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Synthesis, X-Ray Structure Analysis and Topochemical Photopolymerization of 2,5-Dimethoxyphenyl- and Quinone-substituted Octa-3,5-diynes

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Abstract—The octa-3,5-diynes **3a–g** have been synthesized. Subsequent oxidation of **3a–g** gave the 1,8-quinone-substituted octa-3,5-diynes **4a–g**. The molecular structures of the diynes α-**3b**, β-**3b**, **3c**, **3e**, **3f** and **4f** have been determined by X-ray diffraction. UV-irradiation of diyne **3c** afforded in a single crystal-to-single crystal transformation the highly-ordered polymer **5** under topochemical control. The transformation of **3c** into polymer **5** was observed by X-ray diffraction analysis. Irradiation of **4d** yielded the first quinone-substituted intensive-blue poly(but-1-en-3-ynylene) **5**, which turned red after work up. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

In 1969, Wegner first characterized the solid-state polymerization of conjugated diynes.[1] The polymerization, accomplished by heat, irradiation or pressure, was found to lead to highly ordered polymers.[2,3]

The synthesis of organic metals involves the assembly of a molecular solid of crystalline structure, which favors the metallic state.[4] This implies chain-like structures in which donors and acceptors stack in parallel chains, and a uniform structure where each molecule should be equidistant from its neighbor. Such structures are common in the tetracyanobenzoquinodimethane (TCNQ) salts[5,6] or dicyanobenzoquinodiimine (DCNQI) CT complexes.[7]

By combining the favorable aspects of the highly ordered diyne polymers and the geometric dependency of conductivity of organic metals in the case of quinoid compounds, we sought a convenient method for the synthesis of quinone-substituted diynes as precursors for a wide range of dicyanobenzoquinodiimine dialkyne derivatives. In addition the competitive photo- and thermochemical behavior of the topochemical ambident quinone-substituted diynes were of special interest.[8]

Results and Discussion

To prevent the observed oxidation of the methylene-spacer unit between the 2,5-dimethoxyphenyl- and the diyne substituent,[9] which is mainly caused by extension of conjugation, the spacer was expanded by one methylene unit. By introduction of the ethylene-spacer and application of the following synthetic route (Scheme 1) we were able to synthesize the first quinone-substituted diynes starting from the corresponding 2,5-dimethoxybenzyl halogenides **1a–g** in three steps.

The Grignard-coupling of the 2,5-dimethoxybenzyl halogenides **1a–g** with prop-2-ynyl magnesium bromide[10] leads to the temperature sensitive, colorless, liquid respectively low-melting 4-(2,5-dimethoxyphenyl)but-1-ynes **2a–g**, which were obtained free of allene-isomers. Copper(I)-catalyzed coupling of the resulting 3-(2,5-dimethoxyphenyl)but-1-ynes **2a–g** under Hay conditions with CuCl·tmeda in DME in a strong oxygen stream gave the octa-3,5-diynes **3a–g** in yields of 34–85% from which **3c** is light sensitive.

The but-1-ynes **2a–g** and octa-3,5-diynes **3a–g** were fully characterized by their ^{1}H NMR-, ^{13}C NMR-, IR-spectroscopical and mass spectrometrical data. The crystal structure of octa-3,5-diyne **3b**, **3c**, **3e** and **3f** was investigated by X-ray diffraction analysis (Table 3)[11] and showed that **3b** crystallizes in an α- and a β-modification (Figs. 1 and 2).

Bond lengths and angles of the octa-3,5-diynes α-**3b**, β-**3b**, **3c**, **3e** and **3f** in crystal[11] are in the usual range.[12] The packing parameters (Table 1) obtained from the crystal structures of diyne α-**3b**, β-**3b**, **3c**, **3e** and **3f** are in accord with the observed solid-state reactivities. The significance of the intermolecular distances and angles given in Table 1 can be seen in Schemes 2 and 3.

Keywords: diynes; quinones; polymers; photochemistry in solid-state.

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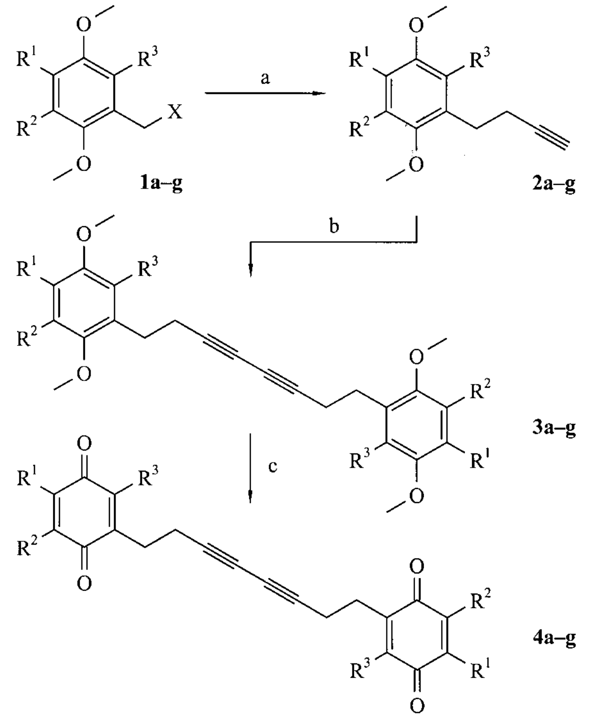


