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Quadruple Functionalization of a Tetraphenylethylene Aromatic Scaffold with Ynamides or Tetracyanobutadienes: Synthesis and Optical Properties

Clotilde Philippe,[a] Maëva Coste,[b] Yann Bretonnière,[c] Loïc Lemiègre,[a] Sébastien Ulrich,*[b] and Yann Trolez*[a]

Ynamides are useful and versatile building blocks in organic synthesis, from which 1,1,4,4-tetracyanobutadienes (TCBD) can be prepared for application in molecular electronics. However, their insertion onto multi-functional molecular scaffold remains a synthetic challenge. In this work, we report the two-steps synthesis in good isolated yield (64% overall, 89% stepwise) of a tetraphenylethylene (TPE) bearing four ynamides, and its further one-step conversion into the tetra-TCBD derivative through a [2+2] cycloaddition-retroelectrocyclization sequence. The concomitant formation of the four ynamides required a specific optimisation of the reaction conditions. Although a poor fluorescent emitter in solution, the tetra-TCBD compound displayed near-infrared luminescence in the solid state, which is an attractive optoelectronic feature when considering future applications in molecular electronic devices.

Introduction

Ynamides have attracted considerable attention in the last two decades.[1–3] Since the seminal works of Danheiser[4] and Hsung[5] groups who described simple methods to access ynamides, numerous synthetics pathways have been developed.[6–9] The fascinating reactivity of ynamides[10–16] justifies the effort brought to the development of new synthetic methodologies and new scaffolds, broadening thus the scope of nowadays-accessible ynamides. In our group, we studied their reactivity with tetracyanoethylene (TCNE) to access new 1,1,4,4-tetracyanobutadienes (TCBDs) in good yields.[17,18] We are particularly interested in these TCBDs for their original optoelectronic properties,[19] and have thus been working on the conjugation of ynamides to π-systems,[20,21] which can pose a challenge when it comes to introducing two ynamide functions within the same molecule.[22] Even though the synthesis of ynamides is well documented, compounds bearing more than two ynamides (or ynamines) remain scarce.[23–26]

We recently synthesized a tris-ynamide (**1**) conjugated to a triphenylamine and reacted it with TCNE to access compound **2** bearing three TCBD units (Figure 1a).[27] In order to go a step further, we wish to challenge the incorporation of four TCBD units derived from ynamides onto a single aromatic compound. We selected a tetraphenylethylene (TPE) aromatic core as scaffold. TPE displays aggregation induced emission,[28,29] a phenomenon which has attracted great interest for various applications in material sciences, biosensing and

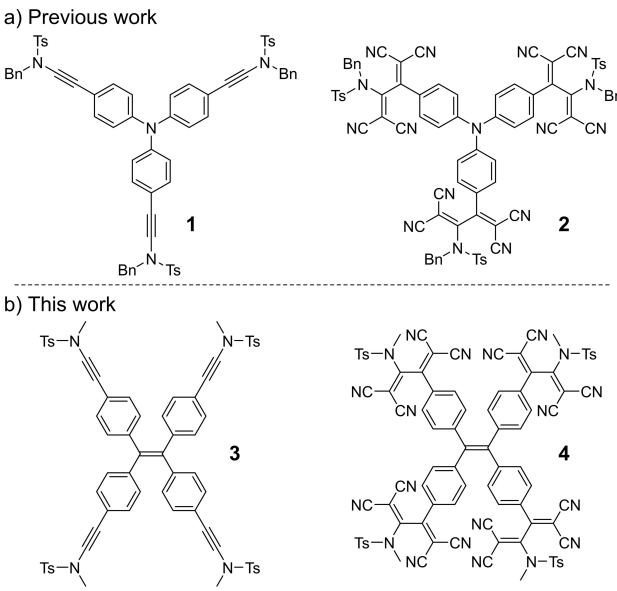

Figure 1. a) Previous work: structure of tris-ynamide **1** and its corresponding tris-TCBD **2**; b) this work: structure of tetra-ynamide **3** and its corresponding tetra-TCBD **4**.

