

Communication

New access to the synthesis of 1,1,4,4-tetracyanobuta-1,3-diene-based push–pull chromophores using tetracyanoethylene oxide via [3+2] cycloaddition–ring opening reactions

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Keywords: tetracyanoethylene oxide, [3+2] cycloaddition, push–pull chromophores, 1,1,4,4-tetracyanobuta-1,3-diene, [2+2] cycloaddition–retroelectrocyclization (CA–RE) reaction

Abstract: Herein we report a new way to access the synthesis of established invaluable push–pull chromophores based on 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs) using tetracyanoethylene oxide (TCNEO) upon reaction with alkynes substituted with an electron-donating group (EDG) via [3+2] cycloaddition (CA) followed by ring-opening (RO) reactions. Further, we uncovered that the facile [3+2] CA–RO reaction under simpler reaction condition is possible due to the presence of EDG group, otherwise, even the formation of [3+2] cycloadduct without EDG requires harsher condition and does not lead to TCBD as reported earlier in 1965 by Linn and Benson.

Introduction

The continuous generation of new organic push–pull chromophores has overwhelmed researchers from across the globe for about a past decade. Because of their immense applications in material fabrications,¹ designing soft molecular device-optoelectronics,² as fluorescence sensors,³ in bio-imaging,⁴ sensitizer in dye-sensitized solar cells,⁵ piezochromic materials,⁶ frequency-upconverted lasing,⁷ and photorefractive organic materials,⁸ etc. The exciting features of all the chromophores arise due to their encounter with the UV/Vis/NIR-radiations.⁹ Interaction of organic push–pull chromophores with light can be easily tuned upon modulating the design of the donor and acceptor groups. This is feasible primarily because of the control by the donor and acceptor groups over the intramolecular charge transfer (ICT) process. Even small structural variation in donor- and acceptor-parts of push–pull chromophores bring a complete transformation in the properties of molecules.¹⁰ Cyano (CN)

group as an acceptor and amines as the donor has secured a prominent place owing to their strong push–pull nature. Synthetic methodology for exploring new acceptors and donors in the push–pull systems is possible with ease thanks to the well-established method pioneered by Diederich and co-workers based on the formal [2+2] cycloaddition–retroelectrocyclization (CA–RE) reaction between alkynes substituted with an electron-donating group (EDG) and electron-deficient olefin yielding EDG-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (Figure 1a).¹¹ The click-type [2+2] CA–RE is a robust method for the preparation of nonplanar, π -conjugated, donor-acceptor (D-A) chromophores that exhibit intense intramolecular charge-transfer (CT) bands with lower energy.¹² Some of them have found applications in devices for all-optical switching,^{2a} organic field-effect transistor,¹³ light-emitting diodes,¹⁴ hole-transporting materials in solar cell,¹⁵ and has also shown remarkable third-order nonlinear optical properties.^{9b}

In general, the previous works reported on the synthesis of TCBDs based push–pull chromophores have mostly changed the donor moiety on the alkyne part, such as metal ylides,¹⁶ thiophenes,¹⁷ amines,¹¹ ferrocene and TTF,¹⁸ azulene,¹⁹ pyrroles,²⁰ carbazole,²¹ ynamide,²² and recently urea.²³ Whereas, in the case of the acceptor part, CN derivatives especially tetracyanoethene (TCNE) has been predominantly used as benchmark starting material.^{11c} Though another functional group such as carboxylic ester group has been used as acceptor but they act as a mild accepting unit and show less reactivity.²⁴ To expand the chemical space for TCBD based push–pull chromophores, it is imperative to look for more tools to synthesize TCBDs apart from the conventional [2+2] CA–RE reaction as the only choice.

We envisaged exploring tetracyanoethylene oxide (TCNEO, **1**) as an alternative to TCNE because the oxirane ring would bring completely different reaction pathways. Further, it is also commercially available and easy to prepare on a large scale.²⁵ In 1965, it has been reported by Linn and Benson that TCNEO undergoes [3+2] cycloaddition (CA) with alkenes as well as alkynes to provide the corresponding cycloadducts of tetracyanotetrahydrofuran and tetracyanodihydrofuran (TCDHF) derivatives, respectively (Figure 1b).²⁶ This cycloaddition reaction occurs by the temperature (≥ 100 °C) assisted formation of carbonyl ylide due to the cleavage of the C–C bond of the epoxide ring of TCNEO.²⁷ Recently, this chemistry has been successfully applied to fabricate graphene-TCNEO adduct and has been found to manipulate the electronic properties of graphene.²⁸

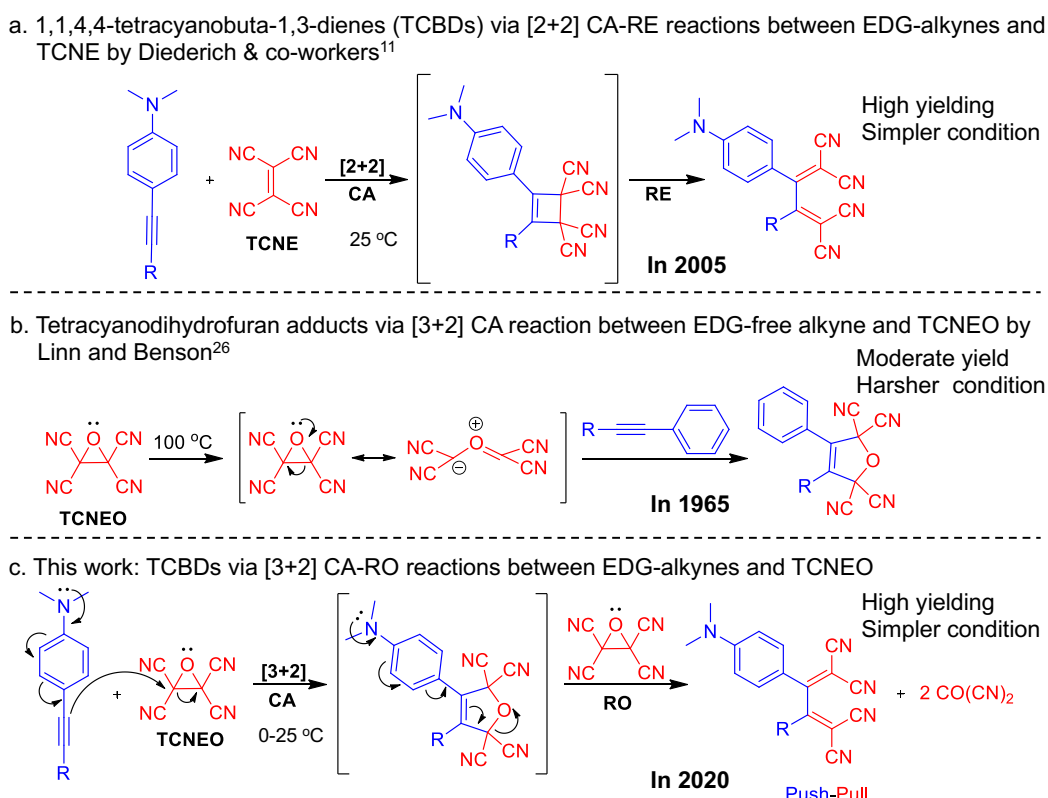


Figure 1. a) Push–pull TCBDs synthesis from EDG-alkynes and TCNE using formal “click”-type [2+2] CA–RE reaction.¹¹ b) [3+2] CA reaction between EDG-free alkynes and TCNEO providing stable tetracyanodihydrofurans.²⁶ c) Push–pull TCBDs synthesis from EDG-alkyne and TCNEO via [3+2] CA–RO reaction.

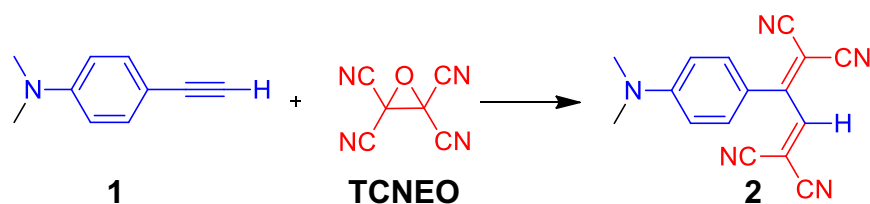
However, it should be noted that the previously reported TCNEO and alkynes having no EDG gave exclusively TCDHF derivatives which were found to be very stable (Figure 1b).²⁶ We hypothesized that incorporating the EDG group in the alkyne part would lead to subsequent ring-opening reactions as indicated in Figure 1c, thus possible to obtain some interesting new and useful products, for example, TCBD. With this hypothesis, we started to explore TCNEO as a potential precursor for the organic acceptor to undergo [3+2] CA reaction with electron-rich alkynes such as *N,N'*-dimethylamino (DMA)-substituted phenylacetylenes and the results are presented herein.