	R^1	R^2	R^3	X
a	H	H	H	Cl
b	CH_3	H	H	Cl
c	CH_3	CH_3	H	Br
d	CH_3	CH_3	CH_3	Br
e	F	H	H	Br
f	Cl	H	H	Br
g	Br	H	H	Br

Scheme 1. Synthesis of **4a–g**; reagents and conditions: (a) C_3H_3MgBr, diethyl ether, rt, 1 day; (b) CuCl·tmeda, DME, 35–36°C, 1–2 days; (c) CAN, CH_3CN, H_2O, 25–30°C, 45 min.

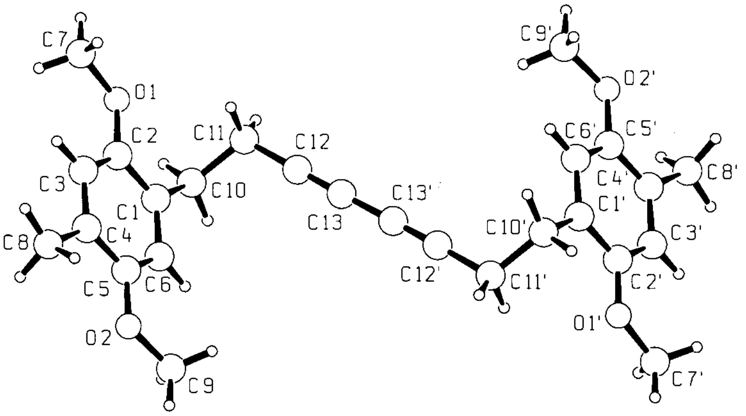


Figure 1. Molecular structure of α-**3b** in the solid state; H atoms are not numbered for clarity.

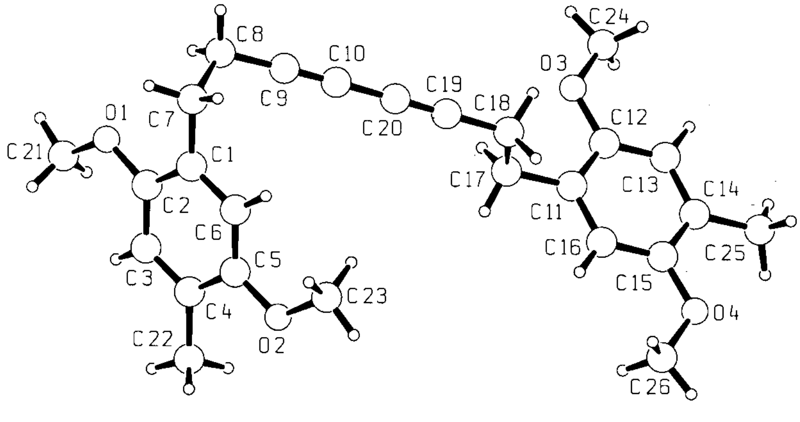


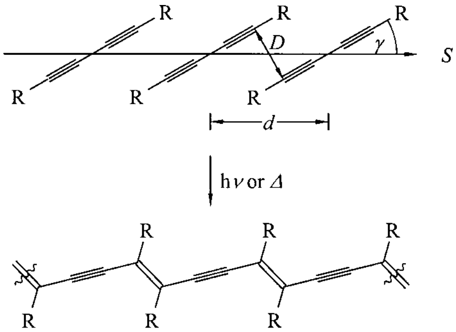
Figure 2. Molecular structure of β-**3b** in the solid state; H atoms are not numbered for clarity.

Table 1. Stacking parameters of α-**3b**, β-**3b**, **3c**, **3e** and **3f**. For definition of *D*, *d* and γ see Schemes 2 and 3, for $\Delta\gamma$ and *s* see text

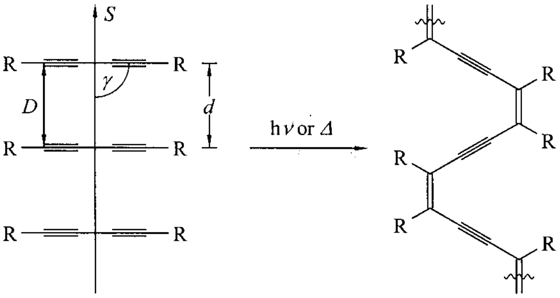
	D [Å]	*D* [Å]	γ [°]	$\Delta\gamma$ [°]	*s* [Å]
α-**3b**	4.155(4)	6.076(4)	53.2(3)	8.2(3)	4.865(4)
			31.0(3)	12.0(3)	3.129(4)
3c	3.574(3)	5.023(1)	45.4(2)	0.4(2)	3.577(2)
3e	4.248(3)	4.498(1)	60.4(2)	15.4(2)	3.911(4)
Tolerance range[a]	3.4–4.3	4.7–5.2	45±10	0–10	3.4–4.0
β-**3b**	3.746(2)	3.729(2)	74.5(2)	–	–
3f	3.716(3)	3.707(3)	71.4(2)	–	–
Tolerance range[b]	3.4–4.3	3.4–4.3	90±10	–	–

[a] Formation of all-*E*-poly(but-1-en-3-ynylene).