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bioimaging.[30–33] In particular, extension of the conjugation with electron-deficient groups has revealed particular photophysical properties such as efficient singlet oxygen generation, making these compounds suited for use as photosynthesizers in photodynamic therapy.[34–36]

Herein, we report the successful synthesis of the tetra-ynamide TPE **3** and the tetra-TCBD TPE **4**, as well as the characterization of **4** by UV-visible and fluorescence spectroscopy, and describe the synthetic approach we implemented to optimize the reaction conditions previously used for the formation of compounds **1** and **2** to obtain the newly tetra-functionalized compounds **3** and **4**.

Results and Discussion

The reaction conditions described by the groups of Hsung[37] and Evano[38] are probably the most popular in the field, and certainly in our research group. The reasons for this are (i) the easy synthesis of the precursors, (ii) the simple reaction conditions and (iii) the broadness of the scope. These two methods are nevertheless very complementary and allowed us to synthesize most of our targeted ynamides.[17–22,27] For Hsung conditions, the precursor is a brominated alkyne that is usually easily synthesized using a mixture of N-bromosuccinimide and silver nitrate in acetone at room temperature. The main limitation of Hsung's method is probably the possible poor stability of brominated alkynes when connected to an electron-donating group, as we observed in the past.[22] This is the reason why we first considered the Evano's method, which

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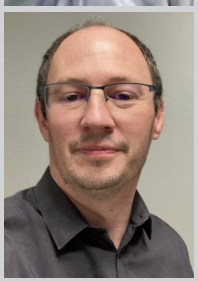
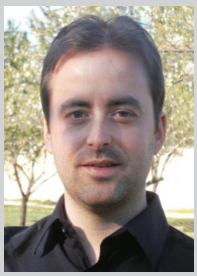
Maëva Coste carried out a Bachelor degree in organic chemistry and a Master degree in chemistry of biomolecules (2018) at the University of Montpellier, France. She carried out her PhD in biomolecular engineering at the Institut des Biomolécules Max Mousseron (IBMM), Université de Montpellier, under the supervision of Dr. Sébastien Ulrich. Her thesis projects focused on the design, synthesis and characterization of programmed and DNA-templated self-assemblies of aromatic conjugates. She has just joined the group of Prof. Rein Ulijn as a post-doctoral fellow at the CUNY Advanced Science Research Center, New York, USA.

After a PhD received in 2001 from the University of Grenoble and a post-doctorate at the University of Durham (UK) in the group of Prof. D. Parker, Yann Bretonnière joined Chantal Andraud's group at ENS Lyon as a CNRS Research Fellow in 2004. His research interests cover the areas of fluorescent molecular probes, luminescent organic materials and their applications.



Loïc Lemiègre obtained his PhD degree from the University of Rouen (2002) under the supervision of Dr. Jacques Maddaluno and Prof. Jean-Claude Combret. He then joined the group of Prof. Eiichi Nakamura (The University of Tokyo) as a JSPS postdoc working on fullerene chemistry (2002–2004) and he then moved to the group of Prof. Jonathan Clayden (The University of Manchester) working on molecular helices (2004–2005). He started his academic career in 2005 at the ENSC-Rennes where he is now associate professor. In addition to fluorescent molecules, he is mainly interested in the synthesis of amphiphilic molecules related to carbohydrates and their self-assemblies, and in bio-based polymers.



Sébastien Ulrich carried out his PhD with Prof. Jean-Marie Lehn (Université de Strasbourg, France), and post-docs with Prof. Harry L. Anderson (Oxford University, UK) and Prof. Eric T. Kool (Stanford University, CA, USA). In 2011, he was awarded an ANR starting grant and joined the group of Prof. Pascal Dumy in Grenoble, before moving in 2012 to Montpellier, France, where he was recruited by the CNRS to develop his research interests in the field of supramolecular bioorganic chemistry. Since then, he has contributed to developing dynamic self-assemblies for nucleic acid recognition and delivery applications. In 2017, he was awarded the CNRS Bronze Medal.

Yann Trolez obtained his PhD degree from the University of Strasbourg (2010) under the supervision of Dr. Jean-Paul Collin and Prof. Jean-Pierre Sauvage. His PhD work dealt with the synthesis of cyclic and linear multi-rotaxanes. He then joined the group of Prof. François Diederich (ETH Zurich) where he worked on alleno-acetylenic chemistry. In 2011, he was appointed Assistant Professor at the Ecole Nationale Supérieure de Chimie de Rennes (Univ Rennes) where he is now Associate Professor. His current research focuses on organic synthesis in various fields, from interstellar chemistry to materials chemistry, passing by supramolecular chemistry.