Results and Discussion

Initially, we investigated the reactivity of TCNEO with mono-substituted alkyne such as 4-ethynyl-*N,N'*-dimethylaniline **1** and explored its synthetic paths under different solvents and temperatures (Table 1). As we wish to check and identify whether the more useful TCBD **2**

would form under this condition, an authentic sample was prepared according to the literature procedure and compared.^{11b} First, the reaction was conducted in CH₂Cl₂ at ambient condition (entries 1–3, Table 1), as indicated by the thin-layer chromatography (TLC) that the reaction occurred even without heating and showed not so clean with multiple spots (Figures S1–S3, Supporting Information (SI)). We were pleased to see that a trace amount of purple color spot appeared and matched with the authentic sample. This suggests that unlike the EDG-free alkyne which gives the stable [3+2] cycloadduct of TCDHF derivatives,²⁶ this adduct with EDG undergoes further reaction paths leading to a complex mixture of products.

Table 1. Optimization studies for mono-substituted alkyne with TCNEO^a



entry	TCNEO equiv	Temp (°C)	Solvent	Additive	TCBD 2 Yield (%) ^b
1	1	25	CH ₂ Cl ₂	none	trace
2	2	25	CH ₂ Cl ₂	none	10
3	2	0	CH ₂ Cl ₂	none	5
4	2	25	CH ₃ CN	none	3
5	1	60	CH ₃ CN	none	2
6	2	25	CH ₂ Cl ₂	LiClO ₄	Complex mixture
7	2	0	CH ₃ CN	LiClO ₄	Complex mixture
8	2	60	CH ₃ CN	LiClO ₄	Complex mixture

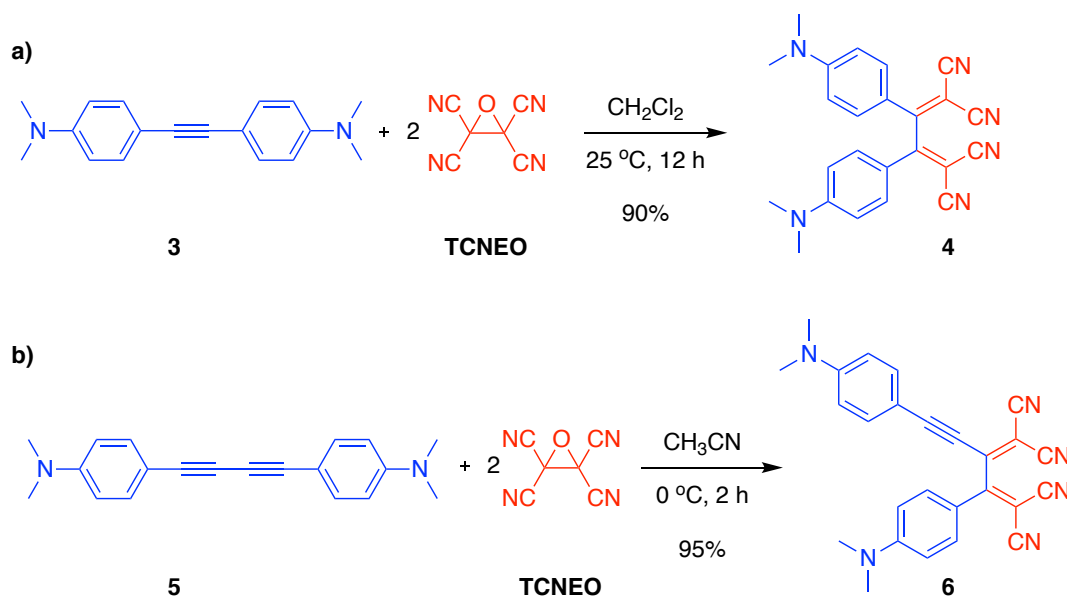
^a Reactions were carried out on a 0.1 mmol scale.

^b Isolated yield.

Further, to improve the yield of TCBD **2** instead of an equimolar (equiv) amount of TCNEO, 2 equiv was reacted and found significant product formation of TCBD up to 10% yield (entries 2–3, Table 1). Changing the solvent from non-polar to polar and also the high temperature resulted in a low yield of TCBD **2**. It has been reported by Diederich et al. that additive such as LiClO₄ assists similar reactions like [3+2] cycloaddition–rearrangement and sometimes different reactivity.^{29,24b} The addition of Lewis acid LiClO₄ also did not improve the reaction and resulted in a more complex reaction mixture. Various attempts to improve the

yield of TCBD were failed including changing the strong EDG ($-NMe_2$) into weaker EDG ($-OMe$) group such as 4-ethynyl anisole, though the TCNEO consumption occurs at high temperature and gave complex mixture. We infer that the over-reactions could be ascribed to the unsubstituted dicyanovinyl group in the 2-substituted 1,1,4,4-tetracyanobuta-1,3-dienes over 2,3-disubstituted 1,1,4,4-tetracyanobuta-1,3-dienes which is not stabilized by the EDG group.³⁰

Hence, we turned our attention to synthesize bis-DMA-substituted alkynes **3** and **5** derivatives to further investigate its effect on TCNEO and possible generation of TCBD chromophores (Scheme 1). While using compounds **3** and **5** as donor alkynes and two equiv of TCNEO, we had observed the almost complete transformation of alkynes into the corresponding TCBDs **4** and **6** with a yield of 90 and 95%, respectively without the use of any additives.



Scheme 1. Synthesis of 2,3-disubstituted TCBDs using TCNEO and bis-substituted alkynes via [3+2] CA followed by RO reactions.

The following observations were noticed upon screening for the best conditions. Regardless of TCNEO equivalents, only the TCBD products were formed and no [3+2] cycloadduct of tetracyanodihydrofuran was observed by TLC. Also, we found that 2 equiv of TCNEO was the optimum amount for the formation of TCBD products. Further, increasing more equiv of TCNEO did not significantly improve the yield. While chlorinated solvent CH_2Cl_2 provided the best yield for **4**, the slightly lower yield was obtained for **6** (85% yield), whereas the polar solvents such as CH_3CN and N,N' -dimethylformamide provided a better

yield of 95% for **6**. Though the reaction can be performed without the inert atmosphere the presence of air leads to a ~20% decrease in the TCBD yield.

It was known that alkyne attached with TCBD tends to undergo a second CA–RE reaction at high temperature to provide the octacyano[4]dendralenes as a new class of cyano-rich non-planar organic acceptor.³¹ Compound **6** was subjected to further reaction with TCNEO to test whether the **6** having similar features would undergo additional [3+2] CA–RO reaction and provide the corresponding octacyano[4]dendralene *i.e.*, 3,4-Bis(dicyanomethylidene)-2,5-bis[4-(dimethylamino)phenyl]hexa-1,5-diene-1,1,6,6-tetracarbonitrile. However, both TLC and LC–MS have confirmed that such octacyano[4]dendralene did not form (Figures S4 and S5, SI). Nevertheless, a new blue-colored compound formed as major and its structural identity with different chemistry needs to be established with a greater detailed investigation which will be reported elsewhere.

The identity of the compounds was checked against the authentic sample of respective product formation in the reaction mixture using silica TLC prepared using TCNE, since all the TCBD products were already known through the [2+2] CA–RE reaction. Further, the successful formation of TCBDs **4** and **6** was characterized by melting point, ¹H-NMR, and unambiguous proof for the TCBD constitution obtained from the single-crystal study. While compound **4** provided the same structure as previously reported CCDC deposition number 256339,^{11a} in the case of TCBD **6**, the obtained crystal structure (CCDC deposition number 2009612) is a new polymorphism (II) with monoclinic unit cell and *P* 2₁/c (14) space group (Figure 2, for details, see Section E, SI), unlike the previously reported polymorphism (I) showing triclinic lattice with *P* $\bar{1}$ space group (CCDC deposition number 56338).^{11a} The comparison table of these two polymorphs is provided in Table S1, SI.