[b] Formation of all-*Z*-poly(but-1-en-3-ynylene).



Scheme 2. 1,4-Polyaddition of conjugated diynes to all-*E*-poly(but-1-en-3-ynylene)s.



Scheme 3. 1,4-Polyaddition of conjugated diynes to all-*Z*-poly(but-1-en-3-ynylene)s.

The correlation between *d* and distance *s* usually found in the literature[16] is given by the formula $s=d\sin(\gamma)$. The deviation from γ is $\Delta\gamma$, which is calculated from the formula $\Delta\gamma=|\gamma-45|$. For significant reactivity of slipped diyne stacks, the upper limit for *D* is 4.3 Å and for *d* is 5.2 Å, γ should be close to 45°, and *s* should be in the range 3.4–4.0 Å.[13–16]

In the case of vertical packing arrangement of the monomers another kind of topochemical 1,4-polyaddition of diynes may be observed which leads to the formation of all-*Z*-poly(but-1-en-3-ynylene)s (Scheme 3).

Interestingly, there is no certain example of an all-*Z*-polymer reported in the literature with diyne monomers stacked as steps of a ladder. A crystal of hexa-2,4-diynedioic acid dihydrate became violet then black in the course of the X-ray diffraction analysis, suggesting that the compound polymerize during X-ray diffraction.[17] For vertical diyne stacks *D* and *d* should be in the range 3.4–4.3 Å and γ should be close to 90°.[16]

The structure determination of a single crystal of **3c** (Fig. 3) crystallized from *n*-hexane/benzene (10:1) in space group $P2_1/c$ (Table 3). The monoclinic cell unit exhibits cell constants of a=5.023(1) Å, b=35.63(1) Å, c=6.655(2) Å and a β-angle of 92.45(2)°. The corresponding cell volume is V=1190.2(6) Å^3 with Z=2 and a calculated density of $D_{\mathrm{calc}}=1.21\times10^3$ kg m^{-3}.

The centrosymmetrical molecular units of **3c** are arranged in stacks along the crystallographic axis *a* and *c*. While stacking arrangement in the *c* direction exhibits no topochemical relevant contacts, along axis *a* a short contact of D=3.574(3) Å is observed (Fig. 4). The stacking distance of the molecular units of **3c** amounts to d=5.023(1) Å. The angle between the diyne-rods and the stacking axis *a* is γ=45.4(2)°. With $\Delta\gamma$=0.4(2)° and s=3.577(2) Å the diyne units are ideally arranged for a topochemical 1,4-polyaddition. The observed light-sensitivity of **3c** is hereby explained and is discussed in the following paragraph.

In irradiation experiments and under thermal annealing of the investigated diynes **3a–g** solely **3c** showed a detectable topochemical reactivity. Octa-3,5-diyne **3c** either photochemically or thermally forms the bronze-orange colored polymer **5**. The crystalline structure of poly(but-1-en-3-ynylene) **5** was proven by the partial single crystal-to-single

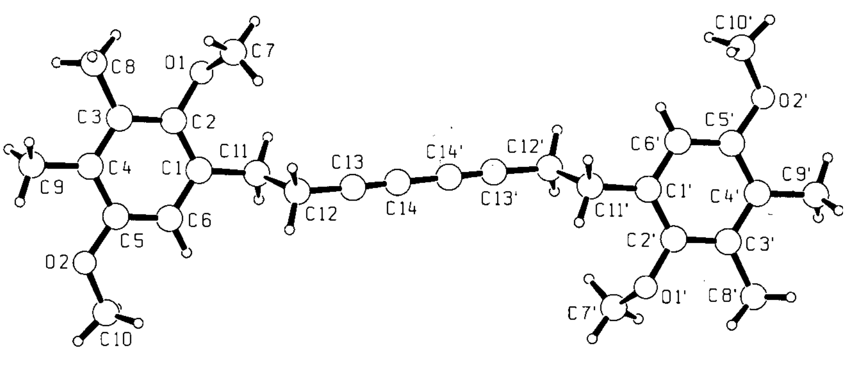


Figure 3. Molecular structure of **3c** in crystal. H atoms are not numbered for clarity.

