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Letter

1,1,4,4-Tetracyanobutadiene-Functionalized Anthracenes: Regioselectivity of Cycloadditions in the Synthesis of Small Near-IR Dyes

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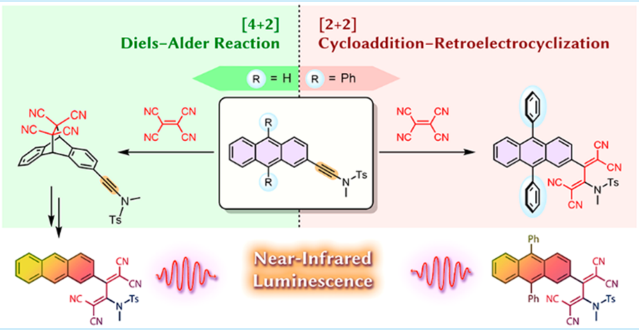
ABSTRACT: Two small 1,1,4,4-tetracyanobutadiene-functionalized chromophores were obtained by careful leverage of the regioselectivity of the cycloaddition reaction of tetracyanoethylene with anthracene−ynamide derivatives, inducing either a [2 + 2] or a [4 + 2] Diels−Alder process. DFT calculations unraveled the mechanism of the [2 + 2] cycloaddition−retroelectrocyclization reaction sequence with ynamides and elucidated the differing mechanisms in the two substrates. The synthesized dyes presented panchromatic absorption extending into the near-IR and far-red/near-IR photoluminescence in the solid state up to 1550 nm.



Push−pull chromophores, consisting of electron donor and acceptor groups bridged together by a π-conjugated backbone, are a class of molecules that play a prominent role in organic molecular materials.[1] Thanks to their particular arrangement that facilitates intramolecular charge transfer (ICT) interactions, they feature in scores of applications including nonlinear optics (NLO)[2] and organic photovoltaics (OPVs).[3] This persistently intriguing topic has stimulated the exploration of 1,1,4,4-tetracyanobutadiene (TCBD) derivatives and their chemistry by several groups in the past decade.[4−12] The elegance of their approach stems from the simplicity of its synthetic route: the TCBD motif can indeed be installed via a facile, high-yield, catalyst-free [2 + 2] cycloaddition-retroelectrocyclization (CARE) sequence, using tetracyanoethylene (TCNE) and an electron-rich alkyne,[10] thus allowing for practical synthetic strategies such as postpolymerization functionalizations.[13] TCBD is now established as a valuable strong electron acceptor group, with a rapidly expanding family of dyes including this motif. Beyond its straightforward incorporation in push−pull chromophores, other advantages of TCBD were put forward: its twisted conformation was shown to increase chromophore solubility and reduce aggregation, thereby improving the poling process efficiency in NLO materials.[14] Despite a number of studies that have promisingly demonstrated photoinduced charge separation in TCBD-appended chromophores, fast nonradiative deactivation of the excited state in these molecules constitutes a major drawback to their implementation in optoelectronic applications. As suggested by Armaroli et al., in anilino-TCBDs, torsional motions following photoexcitation give rise to a low-energy twisted intramolecular charge transfer (TICT) state that can deactivate to the ground state through accessible conical intersections.[15] As a direct consequence, these molecules are generally nonluminescent and fluorescence that involves a TCBD moiety has seldom been reported.[16]

In an effort to modify the prototypical anilino-TCBD fragment, our group discovered that ynamides can engage in the [2 + 2]-CARE reaction with TCNE to form a sulfonamido-TCBD motif, producing dyes with markedly altered optoelectronic properties.[17−19] We recently revealed that such chromophores could exhibit near-infrared (NIR) luminescence in the solid state, extending to 1350 nm.[20] This surprising result prompted us to further investigate compounds based on a similar design, i.e. sulfonamido-TCBD-PAH (polycyclic aromatic hydrocarbon). Interestingly, others have also described solid-state fluorescence involving an ICT to TCBD in push−pull chromophores bearing a PAH.[21]