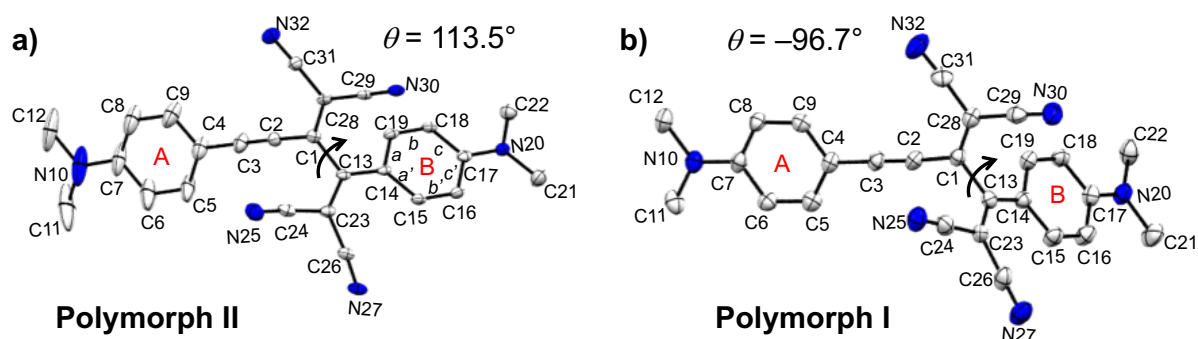


Figure 2. ORTEP plots of a) **6** polymorph II, b) **6** polymorph I^{11a} (arbitrary numbering, H-atoms are omitted for clarity). Atomic displacement parameters are drawn at a 25% probability level.

The protocol established in the previous study shows that TCNEO acts as 1,3-dipolar species at above 100 °C and the generated carbonyl ylide undergoes [3+2] CA reaction with EDG-free alkyne to give stable TCDHF product under relatively harsher condition (Figure 3a).^{26,27} The mechanistic proposal for the present reaction is outlined in Figure 3b. The fact that the TCBDs formation by EDG-alkynes **3** and **5** proceeds at ambient and even at low (0 °C) temperatures, respectively, indicates that the first step initiated by the nucleophilic attack by the EDG-activated alkyne assisted by the electron delocalization. This generates to form a zwitterionic intermediate **I**, in which the cationic charge is favorably stabilized as an iminium ion and such step occurrence has postulated to form in the first step of the CA–RE reaction.³² Upon cyclization by the dicyanomethide anion generate the [3+2] cycloadduct intermediate *i.e* TCDHF derivative **II** (Figure 3b). Unlike the isolable furan adduct formed in the non-activated alkyne,²⁶ the facile furan ring-opening and generation of oxide ion **III** are facilitated by the presence of electron delocalization from the EDG as well as the stabilization by the generation of donor-substituted dicyanovinyl (D–A) moiety. The removal of an oxygen atom (deoxygenation) from this derivative is a prerequisite for the formation of TCBD. This is achieved by without any extra reagent but with additional TCNEO molecule, which undergoes nucleophilic attack by the oxide anion at the electrophilic carbon atom generating the new oxide anion intermediate **IV**. The generation of push–pull TCBD may be formed *via* two pathways **a** and **b**. In pathway **a**, the oxide anion intermediate **IV** undergoes a nucleophilic attack on the electrophilic oxygen atom to form the dioxetane ring and the stable push–pull TCBD molecule. The electrophilic character of the oxygen atom bonded between two –C(CN)₂ has been proven before for the reaction between the TCNEO and anthracene.^{27b} The generated unstable dioxetane further may decompose into two molecules of carbonyl cyanide (CO(CN)₂) *via* retro-electrocyclization. On the other hand, in pathway **b** the elimination of two CO(CN)₂ and push–pull TCBD molecules may occur in a single step. To gain insights on which pathway is being governed in this reaction, we tested the in-situ reaction mixture and analyzed using LC–MS and ATR FT–IR studies to see whether the characteristic peaks corresponding to the dioxetane and CO(CN)₂ are present. The ATR FT–IR spectrum of the crude reaction mixture has shown the characteristic peak corresponding to the dioxetane ring O—O stretching frequency at 670 cm^{–1} which is absent in both TCBD and TCNEO (Figure S11, SI).³³ Similarly, the LC–MS spectrum of the crude reaction mixture showed the presence of molecular ion (*m/z* 160.06 Daltons) peak corresponding to the 3,3,4,4-tetracyano-1,2-dioxetane (Figure S12, SI). Since both paths would eventually lead to the formation of CO(CN)₂, the

evidence for the presence of 3,3,4,4-tetracyano-1,2-dioxetane, in particular, suggests that path **a** is operated in the reaction.

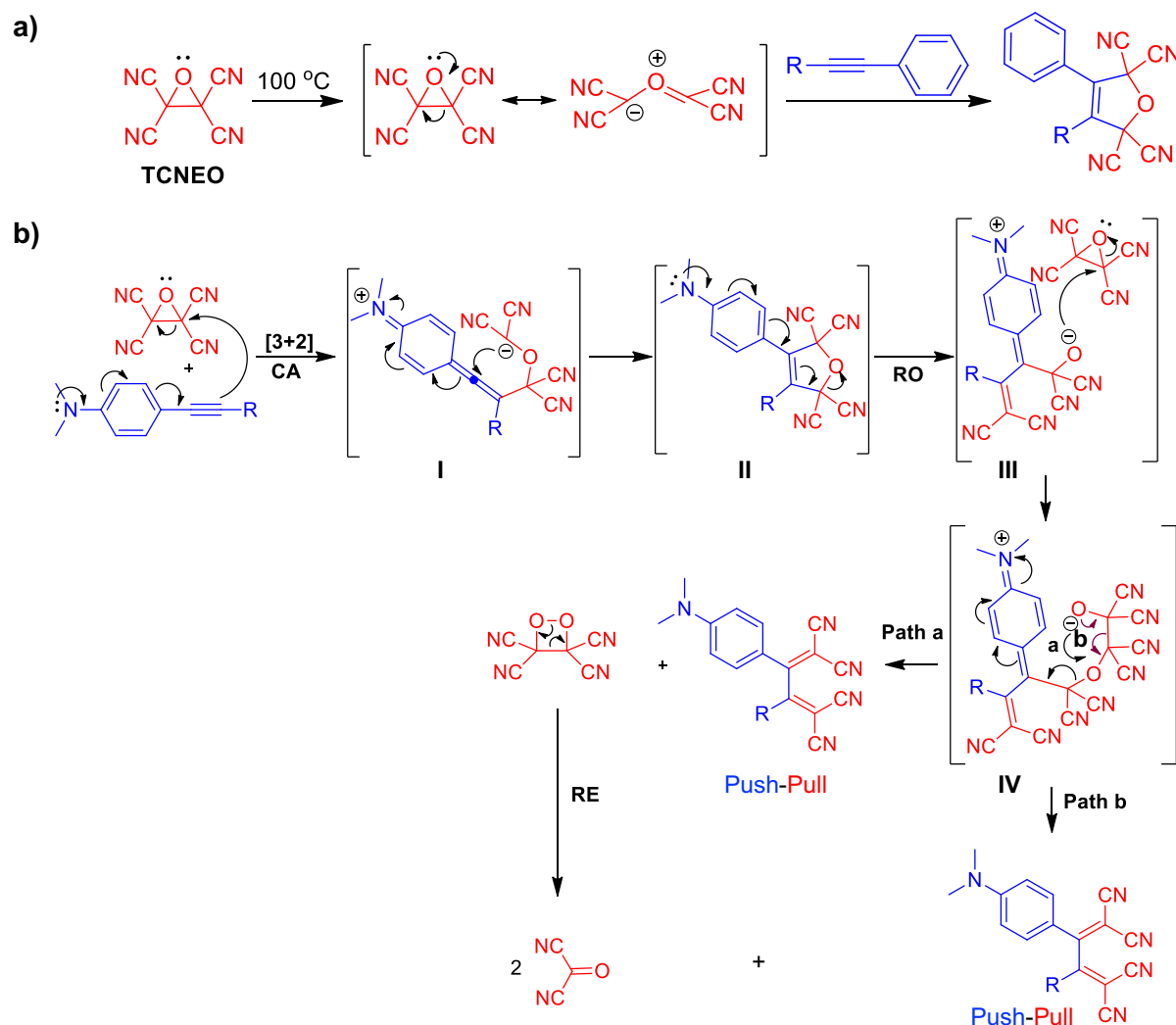


Figure 3. a) Temperature assisted-carbonyl ylide formation in EDG-free alkyne.²⁷ b) Proposed mechanism for [3+2] CA–RO reaction for EDG-alkyne.