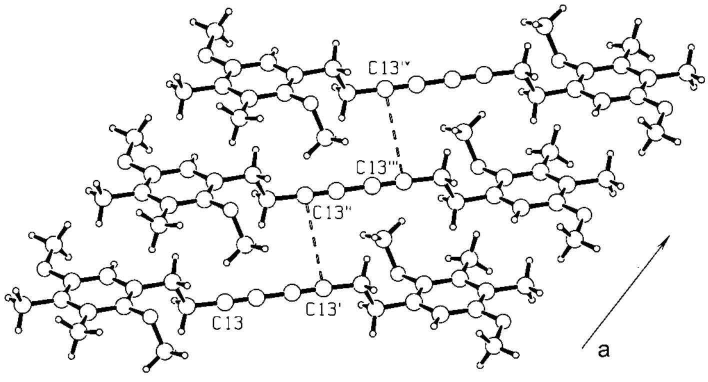
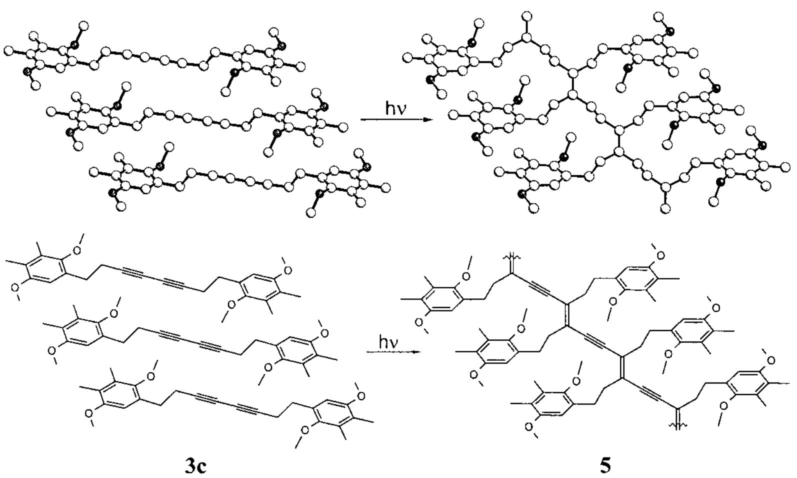


Figure 4. Stacking arrangement of **3c** in the crystal along axis *a* with the short distances of D=3.574(3) Å between alkyne C atoms C13^{I}, C13^{II}, C13^{III} and C13^{IV} of neighboring molecules. Symmetry operations: $(-x+2, -y+1, -z+2)$; $(x+1, y, z)$; $(-x+3, -y+1, -z+2)$; $(x+2, y, z)$.



3c **5**

Figure 5. Single crystal-to-single crystal transformation of octa-3,5-diyne **3c** to the crystalline poly(but-1-en-3-ynylene) **5**.

crystal transformation of **3c** to **5** (Fig. 5) detected by X-ray diffraction.

For identification of the structure of polymer **5** first the structure of monomer **3c** was determined by X-ray diffraction analysis. Then the same monomer single crystal was irradiated with light ($\lambda \geq 450$ nm) for 6 h at 15°C and measured by X-ray diffraction analysis a second time. The refinement was started with the previous obtained data of the monomer and the resulting difference electron density was assigned to the structure of the polymer. On the basis of the resulting occupation numbers of k_{monomer}=0.82 and k_{polymer}=0.18 obtained from refinement of the irradiated crystal the crystallographically determined yield of the single-crystalline poly(but-1-en-3-ynylene) **5** was 18%. Work-up of the irradiated monomer crystal of **3c** by THF extraction for 3 h to remove unreacted monomer gave 37% yield of poly(but-1-en-3-ynylene) **5**. The irradiated single crystal was found to crystallize in the space group $P2_1/c$ (Table 4). The cell constants at 193 K are a=4.940(1) Å, b=35.67(5) Å and c=6.733(4) Å with a β-angle of 92.53(3)°. The cell volume is V=1185(2) Å^3 with Z=2 and the calculated density is D_{calc}= 1.22×10^3 kg m^{-3}. Because of the conventional R-value of

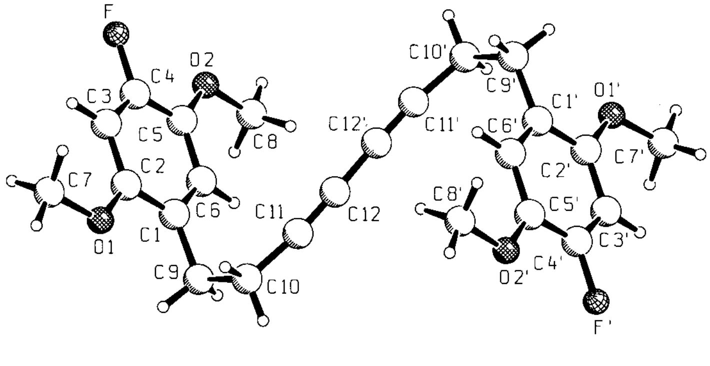


Figure 6. Molecular structure of **3e** in the crystal. H atoms are not numbered for clarity.

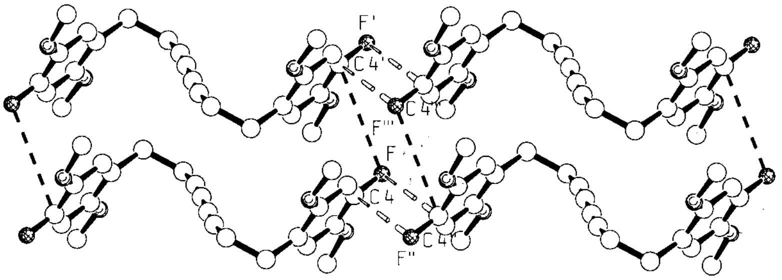


Figure 7. Packing arrangement of **3e** in the crystal along the *bc*-diagonal plane with distances of C4′···F‴ 4.048 Å (broken-lined, outlined) and C4′···F 3.988(2) Å (broken-lined, filled) of neighboring molecules. H atoms are omitted for clarity. Symmetry operations: ($x+1$, y, z); ($-x$, $-y+1$, $-z+1$); ($-x+1$, $-y+1$, $-z+1$).

