acetylides.



Scheme 2. The formation of metal-acetylides of 4 and their reaction with TCNE. Reagents and conditions: a) *n*-BuLi (1.6 M in hexanes, 1.0 equiv), – 30 °C, 0.5 h, then Me₃SnCl (1.0 equiv), –30 to 20 °C, 1 h; b) neat or in CH₂Cl₂, ambient conditions; c) TCNE (1.0 equiv), MeCN, 20 °C, 1 h; d) *n*-BuLi (1.6 M in hexanes, 1.0 equiv), –30 °C, 0.5 h, then TCNE (1.0 equiv), – 30 to 20 °C, 1 h; e) EtMgBr (1.0 M in THF, 1.1 equiv), 0 to 50 °C, 2.25 h, then TCNE (1.0 equiv), 20 °C, 1 h; f)1) *n*-BuLi (1.6 M in hexanes, 1.0 equiv), –30 °C, 0.5 h, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 equiv), –30 to 20 °C, 1 h; 2) TCNE (1.0 equiv), MeCN, 20 °C, 1 h.

Considering we were already forming the lithium-acetylide, we first examined how this may react with TCNE. The only product isolated was **7**, which presumably arises from a CA–RE reaction to form **3**, followed by conjugate addition of *n*-butylide. Despite the multiple electrophilic sites present on **3**, only one product was observed. Compound **7** could be easily identified by its ¹H NMR spectrum which featured a doublet (J = 11.0 Hz, 1 H) at 4.16 ppm and a second doublet (J = 11.0 Hz, 1 H) at 7.64 ppm. The high-resolution mass spectrum also agreed with a mass of 332.1870 ($[M + H]^+$, calculated for C₂₀H₂₂N₅: 332.1870).

We subsequently focused on the magnesium-acetylide prepared from EtMgBr. In a one-pot reaction, the Mg-acetylide was formed, then treated with TCNE. The only organic product isolated was **8** in 24% yield. This is a known compound, previously prepared in 3 steps and 30% overall yield.^{3a} It is interesting to note that despite the 1:1 ratio of Mg-acetylide to TCNE, double, regioselective addition occurs to give the isolated product.

The alkynylboronic ester was next prepared through lithiation of **4** and quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, following a reported procedure.⁷ The subsequent reaction with TCNE only gave the CA–RE product **3** and in lower yields than normally observed. It is likely that the mechanism by which it forms is an initial CA–RE reaction followed by proto-deborylation.

Considering the softer metals tin and copper gave the desired product and to avoid the toxic organotin reagents, we investigated Zn-acetylides for the preparation of TDMEE (Scheme 3). Lithiation, followed by treatment with $ZnCl_2$ in THF afforded the Zn-acetylide, which, in a one-pot reaction, was treated with TCNE. Gratifyingly, the target compound **2** was obtained cleanly, with no CA–RE side product, in reproducible yields (60–65%). This transformation could be scaled up, allowing access to significant, multi-gram quantities of TDMEE in one run. Attempts to extend the methodology to phenylacetylene derivatives were unsuccessful suggesting that a donor-activated alkyne was required. Using $ZnBr_2$ or ZnI_2 were also successful, but did not show a change in the yields, therefore $ZnCl_2$ was maintained.

Encouraged by these simple and high-yielding conditions for the addition of acetylides to TCNE, we applied it to enhance the charge-transfer properties of this class of compounds, namely donor-substituted cyanoethynylethenes (CEEs).^{3a} We prepared the dialkyne **9** by Glaser-Hay coupling of **4** with TMS-acetylene and subsequent deprotection using previously reported procedures.⁷ Forming the Zn-acetylide and treatment with TCNE gave the expected product **10** in a similar yield to that observed with the mono-alkyne (Scheme 3).



Scheme 3. Zinc-acetylides and their reaction with TCNE. Reagents and conditions: a) *n*-BuLi (1.6 M in hexanes, 1.0 equiv), -30 °C, 0.5 h, then ZnCl₂ (1.0 M in THF, 1.2 equiv), -30 to 20 °C, 1.5 h, then TCNE (1.0 equiv), 20 °C, 0.5 h.