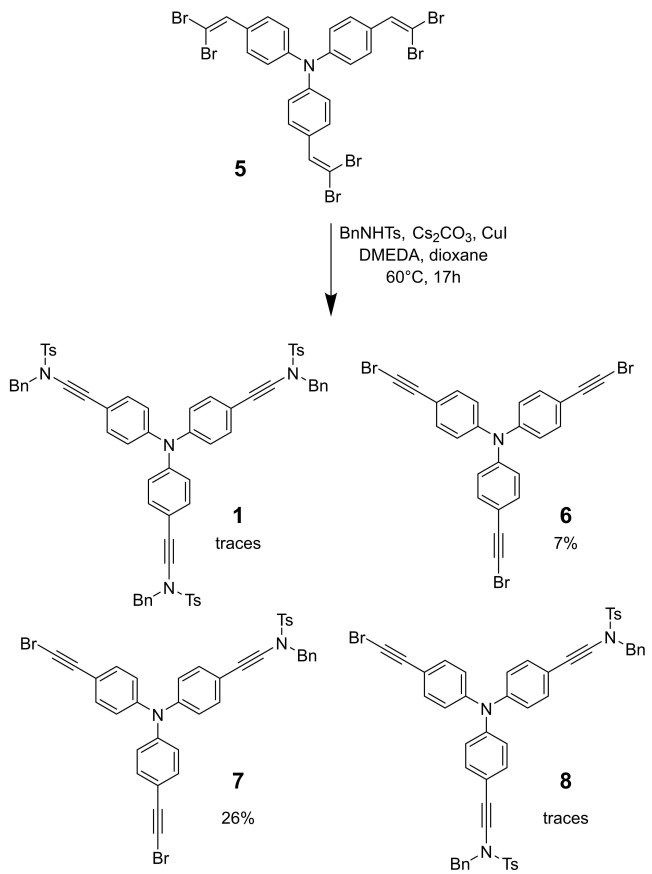
starts with *gem*-dibromovinylic substrates, to tackle the synthesis of compound **1**. Therefore, compound **5** was reacted with benzyltosylamide, copper iodide, cesium carbonate (Cs_2CO_3) and dimethylethylenediamine (DMEDA) in dioxane at 60 °C for 17 hours. Total conversion of compound **5** was observed and the reaction was treated and purified. However, four different products were formed (Scheme 1): the desired compound **1** which could not be isolated, compound **6** which results from three HBr eliminations (7% yield), compound **7** containing one ynamide and two brominated alkynes (26% yield), and compound **8** containing two ynamides and one brominated alkyne (not isolated). One can notice that brominated alkynes were much more stable than we anticipated since they survived the reaction conditions and a column chromatography. Nevertheless, they are not supposed to be formed under these conditions since the mechanism should first involve a C–N coupling and subsequently an elimination, as proposed in the seminal paper of Evano and coworkers.[38] We thus supposed that forming brominated alkynes is a dead-end for the desired reaction using these conditions. Actually, changing the base to potassium carbonate (K_2CO_3) did not help and no conversion was observed.

Although compound **1** could not be isolated, its identification by NMR spectroscopy and LC–MS did let some hope. Given that no *gem*-dibromovinylic function could be observed after reaction but only brominated alkynes resulting from HBr elimination in the presence of cesium carbonate, we assumed that we could take profit of this unexpected event to switch the reaction conditions from Evano's to Hsung's in addition to the use of cesium carbonate which should be able to efficiently generate the required brominated alkynes *in situ*, as previously observed. Thus, compound **5** was reacted with benzyltosylamide, cesium carbonate, potassium carbonate (required in the Hsung's conditions), pentahydrate copper sulfate and 1,10-phenanthroline in toluene at 60 °C for 88 hours. To our delight, the desired compound **1** was then isolated in 38% overall yield (72% stepwise yield) (Scheme 2). In addition, traces of compounds **7** and **8** could also be identified in the reaction mixture but were not isolated.