Table 2. Correlation of the volume increment ΔV [Å^3] of the substituents R^1 and R^2 [21,22] with the conformation of the ethylene spacers $\theta(CH_2–CH_2)$ [*sc*=*synclinal*; *ap*=*antiperiplanar*] of α-**3b**, β-**3b**, **3c**, **3e** and **3f** in the solid state

	3e: R^1=F; R^2=H	α-**3b**: R^1=CH$_3$; R^2=H	β-**3b**: R^1=CH$_3$; R^2=H	**3f**: R^1=Cl; R^2=H	**3c**: R^1=CH$_3$; R^2=CH$_3$
$\theta(CH_2–CH_2)$	*sc*, *sc*	*sc*, *sc*	*sc*, *ap*	*sc*, *ap*	*ap*, *ap*
$\Delta V(R^1+R^2)$ [Å^3]	11.6	25.5	25.5	21.9	47.0

0.137, a discussion of the bonding geometry of **5** is not meaningful.

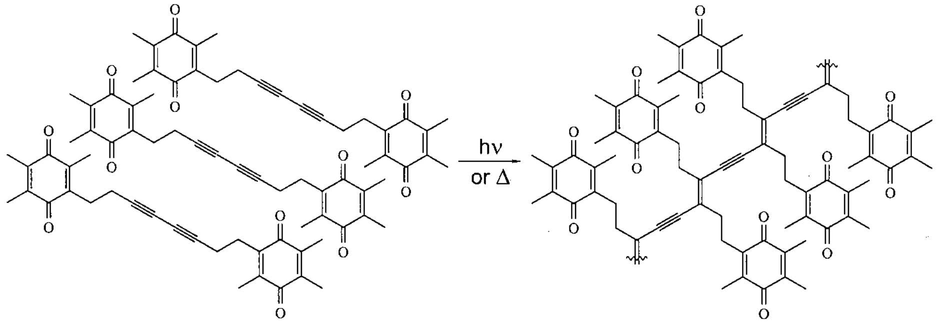
Compared to monomer **3c**, the irradiated crystal showed a reduction of axis *a* by 0.083(1) Å and an elongation of axis *c* by 0.078(4) Å. The length of axis *b* and the value of the *β*-angle remained the same. Before and after irradiation the determined cell volumes stay within the same scope of calculated deviation. By the 'principle of least motion'[18–20] the crystal systems of **3c** and **5** exhibit a very similar arrangement of atoms. In the irradiated crystal of **5** the 2-(2,5-dimethoxy-3,4-dimethylphenyl)ethyl-substituents in the monomeric and polymeric part of the crystal nearly have identical positions. The atoms of the diyne unit, however, changed their positions in the course of bond formation to the polymeric backbone in the ratio described above.

The crystal structure of **3e** (Fig. 6) was determined by X-ray analysis of a single crystal of **3e** obtained from a solution of [D$_6$]-benzene. The space group is $P\bar{1}$ with Z=1 (Table 3).

The dipole character of the C4–F bond of **3e** exerts by intermolecular contacts of C4···F′ 4.048(2) Å and C4···F″3.988(2) Å a strong influence on the arrangement of the molecules in the crystal (Fig. 7). The antiparallel oriented C4–F and C4″–F″ dipoles seem to determine the crystal packing arrangement. The CF dipoles in octa-3,5-diyne **3e** are oriented stair-like head-to-tail. The resulting attractive dipole–dipole interactions create crystal packing forces which cause an S-like deformation of the C10–C11–C12–C12′–C11′–C10′-hexa-2,4-diyne-1,6-ylene-group with angles of C10–C11–C12 173.5(2)° and C11–C12–C12′ 178.4(2)° and lead to a high crystal packing density, which is reflected by the calculated density of $D_{calc}=1.4\times10^3$ kg m^{-3}.

The structure of the octa-3,5-diynes α-**3b**, β-**3b**, **3c**, **3e** and **3f** differ by the conformations of their ethylene-bridges. By correlating the volume increment of the substituents R^1 and R^2 [21,22] with the conformation of the ethylene spacer of the octa-3,5-diynes α-**3b**, β-**3b**, **3c**, **3e** and **3f** in the solid state (Table 2) the following tendency is observed.

With increasing space requirement of substituents R^1 and R^2 and independent of their inductive effects, the conformation of the ethylene spacer alters from *synclinal* to *antiperiplanar*.



4d **6**

Scheme 4. Topochemical polymerization of **4d** to poly(but-1-en-3-ynylene) **6**.

