A multistep single-crystal-to-single-crystal bromodiacetylene dimerization

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Packing constraints and precise placement of functional groups are the reason that organic molecules in the crystalline state often display unusual physical or chemical properties not observed in solution. Here we report a single-crystal-to-single-crystal dimerization of a bromodiacetylene that involves unusually large atom displacements as well as the cleavage and formation of several bonds. Density functional theory computations support a mechanism in which the dimerization is initiated by a [2+1] photocycloaddition favoured by the nature of carbon-carbon short contacts in the crystal structure. The reaction proceeded up to the theoretical degree of conversion without loss of crystallinity, and it was also performed on a preparative scale with good yield. Moreover, it represents the first synthetic pathway to (*E*)-1,2-dibromo-1,2-diethynylethenes, which could serve as synthetic intermediates for the preparation of molecular carbon scaffolds. Our findings both extend the scope of single-crystal-to-single-crystal reactions and highlight their potential as a synthetic tool for complex transformations.

rganic molecules often display surprising physical or chemical properties in a confined environment, such as the crystalline state, because of the precise arrangement of functional or reactive groups, the constrained degrees of conformational freedom, defined and close supramolecular interactions, and the absence of other molecules^{1–7}. Topochemical single-crystal-tosingle-crystal reactions, for instance, often occur under mild conditions with perfect chemo-, regio- and stereoselectivity^{8–10}; prominent examples are the topochemical polymerizations of di- and triacetylenes^{11–17} or di- and trienes^{18,19}, as well as the [2 + 2] photodimerization of alkenes to give cyclobutanes or ladderanes^{20–26}. With the exception of certain unimolecular rearrangements²⁷, however, previously reported examples of single-crystal-to-single-crystal reactions proceeded as single-step transformations, typically following the topochemical postulate of minimal atomic displacements¹⁰.

Here we report the novel atom-efficient and reagent-free topochemical dimerization of bromoacetylenes, such as 1 or 2, which yields the corresponding unsymmetric (E)-1,2-dibromoeneynes 3 and 4, respectively, after 1,2-shifts of both bromine atoms (Fig. 1). A detailed investigation of the reaction in the case of 1 revealed that it proceeded as a single-crystal-to-single-crystal reaction with minimal changes of the lattice parameters and without loss of crystallinity up to the theoretical maximum degree of conversion, although it involved both multiple bond rearrangements and unusually large atomic displacements.

Although the formation of oligoynes via oxidative or reductive dimerizations of terminal acetylenes or haloacetylenes, respectively, is well established, these reactions require chemical reagents whether carried out in solution or in the solid state and, hence, cannot be performed as single-crystal-to-single-crystal transformations²⁸. Similarly, encyne-forming dimerizations of terminal acetylenes under a 1,2-hydrogen shift rely on organometallic reagents or catalysts and proceed in complex multistep solutionphase reactions^{29,30}. However, the topologically related 1,2-dihaloeneyne-forming dimerizations of haloacetylenes under a 1,2-halogen shift, such as those reported here, are generally unknown³¹. According to density functional theory (DFT) computations and in agreement with experimental evidence, the dimerization of 1 appears to be initiated by a [2+1] photocycloaddition 'templated' by the molecular arrangement in the crystal structure followed by a series of bond rearrangements. This reaction represents the first example of a reagent-free transformation of this type and may be regarded as the first complex intermolecular multistep singlecrystal-to-single-crystal reaction. The transformations of 1 and 2 were conducted on a preparative scale with good yields and constitute a synthetic pathway to the otherwise unknown (E)-1,2bis(ethynyl)-1,2-dibromoolefins that are valuable intermediates en route to carbon scaffolds³²⁻³⁴.