In conclusion, we demonstrated for the first time that EDG-substituted TCBDs can be synthesized from an unconventional method using TCNEO as the precursor instead of TCNE *via* [3+2] CA–RO reaction. Though mono-substituted alkynes gave very poor yield due to overreaction, di-substituted EDG-alkynes underwent smooth conversion under simpler conditions. Overall, the procedure is much simpler, greener, additive-free, and gives access to useful TCBDs in just a single step with excellent yields for di-substituted alkynes. The presence of EDG in the alkyne is the key to the successful synthesis of TCBDs which facilitated the RO reaction following the first step [3+2] CA reaction. A mechanism is proposed for the deoxygenation from the tetracyanodihydrofuran derivative is driven by the nucleophilic

addition of another molecule of TCNEO leading to the formation of 3,3,4,4-tetracyano-1,2-dioxetane that may decompose to carbonyl cyanide. FT-IR and LC-MS studies do indicate the formation of this key product. Though some shortcomings exist with the present methodology to synthesis TCBDs, such as mono-substituted alkynes does not yield clean product and not being atom-economical, but offers advantages like an alternative way to make TCBDs, disubstituted alkyne give chromophores with excellent yield, generally works with a very milder condition which means can be useful for those reactions requires harsher conditions under [2+2] CA-RE reaction, and lastly opens up a new window to explore different reactivity products to expand the chemical space for push-pull chromophores.

Experimental section

General procedure. A solution of TCNEO (0.14 mmol) in an appropriate anhydrous degassed solvent (10 mL) was either cooled to 0 °C or at 25 °C, treated dropwise EDG-alkyne **3** or **5** (0.07 mmol), in a degassed appropriate solvent (10 mL) stirred at the same temperature for completion of reaction time upon monitoring the reaction by TLC (SiO₂). The solution color changes occur approximately after 3 h. After evaporation of the solvent, CH₂Cl₂ and water were mixed and extracted with CH₂Cl₂ (3× 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The crude product was columned using silica (hexane/CH₂Cl₂ 7:3) and recrystallized by slow diffusion of hexane into CH₂Cl₂ solution to afford the pure product.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgments

This work was supported by SERB, Department of Science and Technology (DST), grant nos. ECR/2016/000441 and SB/S2/RJN-047/2015. G.J. thanks DST-SERB for Ramanujan Fellowship. The authors thank Kamlesh Satpute and Dr. Nagaraja C. Mallaiah for access to the X-ray facility at IIT-Ropar for the single crystal data collection and refinement and Panjab University (SAIF facility) for NMR data.

Supporting Information

Supporting Information is available.

Notes

The authors declare no competing financial interest

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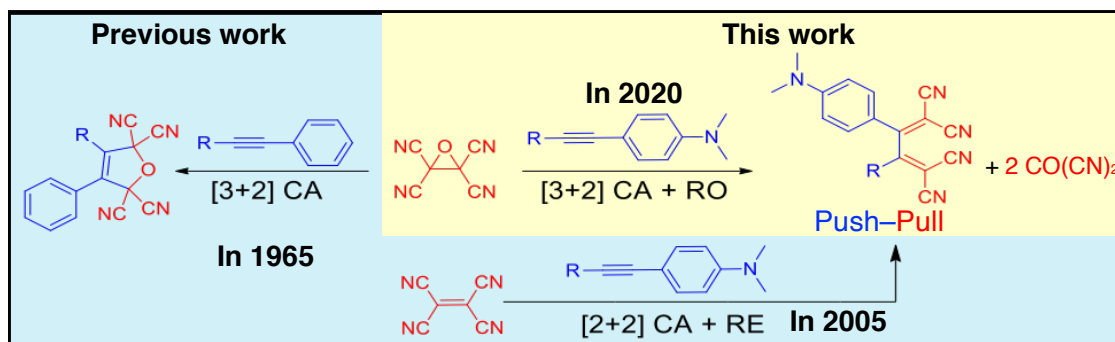
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New access to the synthesis of 1,1,4,4-tetracyanobuta-1,3-diene-based push–pull chromophores using tetracyanoethylene oxide via [3+2] cycloaddition-ring opening reactions

Table of Contents (TOC):



Unlike the [3+2] cycloadduct of the electron-donating group (EDG)-free alkynes with tetracyanoethylene oxide (TCNEO), the EDG induced [3+2] cycloadduct underwent facile ring-opening reaction to provide the very useful non-planar 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs) push-pull chromophores. This is the first report that provides access to TCBDs other than the [2+2] CA–RE reaction with TCNE.

Supporting Information

New access to the synthesis of 1,1,4,4-tetracyanobuta-1,3-diene-based push–pull chromophores using tetracyanoethylene oxide via [3+2] cycloaddition-ring opening reactions

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Section	Table of Contents	Page
A.	General Methods and Materials	S2
B.	Monitoring of some reaction of alkynes with TCNEO by TLC and LC	S3
C.	Synthetic Procedures and Characterization of the Products	S6
D.	¹H NMR spectra of TCBDs 4 and 6	S7
E.	X-ray Data for Compound 6	S8
F.	LC-MS and FT-IR studies of the crude reaction mixture	S11
G.	References	S12

Experimental Section

A. General Methods and Materials.

All reagents and solvents were obtained from commercial suppliers (Aldrich and TCI-India) and used without further purification. CH₃CN, CH₂Cl₂ was freshly distilled from CaH₂ under the nitrogen (N₂) atmosphere. Column chromatography (CC) was carried out with neutral silica gel. Thin-layer chromatography (TLC) was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (MachereyNagel, Germany) using appropriate solvents and visualized with UV light ($\lambda = 254$ nm). Melting points (M.p.) were measured in open capillaries with a Stuart (automatic melting point SMP50) apparatus and are uncorrected. “Decomp” refers to decomposition. ¹H NMR spectra were measured on Bruker Avance II 400 MHz instrument at 25 °C in CDCl₃ or DMSO-*d*₆. Residual solvent signals in the ¹H NMR spectra were used as an internal reference. Chemical shifts (δ) are reported in ppm downfield from SiMe₄, with the residual solvent signal. Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), t (triplet), and m (multiplet). Transmission Spectra were measured using ATR-FT-IR Bruker Vertex 70; signal designations; s (strong), m (medium), and w (weak). Single-crystal X-ray diffraction data were collected using a Rigaku XtaLABmini Xray diffractometer equipped with a Mercury charge-coupled device detector with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) at 100.0 (2) K using ω scans. The data were reduced using CrysAlisPro 1.171.38.46, and the space group determination was done using Olex2.37 The crystal structures were solved by using ShelXT38 and were refined using ShelXL39 through Olex2 suite. All of the hydrogen atoms were geometrically fixed and refined using the riding model. Absorption correction was done by a multiscan method. All of the packing and interaction diagrams have been generated using Mercury. Liquid chromatography (LC) was performed on a Waters ACQUITY UPLC M-Class LC instrument using a Zorbax Eclipse Plus C18 column (250 \times 4.6 mm; 5 μ m pore size) from Agilent.