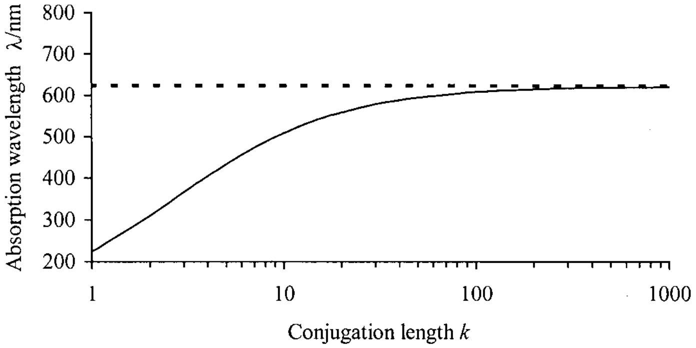


Figure 8. Absorption wavelength λ of poly(but-1-en-3-ynylene)s compared by their conjugation length k. The calculated maximum absorption wavelength λ_{max} is about 622 nm.[24]

The CAN-oxidation of the octa-3,5-diynes **3a–g** in aqueous acetonitrile at 25–30°C gave the yellow to yellow-orange colored crystalline quinone-substituted octa-3,5-diynes **4a–g** which was found to be light sensitive in the case of **4d**.

In daylight, **4d** turned blue after few minutes and became deep blue within 2 h. Irradiation of **4d** with UV light ($\lambda \geq 254$ nm) produced similar colors within 15 min. The aforementioned color is those of the irradiation product prior to work-up. After 3 h of irradiation, work-up of the blue polymer by ethyl acetate extraction yielded 30% of **6** (Scheme 4) as a red, insoluble solid.

Because of the known insolubility of poly(but-1-en-3-ynylene), only oligomers of up to n=4 were observed by field desorption-mass spectrometry (FD-MS), with correct isotopic peak distribution for $[\mathbf{4d}]_n^+$ (n=1–2). The IR-spectrum of **6** showed peaks at 2161 cm^{-1} (w, C≡C), 1643 cm^{-1} (vs, C═O) and 1625 cm^{-1} (w, C═C). Solid state-Raman experiments resulted in a strong signal at $\tilde{\nu}$ = 2087 cm^{-1} for the C≡C-group and gave a band of medium intensity at 1466 cm^{-1} for the C═C-bond.

An important criterion to determine the chain length of the often insoluble poly(but-1-en-3-ynylene) polymers is their color. In 1976 R. H. Baughman and R. R. Chance formulated for poly(but-1-en-3-ynylene)s a correlation between π–π^*-transition energy and the conjugation length,[23] which is represented by Eq. (1).

$$E_{\pi\rightarrow\pi^*} = \frac{h^2}{8m_eL^2(4k+1)} + 0.83V_0\left(1 - \frac{1}{4k}\right) \qquad (1)$$

where h=6.62618×10^{-34} J s; c=2.997925×10^{8} m s^{-1}; m_e= 9.10953×10^{-31} kg; L=1.36 Å[23]=1.36×10^{-10} m; V_0= 2.4 eV[23]=3.84526×10^{-19} J; k=number of butenyne units; the corresponding maximum absorption wavelength is calculated to

$$\lambda_{\mathrm{max}} = \lim_{k\rightarrow\infty} \lambda(k) = 622.42 \text{ nm} \qquad (2)$$

If an optimal conjugation of the butenyne units is realized the polymer maximally absorbs in the orange–red spectral field and appears blue. In the reverse case, it is possible from the color of the polymer and the corresponding absorption wavelength to deduce a conjugation length and thereby approximately a minimum chain length of the polymer chain (Fig. 8) disregarding color shifts due to torsion of the backbone or electronic effects.[24]

Corresponding to Fig. 8 the polymerization degree of **6** can be estimated to n>70 due to the intensive blue color of the polymer. The observed color-change from blue to red after the work-up is not unusual for poly(but-1-en-3-ynylene)s.[24,25] The chromophore backbone reacts sensitive to conformational changes with an absorption field shift.[26,27] In the case of **6**, destruction of the host lattice, by addition of solvent in the work-up process, leaded to a sterical relaxation of the bulky-substituted polymer under twisting of the polymer backbone. In consequence, the absorption maximum is shifted to a lower wavelength and the worked-up polymer **6** has a red color.

The quinone-substituted octa-3,5-diyne **4f** (Fig. 9) crystallized from benzene in space group $C2/c$ with Z=4 as a 1:1-benzene adduct in orange colored plates. The molecular structure of **4f** shows an inversion center. Within the scope of deviation the observed bond lengths[11] are comparable to bond lengths reported in the literature.[12] With bond angles of C3–C4–Cl1 123.3(5)°, C5–C4–Cl1 114.4(4)° and C2–C1–C7 116.7(5)°, C6–C1–C7 122.7(5)°, respectively, a significant shift is observed for the atoms Cl1 and C7 in direction to adjacent carbonyl groups.[28–31] By this, all substituents of the cyclohexa-1,4-dienyl units are arranged like paddles of a millwheel. The hexa-2,4-diynylene unit shows an S-like deformation with bond angles of C8–C9–C10 173.0(7)° and C9–C10–C10′