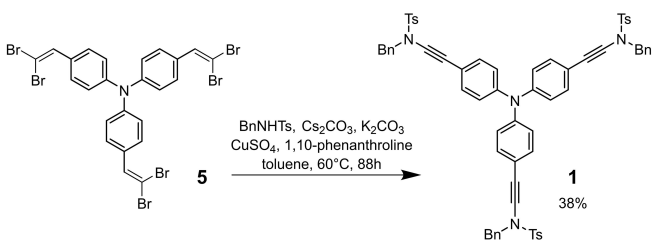
These conditions were then applied to the synthesis of the tetra-ynamide TPE **3**. First, precursor **10** bearing four *gem*-dibromovinylic functions was synthesized from the corresponding tetra-aldehyde **9**[39–41] in the presence of triphenylphosphine and tetrabromomethane in dichloromethane (53% yield). Subsequently, compound **10** was reacted with methyltosylamide under the same Hsung's conditions as previously applied for **1**. The desired compound **3** was thus isolated in a good overall yield of 64% (89% stepwise yield) (Scheme 3). To the best of our knowledge, this is the first example of a molecule bearing four ynamide functions. Compound **3** was then reacted with 5 equivalents of TCNE in dichloromethane at room temperature to afford the desired tetra-TCBD **4** in 78% yield.

For the sake of comparison, we also synthesized the TPE compound bearing only one TCBD moiety. In this case, we started with *gem*-dibromovinyl compound **11**, which was synthesized according to a protocol from the literature.[42] It was reacted with methyltosylamide using standard conditions of the Evano coupling with copper iodide and DMEDA to lead to ynamide **12** in 69% yield (Scheme 4). The latter compound was subsequently reacted with 1 equivalent of TCNE overnight at room temperature in dichloromethane to afford the desired TCBD **13** in 57% yield.

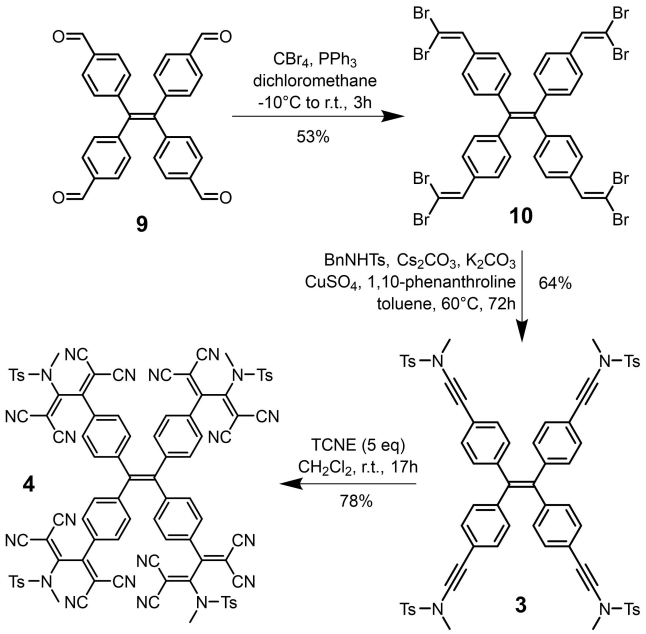
In addition to the characterization of compounds **4** and **13** by NMR spectroscopy and high-resolution mass spectrometry, their electronic absorption and emission properties were also investigated. The UV-visible absorption spectra were recorded from solutions in dichloromethane (Figure 2). In contrast with the starting TPE tetra-aldehyde **9** which exhibits a maximum of absorption of UV light at around 320 nm,[39–41] they both exhibit



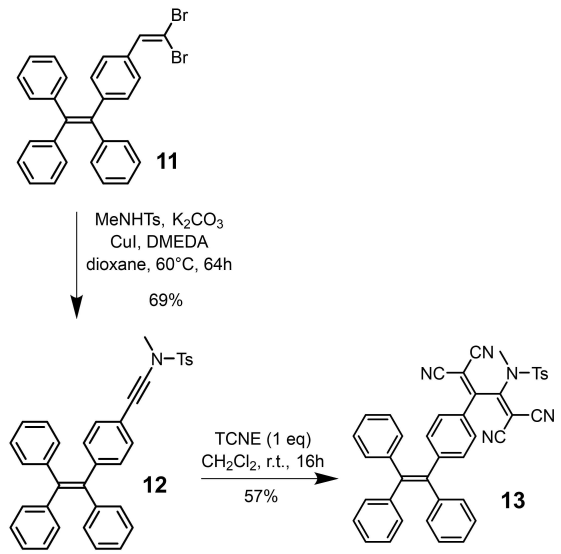
Scheme 1. Reaction of compound **5** with benzyltosylamide under Evano's conditions.