Results and discussion

The bromine-terminated oligo(ethynylene)s 1 and 2 were prepared from the corresponding trimethylsilyl-protected derivatives in excellent yields, following modified literature procedures^{35,36}. In the case of the glycosylated bromodiacetylene 1, light-brown single-crystalline samples suitable for X-ray analysis were obtained by slow evaporation of dichloromethane (DCM) from DCM/heptane solutions at 4 °C. In the crystal structure (Fig. 2a) the molecules were arranged into 'tubular stacks' along the [010] axis that were laterally interconnected by a network of Br···O=C short contacts of 2.96 Å, much less than the respective sum of van

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Figure 1 | Schematic representation of ultraviolet-induced topochemical dimerizations. In the crystalline (cryst.) state, bromodiacetylene 1 yields dimer 3 in a defined single-crystal-to-single-crystal reaction under the displacement of both bromine atoms. Bromotriacetylene 2 was observed to undergo a similar dimerization to yield 4 in the solid state.

der Waals radii^{37,38}. The bromodiacetylene moieties were organized into layers that, in turn, contained two independent arrays. The identity period of the diacetylenes within one such array along the [010] axis amounted to 6.68 Å with an inclination angle of 86°, which is incompatible with a topochemical diacetylene polymerization (Fig. 2b)^{11–13}. However, pairs of carbon–carbon close contacts of 3.64(±0.01) Å and 3.63(±0.01) Å were observed, which suggests a 'three-centre interaction' of a terminal carbon atom of a bromodiacetylene in one array with the terminal acetylene group of an adjacent bromodiacetylene in the other array. These distances are shorter than the reactive carbon–carbon close contacts typically required for topochemical reactions and, as the involved molecules were interrelated via a two-fold screw axis, every molecule participated in two such pairwise short contacts with its two neighbours: once with its terminal carbon and once with its terminal acetylene group. On exposure to light, solid samples of bromodiacetylene 1 underwent a dimerization reaction to yield the (*E*)-1,2-dibromo-1,2-diethynylethene **3** (Fig. 1). Mass spectrometry showed that the product had precisely twice the molecular mass of 1, and both ¹H and ¹³C nuclear magnetic resonance (NMR) spectra of the isolated compound (Fig. 3 and Supplementary Figs S1, S2 and S17) indicated the formation of an unsymmetric product that bears two non-equivalent glucose moieties. Moreover, the disappearance of the two characteristic Br–C≡C carbon resonances in the ¹³C NMR spectrum combined with the concurrent appearance of four new acetylene peaks and two new peaks in the olefin region proved the formation of the (*E*)-4,5-dibromodec-4-ene-2,6,8-triyne fragment in **3**. This interpretation was confirmed unambiguously by two-dimensional (2D) NMR spectroscopy (Supplementary Figs S3–S5).



Figure 2 | Crystal structure of bromodiacetylene 1. a, A view along the [010] axis reveals 'tubular stacks' of the molecules that were interconnected laterally by a network of Br--O=C short contacts of 2.96 Å. Although the significant role of such Br--O=C short contacts was demonstrated recently^{6,38}, only 36 examples were found in a Cambridge Structural Database search. The bromodiacetylene and carbohydrate moieties were arranged into separate 'layers', and the bromodiacetylene layers contained two 'arrays' (A and B) of bromodiacetylenes. **b**, A top view of these arrays shows that the bromodiacetylene packing within each array is inappropriate for a topochemical diacetylene polymerization. However, 'pairs' of carbon-carbon short contacts existed between adjacent molecules across the arrays. Thermal ellipsoids are shown at a 50% probability level, the estimated uncertainty of the distances is <0.03 Å and hydrogen atoms are omitted for clarity (except for the calculated positions of the methylene hydrogens).



Figure 3 | ¹³C NMR spectra (101 MHz, CDCl₃) of the glycosylated bromodiacetylene 1. a,b, The spectra of 1 before (a) and after (b) ultraviolet irradiation show that the characteristic $Br-C \equiv C$ carbon resonances disappeared, whereas new acetylene and olefin peaks emerged, consistent with the structure of the corresponding dimer 3. For a more detailed discussion, see the Supplementary Information.

The observed reaction is, to the best of our knowledge, the first example of a reagent-free dimerization of a haloacetylene derivative to yield the corresponding 1,2-dihaloeneyne after a 1,2-halogen shift. This atom-efficient, non-reductive transformation bears resemblance to the iodonium-mediated solution-phase coupling of iodoacetylenes to yield 1,1-diiodovinylalkynes³¹, and it may be

regarded as topologically related to the palladium-catalysed eneyne-forming dimerizations of terminal acetylenes²⁹. Moreover, whereas cyclic (*Z*)-dibromoenediynes were synthesized previously by Jones and co-workers via an intramolecular carbene dimerization³⁹, this reaction provides the first access to the (*E*)-1,2-bis(ethy-nyl)-1,2-dibromoolefin structural motif.