B Monitoring of reaction of alkynes with TCNEO by TLC and LC

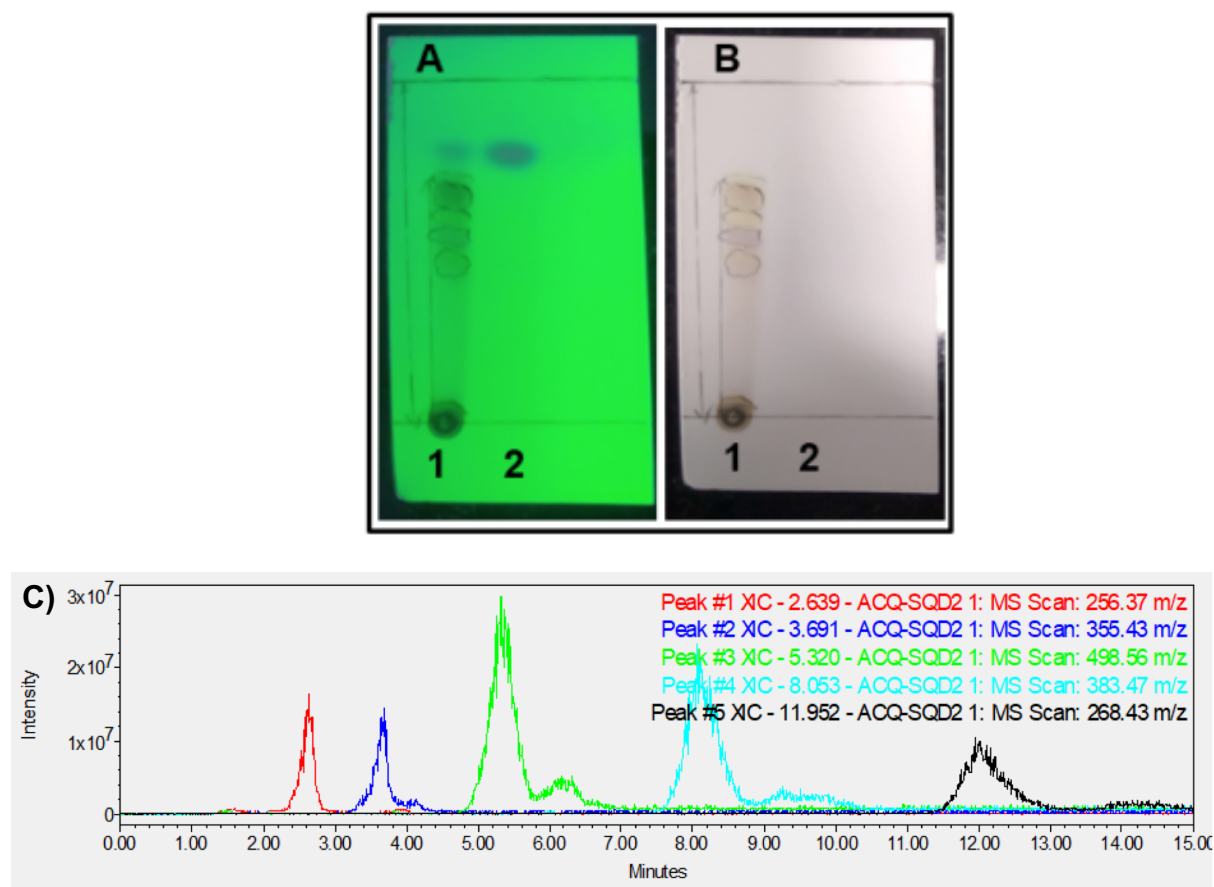


Figure S1. TLC of 4-ethynyl-*N,N'*-dimethylaniline **1** with one equivalent (equiv) of TCNEO in CH_2Cl_2 (TLC eluent: EtOAc/hexane 25:75) visualized in the A) presence and B) absence of UV light (280 nm). Spot 1 indicates the reaction mixture and spot 2 is starting material **1**. Note: some spots are visible with the naked eye than in the photo due to less intensity. C) LC-MS profile for entry 1 in Table 1 (main manuscript).

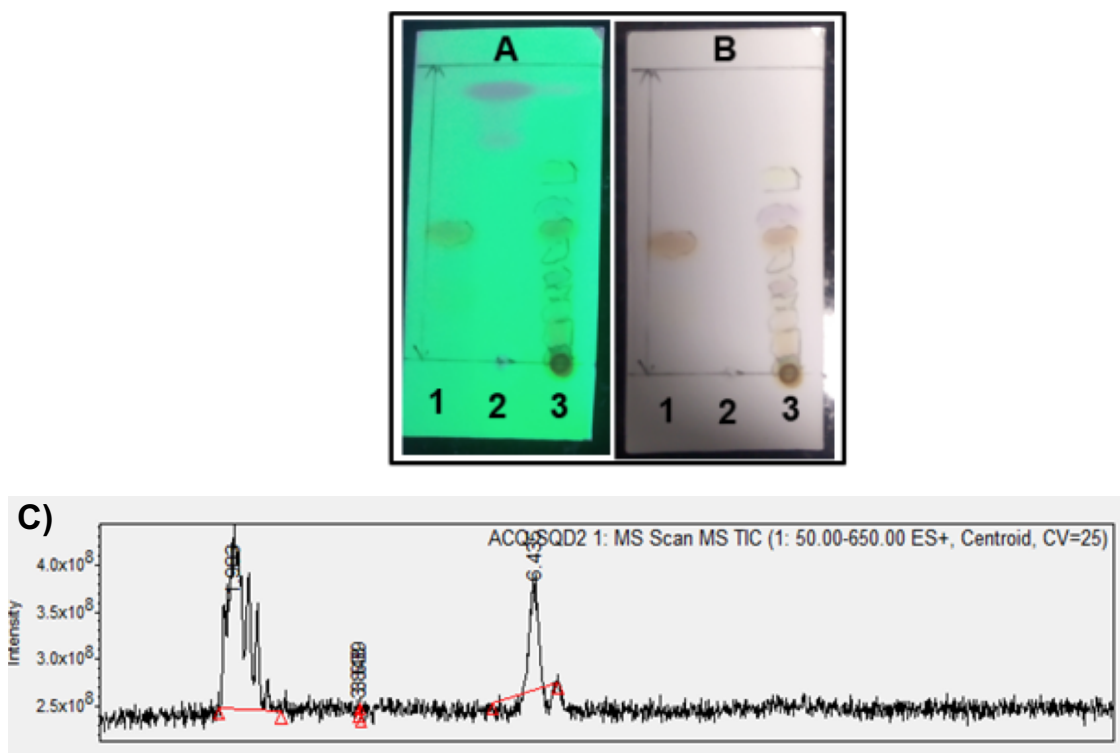


Figure S2. TLC of 4-ethynyl-*N,N'*-dimethylaniline **1** with 1 equiv of TCNEO in CH_3CN (TLC eluent: EtOAc/hexane 25:75) visualized in the A) presence and B) absence of UV light (280 nm). Spot 1 indicates the authentic compound **2**, spot 2 corresponds to the starting material **1**, and spot 3 is the reaction mixture. C) LC-MS profile for entry 2 in Table 1 (main manuscript).

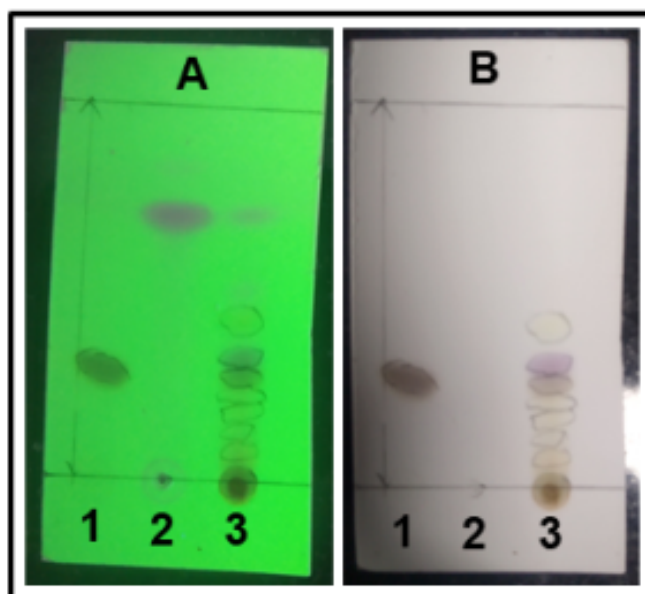


Figure S3. TLC of 4-ethynyl-*N,N'*-dimethylaniline **1** with 2 equiv of TCNEO in CH_2Cl_2 at 25 °C (TLC eluent: EtOAc/hexane 20:80) visualized in the A) presence and B) absence of UV

light (280 nm). Spot 1 indicates the authentic compound **2**, spot 2 corresponds to the starting material **1**, and spot 3 is the reaction mixture for entry 4 in Table 1 (main manuscript).