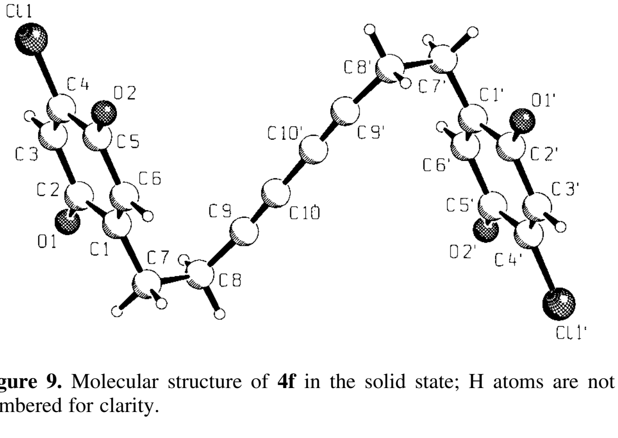


Figure 9. Molecular structure of **4f** in the solid state; H atoms are not numbered for clarity.

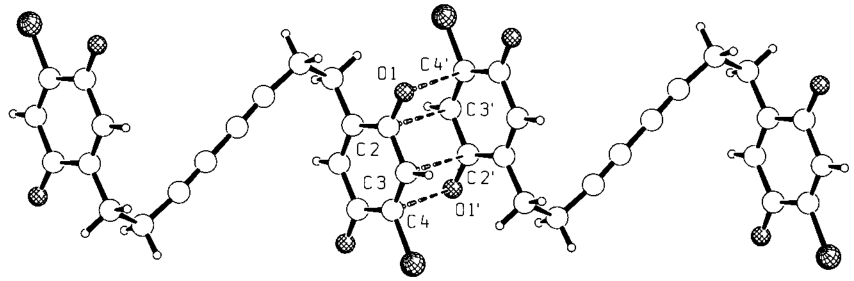


Figure 10. Part of the stacking structure of **4f** in the crystal along the diagonal plane *a*,*b* with intermolecular distances between the carbonyl unit and the vinyl double bond of O1···C4′ [3.328(8) Å] and C2···C3′ [3.414(8) Å]. Symmetry operation: ($-x$, $-y+3$, $-z$).

178.5(7)°. The torsion angles of C7–C1–C6–C5 176.9(6)° and C7–C1–C2–C3 −175.8(5)° indicate that C7 is shifted for 0.070(8) Å out of the quinone plane towards the diyne unit. With a torsion angle of C2–C1–C7–C8 73.8(6)° the quinone substituent is nearly vertically oriented to the ethylene bridge. The ethylene unit shows a *synclinal* conformation in the crystal with a torsion angle of C1–C7–C8–C9 55.2(7)°.

Octa-3,5-diyne **4f** in the crystal represents a stacking structure along the diagonal plane *a*,*b* (Fig. 10). The quinone units of neighboring molecules are oriented parallel to each other and are inclined to the stacking axis by 61°. The O1=C2–C3=C4 unit of one molecule is situated congruent over the C4′=C3′–C2′=O1′ group of an adjacent molecule.

The relative position of two neighboring quinone units of **4f** seems to be mainly steered by attractive intermolecular dipole–dipole interactions between C2–O1 and C4′–C3′ (Fig. 10) corresponding to the allocation of charge density of the β-chloro-substituted vinyloge carbonyl unit Cl–C4=C3–C2=O1. The resulting contacts have distances of O1···C4′ 3.328(8) Å and C2···C3′ 3.414(8) Å. These intermolecular distances are optimal for a topochemically controlled [2+2]photocycloaddition according to Paterno-Büchi.[32,33]

With intermolecular distances of C1···C4′ 3.812(8) Å and C6···C3′ 3.802(8) Å a [2+2]photocycloaddition of the quinone (C=C)-double bonds of neighboring molecules must be taken into account, but the (C1=C6)- and (C3′=C4′)- double bonds are shifted against each other in direction parallel to C1–C6 by 1.79 Å and vertical to C1–C6 by 0.49 Å resulting in an unfavorable orientation for a photoinduced [2+2]cycloaddition in the solid-state.

The solid-state irradiation product of **4f**, obtained by irradiation with UV light at $\lambda \geq 254$ nm for 3 h or $\lambda \geq 520$ nm for 8 h, showed oligomers of up to $n=3$ in MALDI-TOF experiments (Fig. 11). On the other hand, under thermal stress no oligomers were observed. This suggests that no poly(but-1-en-3-ynylene)s were produced by irradiation.