The structure of the new push-pull chromophore **10** was determined by X-ray analysis (Fig. 2). The compound crystallized as a solvate with CHCl₃ in the triclinic space group $P\overline{1}$. Of particular interest was the quinoid character⁹ of the (*N*,*N*-

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dimethylamino)phenyl ring as a measure for ground state pushpull conjugation. A value of 0.036 was calculated for compound 10, while compounds 1^{3b} (DMA ring on the acetylene), 2^{3a} and 3^{3b} have values of $\delta r = 0.056, 0.037, \text{ and } 0.036 \text{ Å}$, respectively (see Supplementary Data for more details). The longer buta-1,3diyne-1,4-diyl spacer in 10 slightly reduces ground-state pushpull conjugation as compared to 2 with an ethyne-1,2-diyl spacer.¹⁰ In the crystal packing, chromophores **10** adopt an antiparallel alignment of dimers, with a π -stacking distance of 3.37 Å.



Figure 2. a) ORTEP plot of 10[°]CHCl₃. Atomic displacement parameters at 100 K are drawn at 50% probability level. The solvent is omitted. For selected bond lengths (Å) and angles (°), see Figs. S1 and S2 in the Supplementary Data. Quinoid character: $\delta r = (((a + a')/2 - (b + b')/2) + ((c + a')/2 - (b + b')/2))$ c')/2-(b + b')/2)/2 = 0.036. b) Antiparallel alignment of dimers of 10 in the crystal lattice, at an average π -stacking distance of 3.37 Å. The solvent is omitted.

The UV/Vis spectrum of 10 in CHCl₃ (see Fig. S15 in the Supplementary Data) features a strong intramolecular chargetransfer (CT) band at $\lambda_{max} = 641$ nm (1.93 eV, $\varepsilon = 30000$ M⁻¹ cm⁻¹), which undergoes a hypsochromic shift as solvent polarity decreases. When protonated with trifluoroacetic acid, the chargetransfer absorption was lost, but the band was fully recovered upon neutralization with Et₃N. The CT band of 10 is substantially bathochromically shifted with respect to the band in 2 ($\lambda_{max} = 591$ nm (2.10 eV, $\varepsilon = 43800 \text{ m}^{-1} \text{ cm}^{-1}$),^{3a} but features a lower molar extinction coefficient, in agreement with previous investigations on the influence of spacer length on optical properties of pushpull chromophores.

The redox properties of compound 10 were studied by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). All electrochemical measurements were carried out in CH2Cl2 containing nBu_4NPF_6 (0.1 M) in a classical three-electrode cell with the potentials given versus the ferrocenium/ferrocene (Fc^{+}/Fc) couple and uncorrected for ohmic drop. The data for the new chromophore 10 in comparison to those previously reported for 1, 2, and 8^3 are given in Table S1 in the Supplementary Data.

For compound 10, reversible oxidation occurs at the (dimethylamino)phenyl moiety at +0.68 V, well in the potential range of the other chromophores. The first reduction potential of 10 is the most anodically shifted, at -0.68 V, showing around a 200 mV increase over the first reduction potentials linearly conjugated compounds 1 (-0.89 V) and 2 (-0.86 V) and a very large increase compared to cross-conjugated 8 (-1.31 V).

In conclusion, we investigated the reaction of different metal-acetylides of N,N-dimethylanilino-acetylene (DMAA) (4) with TCNE and found the zinc-acetylide readily undergoes substitution of a single cyano moiety of TCNE to afford TDMEE (2), a molecule of interest in molecular electronics. This methodology was then extended to form the previously unknown push-pull chromophore **10** with a larger buta-1,3-diyne-1,4-diyl spacer. The substantial reduction in the optical (λ_{max} 2: 2.10 eV; **10**: 1.93 eV) and electrochemical ($\Delta(E_{\text{ox},1}-E_{\text{red},1})$ **2**: 1.65 eV; **10**: 1.36 eV) HOMO-LUMO gap is in full agreement with other study on different chromophore series, 3a,10,11 showing that the opto-electronic properties of push-pull chromophores are enhanced with increasing length of the spacer between donor and acceptor.

Acknowledgments

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Supplementary Material

The supplementary data contains experimental procedures, full characterization of new compounds, copies of ¹H and ¹³C NMR spectra, and X-ray data (PDF).

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• Addition of metal-acetylides to TCNE

- Different products depending on metal used
- Synthesis of push-pull chromophoric compounds
- Improved synthesis of useful materials for molecular electronics