Because bromodiacetylene 1 was converted into the dimer 3 in a single-crystal-to-single-crystal transformation, we were able to study this reaction in more detail. Thus, X-ray analysis of a singlecrystalline specimen exposed to ultraviolet irradiation revealed that the lattice parameters were altered only marginally; the unit cell volume changed by only 2% and the crystal symmetry was preserved. At the same time, significant site disorder was observed in the bromodiacetylene part of the crystal structure of 1. Following the spectroscopic evidence, the latter was interpreted as the coexistence of both starting material 1 and product 3 in the crystal. Accordingly, the crystal structure of 3 was resolved as a superposition of 3 (85%) and 1 (15%). An analysis of the structure showed that the glucose moieties remained virtually unchanged at their original positions in the crystal, although the atom displacements within the bromodiacetylene moieties were exceptionally large for a single-crystal-to-single-crystal reaction (Fig. 4). Thus, the terminal carbon atom of one bromodiacetylene and the terminal carbon atom of the acetylene group of a neighbouring bromodiacetylene were displaced by 1.86 Å and 1.58 Å, respectively, towards one another and connected via a new carbon-carbon single bond. In the process, the two bromine atoms connected to these carbons were displaced by 1.81 Å and 0.80 Å, respectively, and both shifted to the neighbouring carbon atoms. Because every monomer can either react via its terminal carbon atom with one neighbour or with its terminal acetylene group with the other neighbour, two symmetry-related dimers coexisted in the crystal structure of the irradiated sample (labelled as dimers A and B in Fig. 4). The observed relative occupancy of dimers A and B (85% combined) and the remaining monomer (15%) is in excellent agreement with the theoretical maximum conversion of 84% for such single-crystalto-single-crystal reactions in which a molecule can react statistically with one of two neighbours, which leads to 'stranded' monomers left without a reaction partner^{20,40-42}. Moreover, it appears to be impossible to accomplish the observed bond rearrangements in a single concerted reaction step. This renders the fact that the reaction proceeded up to its theoretical maximum conversion more remarkable and prompted us to investigate the possible reaction pathway in more detail.

Ultraviolet/visible, NMR and electron spin resonance (ESR) spectra of carefully degassed solutions of bromodiacetylene 1 in acetonitrile remained completely unaltered on ultraviolet irradiation (Supplementary Figs S11-S14), which corroborates that, indeed, the dimerization towards 3 was limited to the crystalline specimen. Moreover, ESR spectroscopy of microcrystalline samples of 1 at 15 K and 300 K demonstrated that neither single radical nor triplet diradical intermediates were involved in the reaction mechanism (Supplementary Fig. S14), which implies that the photoinduced dimerization reaction proceeded exclusively via singlet species. Based on the available experimental evidence, we performed DFT computations using the geometries of 1 and 3 determined in their respective crystal structures as the starting and end points prior to constrained geometrical optimization. Moreover, to ensure that the same non-optimized geometries were used throughout the reaction pathway, the carbohydrate groups in all intermediates were constructed based on the crystal structure of 3. Because an assignment of bond orders based on bond lengths is ambiguous, we instead used the 'localized orbital locator' (LOL)⁴³ that allows us to describe the electronic structure of the stationary points along the reaction path on the basis that the shape of the LOL basin is related closely to the bond order⁴⁴.