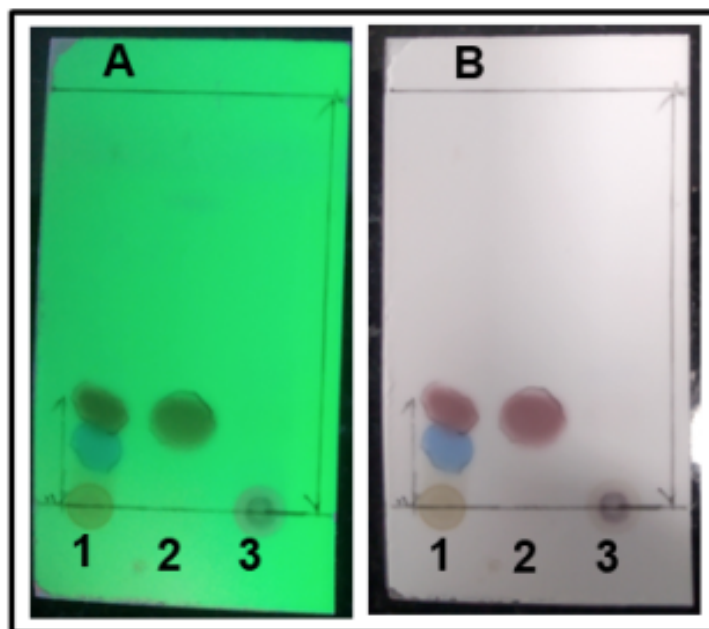


Figure S4. TLC of chromophore **6** with 1 equiv of TCNEO in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 110 °C, 24 h (TLC eluent: EtOAc/hexane 15:85) visualized in the A) presence and B) absence of UV light (280 nm). Spot 1 is reaction mixture, spot 2 correspond to the starting material **6**, spot 3 correspond to the authentic compound octacyano[4]dendralene *i.e.*, 3,4-Bis(dicyanomethylidene)-2,5-bis[4-(dimethylamino)phenyl]hexa-1,5-diene-1,1,6,6-tetracarbonitrile synthesized as per literature.²

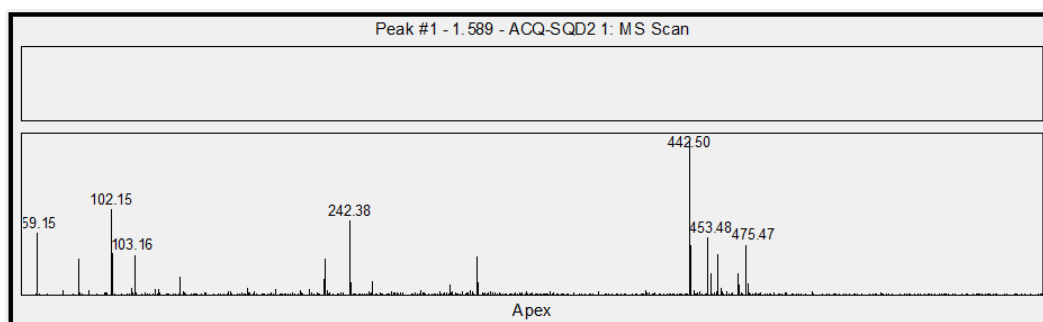
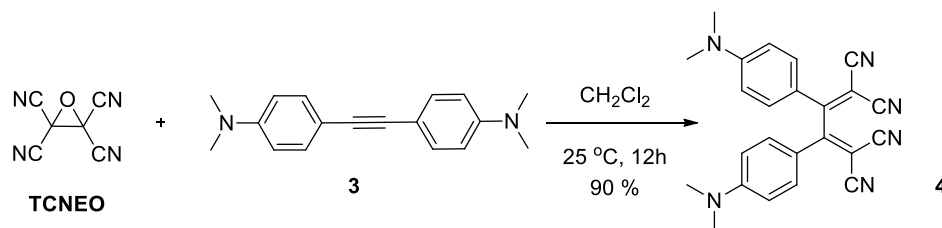


Figure S5. LC–MS profile of the above reaction (Figure S4) indicating the newly formed blue spot does not correspond to the octacyano[4]dendralene *i.e.*, 3,4-Bis(dicyanomethylidene)-2,5-bis[4-(dimethylamino)phenyl]hexa-1,5-diene-1,1,6,6-tetracarbonitrile whose calculated mass is $\{\text{C}_{32}\text{N}_{20}\text{N}_{10}\}$: 544.18.

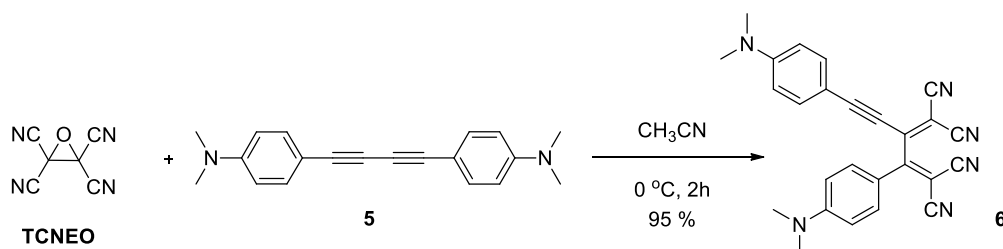
C. Synthetic Procedures and Characterization of the Products

C1. Synthesis and characterization of push-pull chromophore **4**¹ using TCNEO



A solution of TCNEO (20 mg, 0.14 mmol) in anhydrous degassed CH_2Cl_2 (10 mL) was treated dropwise 4,4'-(ethyne-1,2-diyl)bis(*N,N'*-dimethylaniline) **3** (18 mg, 0.07 mmol) at 25 °C, in degassed CH_2Cl_2 solvent (10 mL) stirred at the same temperature for 12 h. The solution color changes occur approximately after 3 h. To the reaction mixture saturated NaCl solution was poured and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The crude product was columned using silica (hexane/ CH_2Cl_2 7:3) and recrystallized by slow diffusion of hexane into CH_2Cl_2 to afford the pure product **4**¹ (49 mg, 90 % yield). R_f = 0.3 (SiO_2 ; hexane/ CH_2Cl_2 7:3) Reddish metallic solid, M. P. 274–275 °C (decomp.);^{1a} $^1\text{H-NMR}$ (400 MHz; 298 K, CDCl_3) δ = 3.14 (s, 12 H), 6.70 (d, J = 9.0 Hz, 4 H), 7.79 ppm (d, J = 9.0 Hz, 4 H).

C2. Synthesis and characterization of push-pull Chromophore **6**¹ using TCNEO



A solution of TCNEO (20 mg, 0.14 mmol) in anhydrous degassed CH_3CN (10 mL) was cooled at 0 °C, treated dropwise 4,4'-(buta-1,3-diynyl)bis(*N,N'*-dimethylaniline) **5** (20 mg, 0.07 mmol), in degassed CH_3CN (10 mL) stirred at the same temperature for 2 h. After completion of the reaction, acetonitrile was vacuum evaporated. The residue was dissolved in CH_2Cl_2 and mixed with water and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The crude product was columned using silica (hexane/ CH_2Cl_2 7:3) and recrystallized by slow diffusion of hexane into CH_2Cl_2 to afford the pure product **6**¹ (55 mg, 95 % yield). R_f = 0.3 (SiO_2 ; hexane/ CH_2Cl_2 8:2) Black coloured solid, M. P. 190–193 °C (decomp.);^{1a} $^1\text{H-NMR}$ (400 MHz,

298 K; CDCl₃) δ = 3.14 (s, 6 H), 3.04 (s, 6 H), 6.62 (d, J = 8.0 Hz, 2 H), 6.70 (d, J = 8.0 Hz, 2 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.78 ppm (d, J = 8.0 Hz, 2 H).

D. ¹H-NMR spectra of TCBDs **4** and **6**

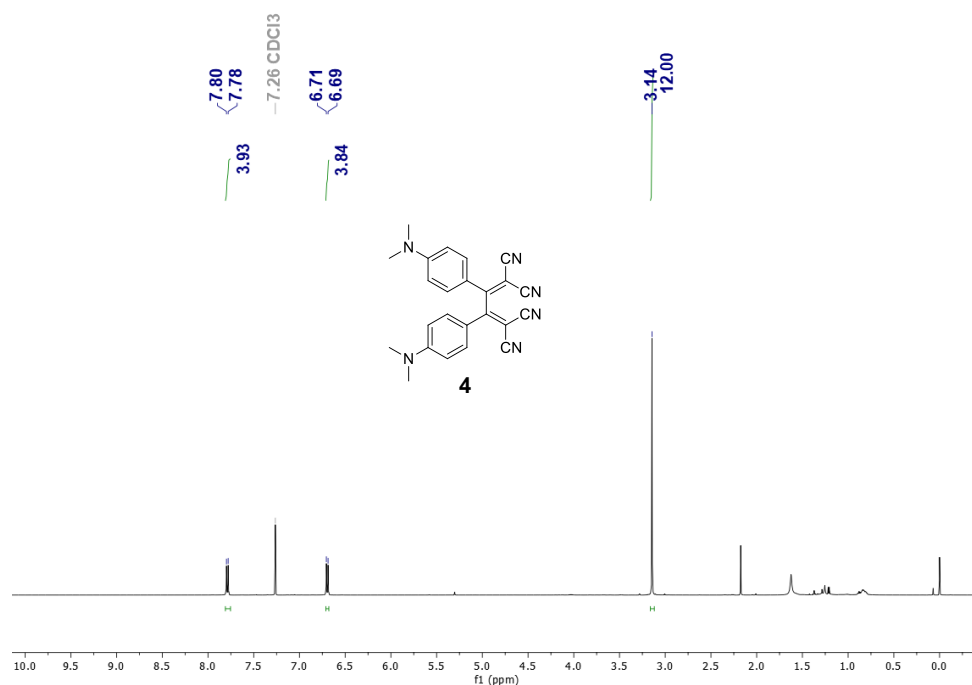


Figure S6. 400 MHz ¹H NMR spectrum of **4** recorded at 298 K in CDCl₃.