Scheme 2. Reaction of compound **5** with benzyltosylamide under Hsung's conditions for the successful synthesis of tris-ynamide **1** from compound **5**.



Scheme 3. Synthesis of TPE derivatives tetra-ynamide **3** and corresponding tetra-TCBD **4**.



Scheme 4. Synthesis of TPE mono-TCBD **13**.

a broad band in the visible range (up to 600 nm), characteristics of TCBDs derived from ynamides linked to polyaromatic cores.[20,21,43] While the absorption coefficient at the maximum of this band for mono-TCBD **13** is about 0.6×10^4 $mol^{-1}.L.cm^{-1}$, the one from tetra-TCBD **4** is around 4-fold this value at 2.8×10^4 $mol^{-1}.L.cm^{-1}$, which amounts to the difference in the number of TCBDs present in the molecule (1 for compound **13** vs. 4 for compound **4**). The band of compound **4** is slightly blue-shifted compared with the one of compound **13**: their maxima are located at 450 nm and 482 nm respectively. This slight but significant difference might originate from the

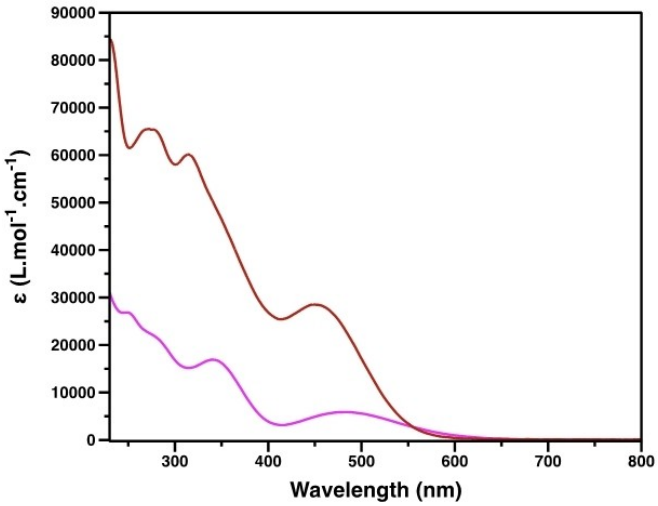


Figure 2. Absorption spectra of compounds **4** (red) and **13** (pink) in dichloromethane.

presence of four electron-withdrawing TCBD groups in **4** compared to only one in compound **13**.

TCBDs[43,44] have long been thought to be non-emissive because of fast non-radiative deactivation pathways.[45] However some groups, including ours,[20,21,46] recently showed that TCBDs could exhibit luminescence, depending on their nature and their environment.[47–50] Therefore, the emission properties of compounds **4** and **13** where examined. While none of them showed a measurable luminescence in dichloromethane, which is in agreement with a previous study on TCBDs derived from ynamides[46], the tetra-TCBD **4** exhibited a weak luminescence in toluene (quantum yield: 0.6%). On the contrary, the mono-TCBD **13** did not show any emission in toluene at all. We reasoned that the absence of luminescence in solution might be due to non-radiative decay promoted by the existence of intramolecular motions on the TPE propeller core. According to the mechanism of aggregation induced emission (AIE) that occurs through the restriction of intramolecular motions prevented in the aggregates,[51] we thought that the optical properties of compounds **4** and **13** may be markedly different once aggregated, and thus recorded the emission spectra of these two compounds in the solid state (Figure 3). In both cases, a weak emission could be recorded from 550 to 1300 nm for tetra-TCBD **4** (with a maximum at 760 nm), and from 650 to 1300 nm for mono-TCBD **13** (with a maximum at 800 nm). These observations are in line with previous reports from our group about the solid-state luminescence in the near-infrared (NIR) range of TCBD connected to polyaromatic cores,[20,21] and, again, in stark contrast with the fluorescence emission of the starting TPE tetra-aldehyde **9** which is centered around 520 nm.[39–41]