Thus, the DFT computations, using a density-dependent dispersion correction developed by Steinmann and Corminboeuf^{45,46} to account for long-range weak-interaction effects, suggested a pathway towards the (*E*)-4,5-dibromodec-4-ene-2,6,8-triyne product. The rate-determining step of this pathway was a [2+1] photocycloaddition (Fig. 5), in excellent agreement with the



Figure 4 | Displacements and structural rearrangements during the dimerization. The crystal structure of an irradiated sample of a singlecrystalline specimen of 1, refined as a superposition of the dimer 3 (85% combined for the symmetry-related dimers A and B) and residual monomer 1 (15%), reveals the drastic displacements and rearrangements of the bromodiacetylene fragment in the course of this single-crystal-to-singlecrystal reaction. Furthermore, each monomer has two reaction possibilities (short contacts given in red), which leads to two symmetry-related populations of 'dimer A' and 'dimer B' as well as a statistical amount of 'stranded' monomers.

existence of the 'three-centre' carbon-carbon short contacts between the terminal carbon atom of one bromodiacetylene and the terminal acetylene group of its neighbour, as observed in the crystal structure of 1 (Fig. 2b). The reaction is initiated by a photoexcitation of 1 to give a singlet excited state S_1 * that, according to the geometry and population analysis, exhibits a pronounced carbene character on carbon atoms C1 and C4 of the diacetylene fragment (Fig. 5). The terminal carbonoid carbon atom of the excited molecule then reacts with the terminal acetylene group of the appropriate neighbour in the sense of a [2 + 1] photocycloaddition without violation of spin-conversion rules. This results in the formation of the cyclopropenyl carbene A that is 23 kcal mol^{-1} higher in energy with respect to the two monomers in their ground state in the crystal structure. In the next step, the bromine atom that neighbours the carbene is shifted towards the latter, accompanied by a C=C double-bond formation to give the methylene cyclopropene intermediate **B**, stabilized by 25 kcal mol^{-1} (relative to the two monomers). A ring opening then leads to intermediate C, which has two resonance forms according to the LOL analysis; that is, an open-shell singlet allenyl ethynyl carbene and an open-shell allenyl cumulene diradical. Finally, the dimerization towards 3 completes by a 1,2-bromine shift under relaxation to an enevne structure. The product is stabilized by 51 kcal mol⁻¹ (relative to the two monomers), consistent with estimations based on the overall bond changes.

In the course of our investigations, different alternative mechanistic routes via, for example, a bromovinylidene carbene or a [2 + 2]photocycloaddition were investigated, but found to be unfavourable (Supplementary Fig. S15). By contrast, the proposed reaction sequence is in good agreement with the experimental findings and is supported further by the fact that the excited state S₁* and intermediate **A** bear resemblance to reactive species observed at low temperatures in argon matrixes^{47,48}. Although the subsequent carbene addition to an alkyne seems reasonable, such reactions



Figure 5 | Reaction pathway, energies of intermediates, LOL functions and structural interpretations for the dimerization of the glycosylated bromodiacetylene 1. The dimerization of 1 to give (*E*)-4,5-dibromodec-4-ene-2,6,8-triyne **3** (separate, paired and angular up/down arrows represent diradical, close-shell singlet carbene and open-shell singlet species, respectively). The energy values (kcal mol⁻¹, shown in red) were obtained at the dispersion-corrected level B3LYP-dDsC/cc-pVDZ and are given with respect to the energy of two adjacent monomers in the ground state. The LOL analysis was performed at the B3LYP/cc-pVDZ level on the optimized structures (**A-C**) (glycosyl residues are replaced by methyl groups for simplicity). The LOL isovalues of 0.6 show triple bonds (blue), double bonds (purple), single bonds (white) and bonds with fractional bond order (yellow).

are observed rarely and the obtained methylene cyclopropenes, such as **B**, are reportedly highly reactive⁴⁹. Sander and co-workers, however, described the addition of difluorovinylidene carbenes to acetylene and proposed the formation of allenyl carbenes similar to intermediate **C** in this context⁵⁰. Moreover, the formation of such intermediates and the subsequent 1,2-halogen shift, as proposed here, have abundant precedence in ring-opening reactions of halogenated cyclopropenes⁵¹.