While examining the structures of photoactive multicomponent systems that integrate TCBD units, one can

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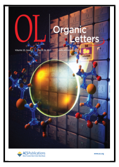
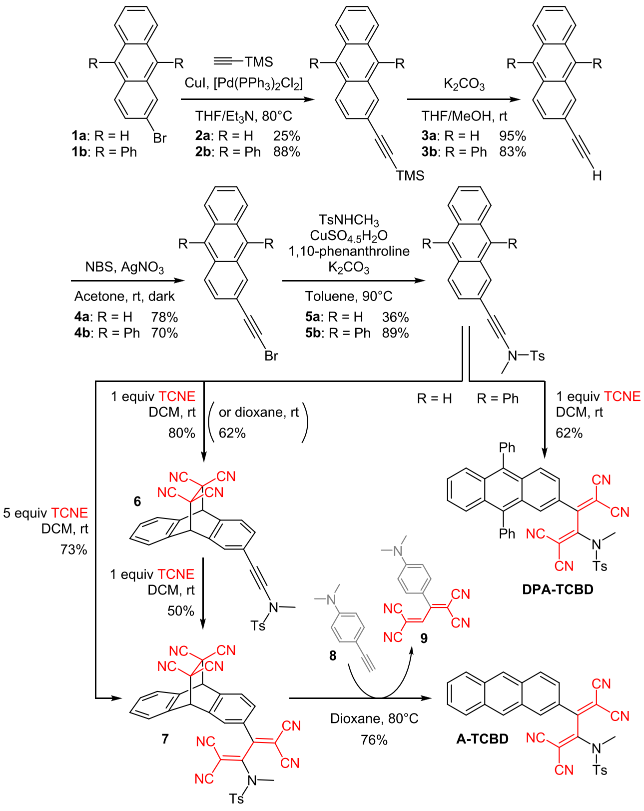


remark that anthracene is a strikingly rare building block, with only two examples (to the best of our knowledge) bearing a TCBD motif attached to strong electron-donating groups and remote from the anthracene moiety.[22,23] A possible explanation is the presence of a competing Diels−Alder (DA) reaction which makes this PAH seemingly incompatible with the [2 + 2]-CARE sequence—a pitfall that was also encountered with other acenes.[24] Herein we report a synthetic strategy to overcome this limitation, a complete mechanistic picture by density functional theory (DFT) calculations, and the optical properties of the synthesized molecules **A-TCBD** and **DPA-TCBD** (Scheme 1).

Scheme 1. Reaction Pathways for the Synthesis of A-TCBD and DPA-TCBD



We have previously identified the lack of reactivity of the triple bond when the ynamide is grafted to the 9-position of anthracene,[18] which prompted us to investigate anthracenes functionalized in a different position. Brominated derivatives **1a** and **1b** were therefore selected as starting molecules to access 2-substituted anthracenes. Sonogashira cross-coupling with trimethylsilylacetylene and subsequent deprotection gave the precursor compounds **3a**[25] and **3b**. The terminal alkynes were brominated to afford compounds **4a** and **4b** in 78% and 70% yield, respectively. The latter underwent copper-catalyzed amidation using Hsung's conditions,[26] leading to ynamides **5a** in moderate yield (36%) and **5b** in very good yield (89%). Compounds **5a** and **5b** were then reacted with one equivalent of TCNE. While 9,10-diphenylanthracene derivative **5b** yielded **DPA-TCBD** (62%), compound **A-TCBD** was not isolated and the DA product **6** was obtained instead (80% yield).