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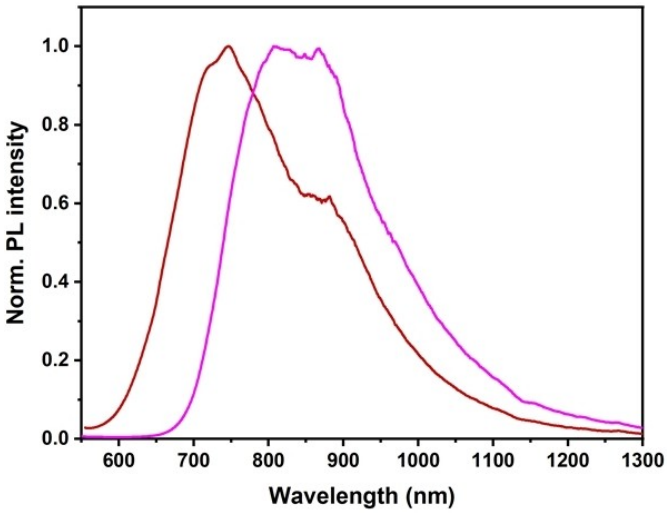

Figure 3. Emission spectra of compounds **4** (excitation: 460 nm; red) and **13** (excitation: 520 nm; pink) in the solid state.

Conclusion

In conclusion, we addressed herein the challenge of synthesizing aromatic compounds bearing multiple ynamide functions, and provide a method to introduce, in one step, four ynamide functions onto a single aromatic scaffold. The tetra-ynamide **3** was then successfully turned into the corresponding tetra-TCBD **4** by reaction with TCNE. The absorption and the emission properties of the latter and its monofunctionalized counterpart revealed very weak fluorescence emission in solution, but significant NIR luminescence in the solid-state. We believe the synthetic methodology described here can pave the way to even more complex structures in the future, possibly leading to the development of novel small organic NIR-emitters.[52,53]

Experimental Section

General procedures

Reagents were obtained from commercial suppliers and used without further purification. Compound **9** was synthesized following a previously-reported procedure.[39] NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Spectra were recorded in deuterochloroform referenced to residual $CHCl_3$ (1H, 7.26 ppm) or $CDCl_3$ (13 C, 77.2 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hz. The following abbreviations are used to describe multiplicity; s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet. HRMS experiments were carried out on a Waters Q-Tof 2 (ESI-Electrospray Ionization, ASAP-Atmospheric Solids Analysis Probe) spectrometer. Analytical TLC was carried out on Merck 60 F245 aluminium backed silica gel plates. Short wave UV radiation (245 nm), $KMnO_4$ and vanillin were used to visualize components. Compounds were purified by flash column chromatography using Geduran® silica gel 60 (0.040-0.063 nm). UV-visible spectra were recorded on a Jasco V-750 spectrophotometer using 1 cm quartz cuvettes for solutions. The luminescence spectra were measured using Horiba-Jobin-Yvon Fluorolog-3 spectrofluorometers. Powders were placed in quartz tubes inserted in a G8 GMP integrating sphere. The steady-state luminescence was excited with unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° with a Peltier cooled Hamamatsu R2658 PMT or a liquid nitrogen-cooled Horiba Symphony II CCD detector. Long-pass filters were used to reject scattered light. Spectra were reference-corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector, filters, and grating).

Synthesis

Compound 12. A solution of dibromoalkene **11** (65 mg, 0.126 mmol), TsNHMe (17 mg, 0.127 mmol), CuI (4 mg, 0.021 mmol), *N,N'*-dimethylethylenediamine (3 µL, 0.028 mmol) and Cs_2CO_3 (165 mg, 0.506 mmol) in dry 1,4-dioxane (3 mL) was heated to 60 °C under a nitrogen atmosphere over 64 h. The reaction mixture was cooled to room temperature and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane: ethyl acetate 1:0 to 9:1) to give ynamide **12** (47 mg, 0.086 mmol, 69%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4, 1.9 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.16–7.08 (m, 11H), 7.07–7.00 (m, 6H), 6.97 (d, J = 8.0 Hz, 2H), 3.13 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 143.7, 143.6, 143.5, 143.5, 141.7, 140.3, 133.4, 131.5, 131.4, 131.4, 131.0, 129.9, 128.0, 127.9, 127.8, 127.8, 126.8, 126.7, 126.7, 120.6, 84.1, 69.3, 39.4, 21.8; HRMS (ESI MeOH/CH_2Cl_2 90/10) calculated for $C_{36}H_{23}NO_2NaS$ $[M+Na]^+$ 562.1811, found 562.1813.