We are not aware of any previous examples of intermolecular multistep single-crystal-to-single-crystal transformations. The observed atom displacements along with multiple bond cleavages and formations in the course of the reaction seem to violate the 'topochemical postulate'¹⁰. Moreover, its progress to the theoretical conversion limit without any mediating reagents is unexpected given that related acetylene dimerizations require organometallic catalysts or reagents^{29,30}. The overall exothermic nature of the process and the notorious reactivity of the proposed primary reaction product, the methylene cyclopropene **B**, may help to explain these ostensive discrepancies. Furthermore, the 'reaction cavity concept' interprets the topochemical principle such that the molecules that participate in a lattice-controlled reaction do so with minimal distortion of the surface surrounding the reaction

environment¹⁰. In this context, the bulky carbohydrate head groups in combination with the flexible OCH_2 linker of 1 are ideal prerequisites, as evidenced by the minimal changes in lattice parameters and the preserved crystallinity during the reaction. It may be the crystallographically observed short contacts that 'template' the initial [2 + 1] photocycloaddition. In this context, a second orthorhombic polymorph of 1 (obtained by recrystallization at a different temperature) that featured numerous carbon–carbon short contacts but lacked the characteristic 'three-centre' interactions described above did not undergo a dimerization reaction on exposure to light (Supplementary Fig. S16).

Interestingly, the dimerization was not limited to bromodiacetylene 1, as microcrystalline powders of bromotriacetylene 2 furnished the corresponding (E)-5,6-dibromododec-5-ene-1,3,7,9,11-pentayne fragment in dimer 4 under ambient conditions in a yield of 66% as determined by NMR spectroscopy (Fig. 1). Contrary to the conversion of 1 into 3 that strictly required photochemical activation, the reaction of 2 was faster upon irradiation, but also proceeded slowly in the dark, which indicates that a second thermally activated pathway may be involved. Moreover, owing to the significantly higher reactivity of 2, all attempts to determine its single-crystal structure were unsuccessful. However, the molecular structure of 4



Figure 6 | 2D NMR spectroscopy for the structural elucidation of 4. The heteronuclear multiple bond correlation NMR spectrum (400 MHz, CDCl₃) of dimer 4 with the corresponding 1D ¹H NMR and ¹³C NMR traces exhibited ten acetylene carbon resonances, a duplication of the propargyl methylene proton resonances that coupled with four and six acetylene carbons, respectively, as well as two new olefin carbon resonances that coupled only with the propargyl methylene protons on the 'shorter' side of the molecule. The inset is a magnified view of the region of the acetylene cross-peaks. For a more detailed discussion, see the Supplementary Information.

was established rigorously by means of mass spectrometry, as well as by 1D and 2D NMR spectroscopy (Fig. 6 and Supplementary Figs S6–S10 and S18).

Finally, to evaluate further the synthetic prospects of the observed dimerization reaction, we performed the ultraviolet-induced dimerization of microcrystalline samples of 1 (0.5 g) and 2 (1.0 g) on a preparative scale and obtained, after column chromatography, the corresponding dimers 3 and 4 in very good isolated yields of 76% and 43%, respectively. Although the yield of dimer 4 was somewhat diminished because of the low stability of the product, dimer 3 was obtained in a yield close to the theoretical maximum conversion, which demonstrates the synthetic potential of this reaction.

Conclusions

We report here the topochemical dimerization of two bromineterminated oligo(ethynylene)s that represents the first example of a reagent-free haloacetylene dimerization to give 1,2-dibromoeneynes. Crystallographic analysis, spectroscopic methods and DFT computations of bromodiacetylene 1 allowed us to conclude that the reaction proceeded in the sense of an intermolecular multistep single-crystal-to-single-crystal transformation that involves both large atom displacements and the cleavage and formation of several bonds. This reaction is even more remarkable as it reaches the theoretical conversion limit within minutes on a preparative scale in an atom-efficient process under a 1,2-halogen shift in a catalyst-, reagent- and solvent-free environment, but related acetylene dimerizations are complex solution-phase reactions that require organometallic catalysts or reagents²⁹⁻³¹. In this way, the reported transformation provides the first synthetic access to the (E)-1,2-bis(ethynyl)-1,2dibromoethylenes in a facile manner compared to the efforts otherwise involved in the synthesis of similar intermediates^{33,34,39}. The obtained compounds are useful functional carbon-rich derivatives for the construction of carbon scaffolds³². This renders our approach one of the few synthetically relevant single-crystal-to-single-crystal reactions beyond [2+2] photocycloadditions, and extends their scope towards complex transformations.