The [4 + 2] cycloaddition of anthracene with TCNE has already been well documented by several groups.[27−29] The modulation of the equilibrium for addition of TCNE to anthracene by the solvent was discussed by Brown and Cookson and the dissociation was found to be favored in dioxane.[30] Furthermore, Sauer et al. demonstrated the recovery of the anthracene addend using a different anthracene derivative to trap TCNE.[31] In the light of these studies, we sought to harness the reversibility of the DA reaction by testing various methods for the recovery of the anthracene structure and formation of the TCBD group. When **5a** was heated at 80 °C in dioxane in the presence of 1 equiv of TCNE, even though the retro-DA reaction is expected to be feasible under these conditions, the ynamide degraded without significant conversion into **A-TCBD**. At room temperature, the same reaction led only to cycloadduct **6** in 62% yield. Under UV irradiation (365 nm) in toluene, compound **5a** did not provide the [4 + 4] photodimerization product and its degradation was exclusively observed, invalidating the preliminary protection of the 9,10-positions of the anthracene core by formation of a dimer as an alternate strategy. We endeavored to construct the TCBD motif from cycloadduct **6** instead. In the presence of a second equivalent of TCNE, compound **6** was successfully converted into bisadduct **7** in 50% isolated yield. Using 5 equiv of TCNE, **5a** could be directly transformed into **7** in a much higher yield (73%) than through the combined two-step procedure (40%). Both cycloaddition products **6** and **7** were moderately stable and decomposed in solution within a few hours. Different conditions for the extrusion of TCNE from the anthracene core were then assessed. When a 0.01 M solution of **7** in dioxane was heated at 80 °C, **A-TCBD** could be isolated in only 3% yield after 3 h. To inhibit the forward [4 + 2] cycloaddition, rather than another anthracene derivative and DA reaction, 1.5 equiv of commercially available 4-ethynyl-*N*,*N*-dimethylaniline **8** were used to scavenge extruded TCNE, considering the known efficiency[32] and irreversibility of the [2 + 2]-CARE reaction. Thus, when stirred for 3 h at 80 °C in the presence of **8**, a solution of **7** in dioxane provided compound **A-TCBD** in a satisfactory yield of 76%. The newly synthesized dyes **A-TCBD** and **DPA-TCBD** were characterized by ^{1}H and ^{13}C NMR spectroscopy, HRMS, and cyclic voltammetry (Supporting Information).

Density functional theory (DFT) calculations at COSMO-(DCM)-BLYP-D3(BJ)/TZ2P using ADF (see the Supporting Information for computational details) were carried out to pinpoint the origin of disparate regioselectivity of **5a** and **5b**. For the calculations, the tosyl group (Ts) of **5a** and **5b** was replaced with mesyl group (Ms) and the substrates are denoted as **5a′** and **5b′**. The energy profiles associated with the [2 + 2]-CARE and [4 + 2] DA sequences of **5a′** and **5b′** are provided in Figure 1 and are in line with others in the literature.[24] It can be seen that **5a′** preferentially reacts via the DA sequence, whereas **5b′** reacts via the [2 + 2]-CARE sequence. The origin of this observed regioselectivity is traced back to the steric bulk at the 9- and 10-position of the anthracene: the unsubstituted **5a′** can facilitate the DA reaction of TCNE at anthracene to afford **6′**, whereas the 9,10-diphenylanthracene **5b′** is too sterically demanding for the DA reaction and the [2 + 2]-CARE pathway becomes more energetically viable.

First, we focus on the reactivity of the unsubstituted anthracene **5a′**. The DA sequence of **5a′** (Figure 1a, go left) begins with the formation of a reactant complex **5a′-INT1*** that is more stable (from enhanced π−π stacking) than the corresponding complex **5a′-INT1** of the [2 + 2]-CARE