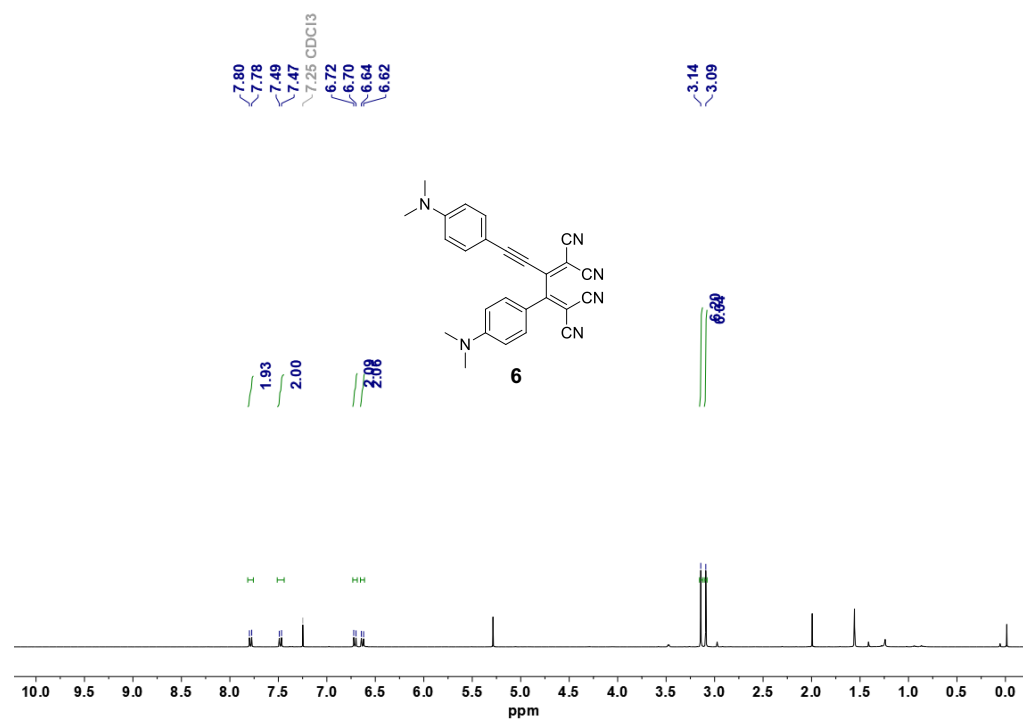


Figure S7. 400 MHz ¹H NMR spectrum of **6** recorded at 298 K in CDCl₃.

E. X-ray Data for Compound 6

The crystal structure obtained in the previous study using TCNE is called here as **polymorph I^{1a}** and in this study using TCNEO is called **polymorph II**.

Table S1. Crystal structure data and experimental details of **polymorph-I^{1a}** and **-II** of **6**.

	Polymorph I	Polymorph II
<i>Crystal data</i>		
CCDC deposition number	256338	2009612
Chemical formula	C ₂₆ H ₂₀ N ₆ •2(CH ₂ Cl ₂)	C ₂₆ H ₂₀ N ₆
<i>M_r</i> (g mol ⁻¹)	586.33	416.48
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$ (no.2)	Monoclinic, <i>P</i> 2 ₁ /c (no.14)
Temperature (K)	263	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3661(1), 9.5653(2), 20.8690(4)	17.2509(19), 17.0756(17), 8.2275(9)
β (°)	95.014(7)	94.912(4)
<i>V</i> (Å ³)	1462.03(5)	2414.7(4)
<i>Z</i>	2	4
Radiation type	Mo K α	Mo K α
μ (mm ⁻¹)		0.071
Crystal size (mm)		0.10 x 0.31 x 0.34
<i>Data collection</i>		
Diffractometer	Bruker-Nonius Kappa-CCD	Bruker D8 Venture PHOTON 100
Absorption correction		Multi-scan
<i>T_{min}</i> , <i>T_{max}</i>		0.592, 0.745
Number of measured, Independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	11122, 6573, and 5258	24495, 4907 and 3253
<i>R_{int}</i>	0.03	0.0568
<i>R_{sigma}</i>		0.0569
(sin θ/λ) _{max} (Å ⁻¹)	0.7107	0.71073
<i>Refinement</i>		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>		0.0963 (3253), 0.2434 (4907), 1.03
Number of reflections	2223	4907
Number of parameters	348	289

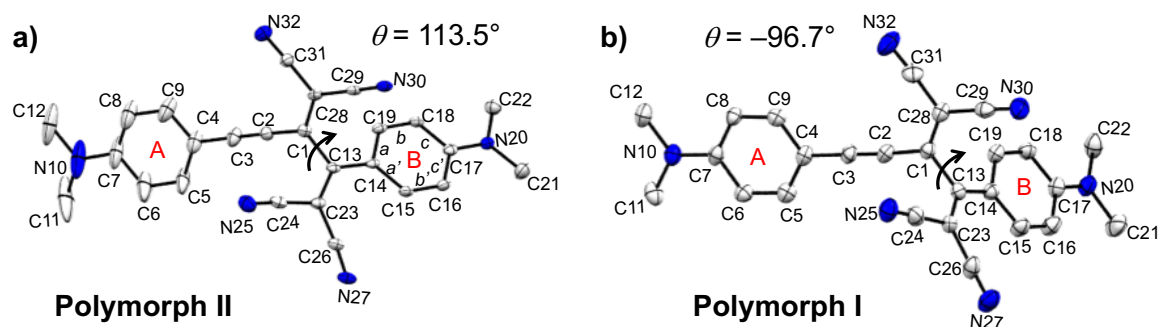


Figure S8. a) ORTEP plot of **6 polymorph II** (arbitrary numbering, H-atoms are omitted for clarity). Atomic displacement parameters are drawn at a 25% probability level. Selected bond lengths [\AA], angles [$^\circ$], and torsional angles [$^\circ$]: C1–C2 1.386(12), C1–C13 1.503(11), C2–C3 1.2092(11), C3–C4 1.434(12), C4–C5 1.383(12), C4–C9 1.3742(12), C5–C6 1.372(11), C6–C7 1.424(11), C7–N10 1.362(10), C7–C8 1.386(11), C8–C9 1.3883(10), C13–C14 1.433(10), C14–C15 1.408(11), C14–C19 1.407(10), C15–C16 1.367(11), C16–C17 1.427(11), C17–N20 1.342(10), C17–C18 1.404(11), C18–C19 1.363(10), C28–C1–C13 120.30(7), C3–C2–C1 177.73(8), C2–C3–C4 178.20(8), C23–C13–C1 114.337(6), C24–C23–C26 111.528(7), C31–C28–C29 116.61(8), C14–C13–C1–C28: -67.26 (8), C15–C14–C13–C23: -15.15 (8), C28–C1–C13–C23: 113.48(8), C31–C28–C1–C2: 2.47(8). b) ORTEP plot of **6•2CH₂Cl₂ polymorph I^{la}** (arbitrary numbering, H-atoms are omitted for clarity). Atomic displacement parameters are drawn at a 25% probability level. Selected bond lengths [\AA], angles [$^\circ$], and torsional angles [$^\circ$]: C1–C2 1.396(12), C1–C13 1.514(11), C2–C3 1.178(11), C3–C4 1.431(12), C4–C5 1.392(12), C4–C9 1.416(12), C5–C6 1.358(11), C6–C7 1.409(11), C7–N10 1.371(10), C7–C8 1.422(11), C8–C9 1.349(10), C13–C14 1.431(10), C14–C15 1.394(11), C14–C19 1.407(10), C15–C16 1.347(11), C16–C17 1.401(11), C17–N20 1.335(10), C17–C18 1.395(11), C18–C19 1.364(10), C28–C1–C13 120.5(7), C3–C2–C1 175.2(8), C2–C3–C4 178.8(8), C23–C13–C1 113.3(6), C24–C23–C26 114.0(7), C31–C28–C29 116.6(8), C15–C14–C13–C23: -4.35 (8), C28–C1–C13–C23: -96.64 (8), C31–C28–C1–C2: 2.53(8).