Methods

All the experimental details, including Supplementary Figs S1–S18, a thorough discussion of the 2D NMR spectra of 1–4, experimental procedures and analytical data for all the compounds, detailed crystallographic information for

 $1 \mbox{ and } 3$ (including CIF files), and computational details are given in the Supplementary Information.

5'-Bromopenta-2',4'-diynyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (1). 5'-Trimethylsilylpenta-2',4'-diynyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (1.0 g, 2.0 mmol, 1 equiv.) and N-bromosuccinimide (0.56 g, 3.1 mmol, 1.5 equiv.) were dissolved in 25 ml dry acetonitrile. The flask was wrapped with aluminium foil, and silver fluoride (0.4 g, 3.1 mmol, 1.5 equiv.) was added at room temperature. After 1.5 hours the resulting suspension was filtered through a paper filter and diluted with DCM. The resulting solution was washed once with water and once with saturated NaCl solution. The organic phase was dried over MgSO4 and evaporated to give 1.01 g (100%) of 1 as colourless crystals. ¹H NMR (400 MHz, CDCl₃): $\delta = 5.22$ (dd, J = 9.4 Hz, 1H), 5.07 (dd, J = 9.6 Hz, 1H), 4.98 (dd, J = 8.0 Hz, 9.5 Hz, 1H), 4.71 (d, J = 8.0 Hz, 1H), 4.40 (d, J = 2.0 Hz, 2H), 4.25 (dd, J = 4.6 Hz, 12.4 Hz, 1H), 4.13 (dd, J = 2.3 Hz, 12.3 Hz, 1H), 3.72 (ddd, J = 2.5 Hz, 4.6 Hz, 10.0 Hz, 1H), 2.10-1.97 (m, 12H). ¹³C NMR (101 MHz, CDCl₂): $\delta = 170.8$, 170.3, 169.6, 169.5, 98.5, 72.8, 72.2, 72.1, 71.0, 69.7, 68.3, 64.7, 61.8, 56.5, 42.4, 20.8, 20.8, 20.7, 20.7. Infrared (KBr): $\nu = 2,959, 2,241, 2,143, 1,753, 1,368, 1,221, 1,061 \text{ cm}^{-1}$. Melting point = 108 °C (decomposition). $[\alpha]_{\rm D} = -37.7$ (c 0.9, CHCl₃). High-resolution mass spectrometry (HRMS) (electrospray ionization (ESI)): calculated for C19H21O10BrNa $([M + Na]^+)$, 511.0210; found, 511.0214.

4-Tritylphenyl 10-bromodeca-5,7,9-triynoate (2). 4-Tritylphenyl 10-(trimethylsilyl)deca-5,7,9-triynoate (0.493 g, 0.908 mmol, 1 equiv.) was dissolved in DCM (12 ml), and acetonitrile (10 ml) was added. The flask was wrapped in aluminium foil, and N-bromosuccinimide (0.172 g, 0.953 mmol, 1.05 equiv.) and silver fluoride (0.122 g, 0.953 mmol, 1.05 equiv.) were added at room temperature. After six hours the reaction mixture was transferred into a separating funnel and diluted with DCM (30 ml). The organic phase was washed six times with 1 M HCl (100 ml) and once with saturated NaCl solution. The organic phase was dried over Na2SO4 and concentrated to approximately 10 ml, thoroughly shielding it from light. For synthetic purposes, toluene was added and the mixture was concentrated in vacuo. For analytic purposes, CDCl₃ (10 ml) was added and the mixture was concentrated *in vacuo*. ¹H NMR (400 MHz, CDCl₃): δ = 7.30-7.20 (m, 17H), 7.02-6.98 (m, 2H), 2.71 (t, J = 7.3 Hz, 2H), 2.48 (t, J = 6.9 Hz, 2H), 2.00 (tt, J = 7.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 171.2, 148.5, 146.6, 144.5, 132.2, 130.1, 127.6, 126.1, 120.4, 78.3, 66.4, 66.1, 64.7, 60.8, 59.6, 53.6, 39.9, 33.0, 23.1, 18.8. HRMS (matrix-assisted laser desorption/ionization (MALDI)): calculated for C35H25BrNaO2 ([M + Na]+), 581.0927; found, 581.0914.