Compound 13. A solution of ynamide **12** (44 mg, 0.081 mmol) and TCNE (10.5 mg, 0.082 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 16 h. The reaction mixture was concentrated and purified by column chromatography (cyclohexane: dichloromethane:ethyl acetate 1:0:0 to 8:2:0 to 78:20:2) to give TCBD **13** (31 mg, 0.046 mmol, 57%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.46 (J = 8.6 Hz, 4H), 7.25 (d, J = 8.7 Hz, 2H), 7.21–7.09 (m, 9H), 7.08–7.02 (m, 6H), 3.39 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 164.2, 151.2, 147.5, 144.6, 142.9, 142.6, 142.5, 139.2, 132.8, 132.5, 131.6, 131.5, 131.4, 131.0, 130.0, 129.2, 128.3, 128.3, 128.3, 127.9, 127.6, 127.3, 127.2, 112.2, 112.1, 110.6, 110.6, 87.7, 80.6, 41.2, 22.0; HRMS (ESI MeOH/CH_2Cl_2 90/10) calculated for $C_{42}H_{29}N_5O_2NaS$ $[M+Na]^+$ 690.1934, found 690.1939.

Compound 10. A solution of aldehyde **9** (95 mg, 0.216 mmol) and PPh_3 (684 mg, 2.604 mmol) in dry CH_2Cl_2 (10 mL) at −10 °C was reacted with a solution of CBr_4 (432 mg, 1.303 mmol) in dry CH_2Cl_2 (10 mL) added dropwise. The reaction mixture was stirred at room temperature for 3 h. The reaction was diluted with pentane, filtered and concentrated in vacuum. The residue was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 8:2) to give compound **10** (123 mg, 0.115 mmol, 53%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 4H), 7.33 (d, J = 8.6 Hz, 8H), 7.00 (d, J = 8.3 Hz, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 141.1, 136.5, 133.9, 131.5, 128.1, 89.5; HRMS (MALDI) calculated for C34H20^{79}Br$_7$^{81}Br $[M]^{+\cdot}$ 1061.5006, found 1061.501.

Compound 3. A solution of dibromoalkene **10** (122 mg, 0.114 mmol), TsNHMe (82 mg, 0.445 mmol), $CuSO_4.5H_2O$ (12 mg, 0.049 mmol), 1,10-phenanthroline (33 mg, 0.182 mmol), K_2CO_3 (297 mg, 2.149 mmol) and Cs_2CO_3 (292 mg, 0.912 mmol) in dry degassed toluene (5 mL) was heated to 90 °C under a nitrogen atmosphere over 72 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 1:1) to give ynamide **3** (85 mg,

0.073 mmol, 64%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 8H), 7.38 (d, J = 8.6 Hz, 8H), 7.11 (d, J = 8.5 Hz, 8H), 6.90 (d, J = 8.7 Hz, 8H), 3.15 (s, 12H), 2.48 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 142.8, 140.7, 133.3, 131.4, 131.1, 130.0, 127.9, 121.3, 84.6, 69.1, 39.4, 21.8; HRMS (ESI MeOH/CH_2Cl_2 95/5) calculated for $C_{66}H_{56}N_4O_8NaS_4$ $[M+Na]^+$ 1183.2873, found 1183.2879.

Compound 4. A solution of ynamide **3** (22 mg, 0.019 mmol) and TCNE (12 mg, 0.095 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 17 h. The reaction mixture was concentrated and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 1:1) to give TCBD **4** (25 mg, 0.015 mmol, 78%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 8H), 7.67 (d, J = 8.5 Hz, 8H), 7.47 (d, J = 8.1 Hz, 8H), 7.32 (d, J = 8.5 Hz, 8H), 3.42 (s, 12H), 2.50 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 163.5, 147.7, 147.1, 142.4, 132.8, 132.2, 131.3, 131.2, 131.1, 128.4, 112.0, 111.7, 110.6, 110.6, 89.4, 81.6, 41.2, 22.0; HRMS (ESI MeOH/CH_2Cl_2 95/5) calculated for $C_{90}H_{56}N_{20}O_8NaS_4$ $[M+Na]^+$ 1695.3365, found 1695.3366.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Cycloaddition · Fluorescence · Synthetic methods · Tetracyanobutadienes · Ynamides

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