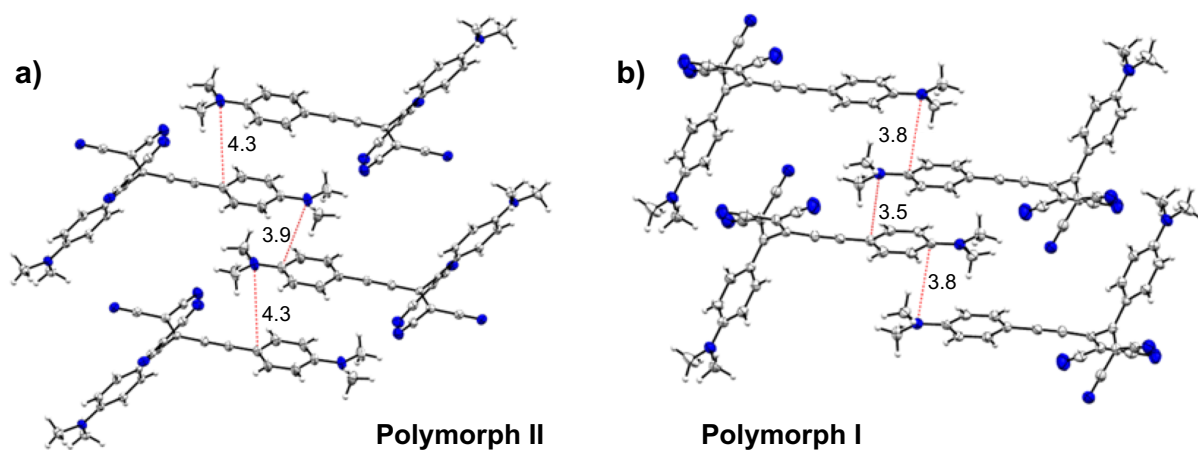


Figure S9. Arrangement of neighboring molecules in the crystal packing of a) **6** in **polymorph II**, b) **6•2CH₂Cl₂^{1a}** in **polymorph I**.

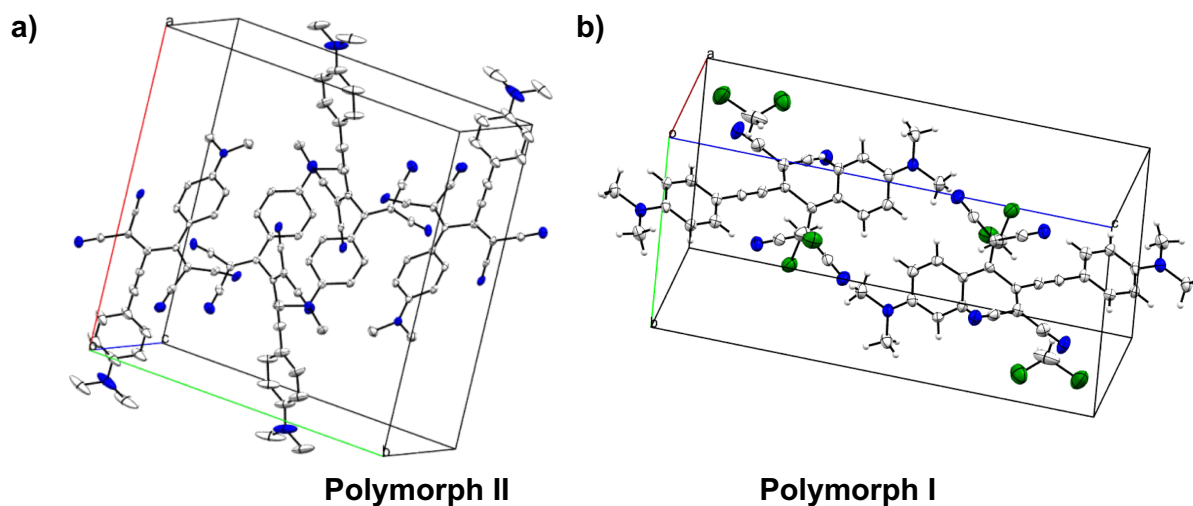


Figure S10. Unit cell lattice showing the number of molecules of a) **6** in **polymorph II**, b) **6•2CH₂Cl₂^{1a}** in **polymorph I**.

F. LC-MS and FT-IR studies of the crude reaction mixture

F1. FT-IR Data:

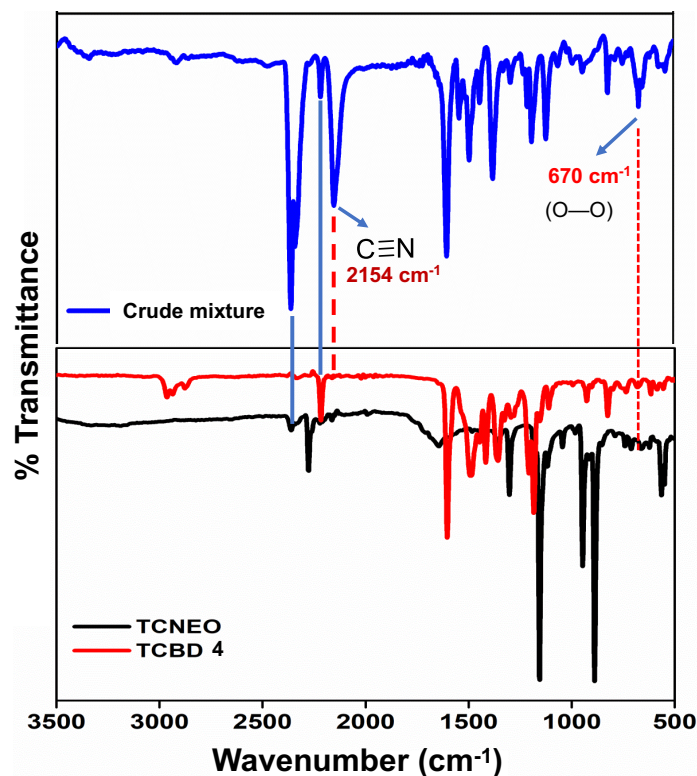


Figure S11. FT-IR (ATR) spectra of the crude reaction mixture, TCNEO, and TCBD 4.

F2. LC-MS Data:

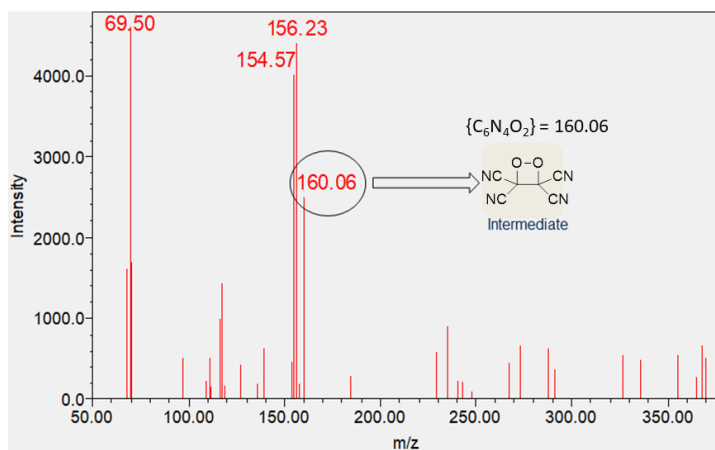


Figure S12. LC-MS spectrum of the crude reaction mixture for the **3** and TCNEO (MS-ESI) m/z Calcd for {C₆N₄O₂}: 160.00, found 160.06.

Liquid chromatography-mass spectrometry (LC-MS): The analysis of reactive intermediates is carried out by using a reverse-phase HPLC system from waters equipped with a photodiode array detector (Waters 2998) (Figure S12).

G. References

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