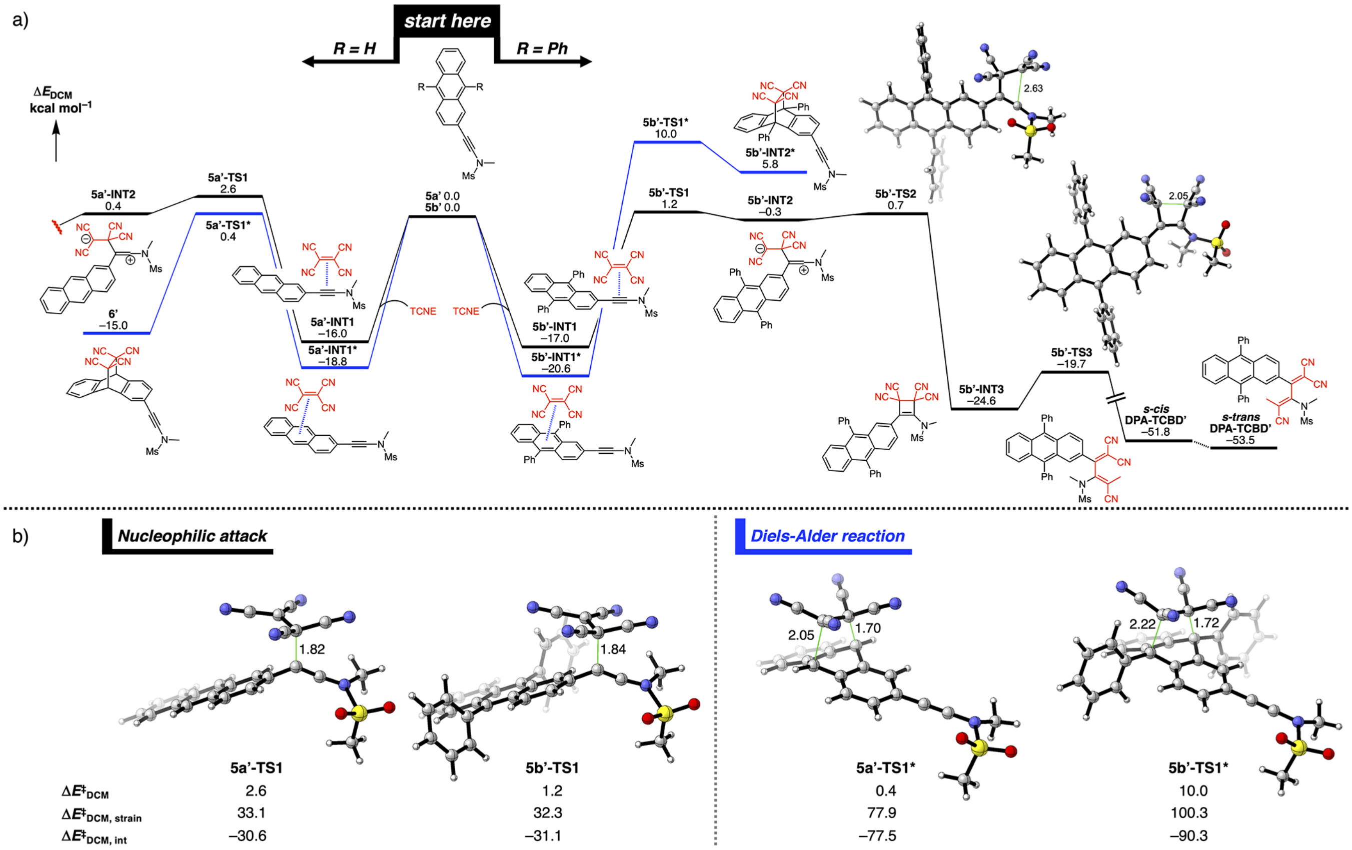


Figure 1. (a) Energy profiles (ΔE_{DCM} in kcal mol^{-1}) for the competing catalyst-free [2 + 2] cycloaddition-retroelectrocyclization (CARE, in black) and [4 + 2] Diels−Alder (DA) reactions (in blue) of **5a′** and **5b′** with TCNE; (b) key transition state geometries (in Å) and activation strain analysis ($\Delta E^{\ddagger}_{\mathrm{DCM}} = \Delta E^{\ddagger}_{\mathrm{DCM,\ strain}} + \Delta E^{\ddagger}_{\mathrm{DCM,\ int}}$, in kcal mol^{-1}). All data computed at COSMO(DCM)-BLYP-D3(BJ)/TZ2P.

pathway. From **5a′-INT1***, the DA reaction proceeds through a concerted asynchronous transition state **5a′-TS1*** ($\Delta E^{\ddagger}$ = 0.4 kcal mol^{-1}) to afford the experimentally isolated analog **6′**. The first step of the [2 + 2]-CARE sequence involves the nucleophilic attack of **5a′** at TCNE, which goes via an unfavorably high energy transition state **5a′-TS1** ($\Delta E^{\ddagger}$ = 2.6 kcal mol^{-1}) and formation of an unstable zwitterionic intermediate.