(*E*)-4,5-Dibromodeca-2,6,8-triyne-4-enediyl-1,10-bis(2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) (3). A solution of 1 (0.434 g, 0.89 mmol) in ethyl acetate/heptane (1:2) was evaporated to dryness. The obtained polycrystalline solid was irradiated with ultraviolet light for five minutes. The crude product was purified by column chromatography to yield 3 (0.328 g, 76%) as a colourless solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 5.26-5.19$ (m, 2H), 5.12-5.07 (m, 2H), 5.04-4.98 (m, 2H), 4.77 (d, J = 7.9 Hz, 1H), 4.73 (d, J = 7.9 Hz, 1H), 4.68-4.58 (m, 2H), 4.54 (s, 2H), 4.29-4.24 (m, 2H), 4.15 (dd, J = 2.4 Hz, 12.4 Hz, 2H), 3.73 (ddd, J = 9.7 Hz, 4.5 Hz, 2.3 Hz, 2H), 2.10-2.05 (m, 12H), 2.03-1.98 (m, 12H). ¹³C NMR (101 MHz, CDCl₃): $\delta = 170.8$, 170.3, 169.5, 169.5, 106.8, 104.3, 99.8, 98.8, 98.5, 86.2, 85.4, 84.6, 74.2, 72.9, 72.8, 72.2, 72.2, 71.1, 71.0, 70.8, 68.3, 68.3, 61.8, 56.8, 56.5, 20.9, 20.7. HRMS (ESI): calculated for C₃₈H₄₂Br₂NaO₂₀ ([M + Na]⁺), 1,000.0513; found, 1,000.0494.

(E)-9,10-Dibromoicosa-9-ene-5,7,11,13,15-pentaynedioic acid bis(4-tritylphenyl) ester (4). 4-Tritylphenyl 10-(trimethylsilyl)deca-5,7,9-triynoate (1.00 g, 1.816 mmol, 1 equiv.) was dissolved in DCM (15 ml), and acetonitrile (16 ml) was added. The flask was wrapped in aluminium foil, and N-bromosuccinimide (0.339 g, 1.906 mmol, 1.05 equiv.) and silver fluoride (0.242 g, 1.906 mmol, 1.05 equiv.) were added successively at room temperature. After five hours the reaction mixture was transferred into a separating funnel and diluted with DCM (100 ml). The organic phase was washed six times with 1 M HCl (100 ml) and once with saturated NaCl solution. The organic phase was dried over Na2SO4 and evaporated to dryness in a 250 ml round-bottom flask to give 2 (1.012 g, 100%) as a red-brown solid. The flask was irradiated with ultraviolet light for one minute, and the resulting compound was purified by column chromatography to yield 4 (0.434 g, 43%) as a light-brown solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.31–7.21 (m, 35H), 7.03–7.00 (m, 4H), 2.74 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 2.63 (t, J = 6.9 Hz, 2H), 2.58 (t, J = 6.9 Hz, 2H), 2.09-2.00 (m, 4H).¹³C NMR (101 MHz, CDCl₃): $\delta = 171.3, 171.2, 148.6, 146.6, 144.5, 132.3, 131.2, 127.7, 126.1, 120.4, 107.2, 107.2, 108.6, 109.$ 105.2, 93.8, 90.5, 89.2, 86.1, 76.0, 71.7, 71.3, 66.6, 65.8, 64.7, 58.9, 33.0, 33.0, 23.1, 23.1, 19.6, 19.2. HRMS (MALDI): calculated for C₇₀H₅₀Br₂NaO₄ ([M + Na]⁺), 1,137.1984; found, 1,137.1984.

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Author contributions

T.N.H. and S.S. synthesized, characterized and crystallized the monomers, conducted the dimerization experiments, characterized the products and contributed to the preparation of the manuscript. R.M. assisted in the synthesis. T.K.T. performed the DFT computations designed and directed by C.C.; both these authors contributed to the preparation of the manuscript. A.S. performed the ESR measurements. R.S. and W.B.S. performed the X-ray crystal structure analyses. H.F. designed and directed the research and wrote the manuscript.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to H.F.

Competing financial interests

The authors declare no competing financial interests.