Now, we analyze the reactivity of the 9,10-diphenylanthracene derivative **5b′** (Figure 1a, go right). The reactant complex **5b′-INT1*** is a resting state on the energy surface and cannot proceed further due to an unsurmountable DA barrier via **5b′-TS1*** ($\Delta E^{\ddagger}$ = 10.0 kcal mol^{-1}) that goes with a highly destabilizing strain ($\Delta E^{\ddagger}_{\mathrm{strain}}$ = 100.3 kcal mol^{-1}) due to steric clash between **TCNE** and the phenyl groups at the 9- and 10-positions of the anthracene (Figure 1b). Instead, **5b′-INT1*** reversibly dissociates to the reactants and then can form the slightly less stable **5b′-INT1**, which undergoes the nucleophilic attack via **5b′-TS1*** to generate a metastable zwitterionic intermediate **5b′-INT2**. The facile rotation and subsequent cyclization via **5b′-TS2** accomplishes the stepwise [2 + 2] cycloaddition and generates the cycloadduct **5b′-INT3**. Retrocyclization via **5b′-TS3** provides the ***s-cis*DPA-TCBD′** which can then isomerize to complete the CARE sequence and furnish ***s-trans*DPA-TCBD′**.

The UV−vis absorption spectra of **A-TCBD** and **DPA-TCBD** were recorded in dichloromethane (Figure 2A). Compared to their ynamide precursors, the clear and characteristic finger-like structured absorption bands of anthracene that were observed between 335 and 400 nm in **5a** and **5b** are now indistinct. New features arose in both TCBD derivatives, causing their absorption spectra to span the whole visible range. Most remarkably, a very broad and structureless low-energy absorption band, attributed to an ICT transition resulting from interactions between the PAH moiety and TCBD, covers the visible region between 450 and 800 nm, with a maximum located at 527 nm ($\varepsilon = 3.5 \times 10^{3}$ M^{-1} cm^{-1}) for **A-TCBD** and at 557 nm ($\varepsilon = 4.3 \times 10^{3}$ M^{-1} cm^{-1}) for **DPA-TCBD**. Comparison with published data on pyrene and perylene derivatives decorated with a TCBD unit[20] reveals a pronounced bathochromic effect as well as a slight hyperchromic effect associated with the increase in the PAH π-conjugation and/or resonance stabilization (Table S2).

Finally, the photoluminescence (PL) properties of **A-TCBD** and **DPA-TCBD** were examined. As reported with analogous dyes,[20] no emission was detected in dichloromethane, but in rigid media, both compounds displayed a very comparable and broad PL band (Figure 2B). In diluted rigid matrices (2-methyltetrahydrofuran at 77 K and PMMA at room temperature, Table S3), where the intermolecular interactions[33] are minimized, this band lied between the red and the first near-infrared window (NIR-I, 700−950 nm). Powders of the products exhibited PL in the NIR-I region with a maximum centered at 865 and 875 nm for **A-TCBD** and **DPA-TCBD** respectively, and a remarkably long tail extending to 1550 nm in the second near-infrared window (NIR-II, 1000−1700 nm), even farther than the upper limit in pyrene and perylene derivatives (ca. 1350 nm). This PL enhancement in the solid-

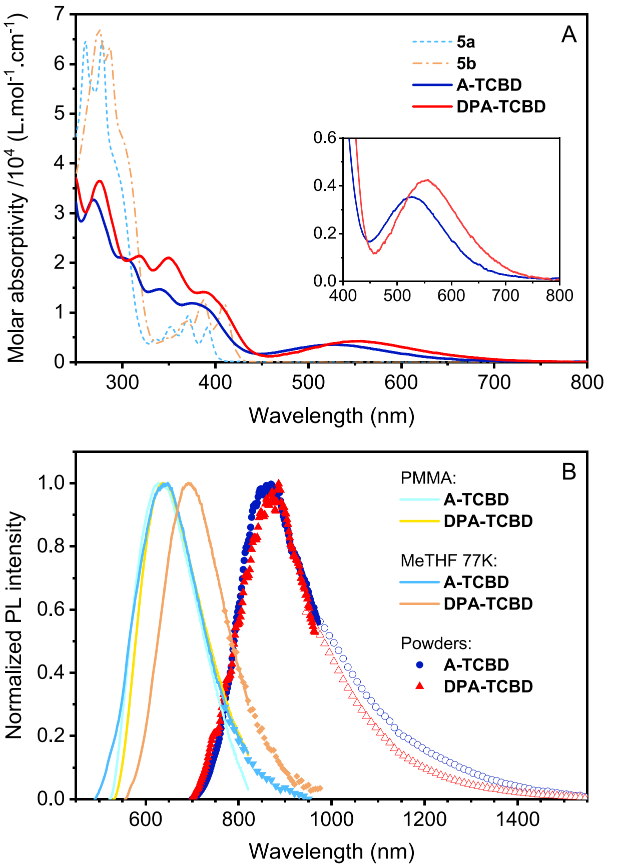


Figure 2. (A) UV−vis absorption spectra of ynamide precursors **5a** and **5b** and compounds **A-TCBD** and **DPA-TCBD** in dichloromethane. Inset: zoom on the low-energy band of **A-TCBD** and **DPA-TCBD**. (B) Normalized photoluminescence spectra of **A-TCBD** and **DPA-TCBD** in PMMA (λ_{exc} = 500 and 515 nm, respectively), organic glass (MeTHF at 77 K, λ_{exc} = 480 and 520 nm, respectively), and powders (λ_{exc} = 585 and 600 nm, respectively). The different detectors used are represented as follows. Continuous line: R928; filled symbols: R2658; open symbols: InGaAs.

state can be ascribed to the restriction of molecular motions following light absorption, which helps reduce the nonradiative losses in these environments.[21]

Besides the successful synthesis of two TCBD-appended anthracene derivatives **A-TCBD** and **DPA-TCBD**, our joined experimental and theoretical investigations showed that the regioselectivity of the cycloaddition reaction of TCNE with **5a** and **5b**, favoring either a [4 + 2] Diels−Alder process with the anthracene core in **5a** or a [2 + 2]-CARE reaction with the triple bond in **5b**, is dictated by steric effects at the 9,10-positions. DFT calculations uncovered the mechanism of the [2 + 2]-CARE sequence with ynamides for the first time, demonstrating that the reaction proceeds through stepwise [2 + 2] cyclization to produce a cyclobutene intermediate which then opens to give the TCBD moiety. When the DA reaction was preferential, it could advantageously be used to deactivate the 9,10-positions prior to the [2 + 2]-CARE, then its reversibility exploited to unmask the anthracene core thanks to a scavenger. In addition to insight into the reactivity of some π-systems with TCNE, we expect the synthetic method developed to obtain **A-TCBD** to be applicable to other acene-TCBD targets. Both **A-TCBD** and **DPA-TCBD** displayed optical properties that were remarkable for such small dyes. They presented panchromatic absorption in DCM that extends into the NIR-I region, and solid-state PL signals lying between the far-red and the NIR-II range. This latter feature, rare in TCBD-functionalized molecules, thus further substantiates that new molecular designs comprising this fragment can offer room for unusual photophysical properties.[34]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00136.

> General and synthetic procedures, characterization data, cyclic voltammograms, complementary UV−vis and photoluminescence data, excitation spectra, and full computational details (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This work is dedicated to the memory of François Diederich.

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