It is assumed that according to the topochemical parameters obtained from X-ray diffraction analysis of **4f** and the results of frontier orbital correlation based on the model compound *E*-3-chloroprop-2-ene-1-one, that a topochemical controlled [2+2]cycloaddition of **4f** under Paterno-Büchi[32,33] had taken place forming different oxetane-derivatives. Subsequent- and side-reactions are to be expected under the selected reaction conditions leading to the formation of further products.[34,35] The exact constitution of the irradiation products could not be determined, because of low yield (2–3%) and problem in separation of the oligomers obtained

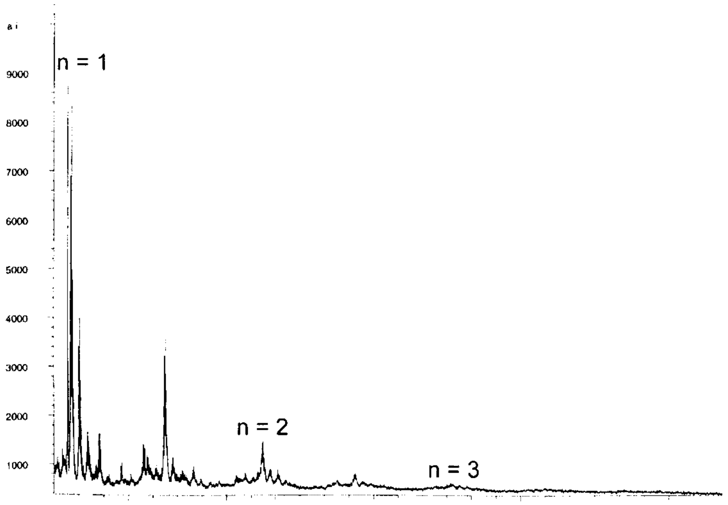


Figure 11. MALDI-TOF-spectrum of the oligomers $[\mathbf{4f}]_n^+$ ($n=1$–3) of octa-3,5-diyne **4f** after UV irradiation ($\lambda \geq 254$ nm). The signal at $m/z=379$ $[(CCA)_2^+ + H]$ is caused by the matrix CCA.

by the irradiation. The quinone-substituted octa-3,5-diynes **4a–c**, **4e** and **4g** showed no significant thermo or photo reactivity in the solid-state.

Experimental

General

Melting points: Büchi Melting Point B-540 (Switzerland); open capillary tube. IR: Bruker IFS 66. UV/Vis: HP 8452 A (diode array). NMR: Bruker AC 300 (300 and 75.5 MHz, for ^{1}H and ^{13}C, respectively); chemical shifts are relative to the solvent signal indicated (internal standard TMS). MS: Finnigan 3200 (low-resolution electron ionization; 70 eV); Vacuum Generators Micromass ZAB-2F (high-resolution electron ionization; 70 eV); and Jeol JMS-700 (fast-atom bombardment). Elemental analyses: Heraeus CHN-O-Rapid.

Diethyl ether, dimethoxyethane (DME); tetrahydrofuran (THF); and benzene were distilled from sodium benzophenone ketyl in a recirculating still prior to use. Dichloromethane, cyclohexane, *n*-hexane, petroleum ether (30–75); and tetramethylethylenediamine (tmeda) were distilled from calcium hydride. All reagents were purified according to standard methods before use unless otherwise indicated. All reactions were carried out under an inert atmosphere of argon.

The following compounds have been reported previously in the literature and were prepared as described or according to published procedures: 1-chloromethyl-2,5-dimethoxybenzene (**1a**),[36] 1-chloromethyl-2,5-dimethoxy-4-methylbenzene (**1b**),[37] 2-bromomethyl-1,4-dimethoxy-5,6-dimethylbenzene (**1c**),[38] 2-bromomethyl-1,4-dimethoxy-3,5,6-trimethylbenzene (**1d**),[39,40] 1-bromomethyl-4-fluoro-2,5-dimethoxybenzene (**1e**),[38] 1-bromomethyl-4-chloro-2,5-dimethoxybenzol (**1f**)[41] and 1-bromo-4-bromomethyl-2,5-dimethoxybenzene (**1g**).[38] Prop-2-yne-1-yl magnesium bromide was prepared from 3-bromoprop-1-yne (80% solution in toluene; purchased from Aldrich and used without further purification) and magnesium-turnings.[10]

General procedure for the synthesis of but-1-ynes 2a–g

To a solution of **1** (10 mmol) in 300 ml diethyl ether was added dropwise a solution of freshly prepared prop-2-yne-1-yl magnesium bromide (20 mmol) in 40 ml diethyl ether over a period of 30 min. After complete addition the reaction mixture was stirred at room temperature for one day, then poured into 200 ml ice water. The organic phase was separated and the watery phase extracted with diethyl ether (3×100 ml). The combined organic phases were dried over magnesium sulfate, concentrated under reduced pressure, and the residue was purified by distillation.

4-(2,5-Dimethoxyphenyl)-but-1-yne (2a). But-1-yne **2a** was obtained from **1a** in 23% yield as a colorless unstable liquid (bp$_{0.5}$ 94–96°C). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 6.89 (d, $^{4}J_{\mathrm{HH}}$=3.1 Hz, 1H, 6-*H*); 6.75 (dd, $^{3}J_{\mathrm{HH}}$=8.8 Hz, $^{4}J_{\mathrm{HH}}$=3.1 Hz, 1H, 4*H*); 6.54 (d, $^{3}J_{\mathrm{HH}}$=8.8 Hz, 1H, 3-*H*); 3.48 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 3.36 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 2.98 (t, $^{3}J_{\mathrm{HH}}$=7.5 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CCH}$); 2.52 (td, $^{3}J_{\mathrm{HH}}$=7.5 Hz, $^{4}J_{\mathrm{HH}}$=2.7 Hz, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CCH}$); 1.86 (t, $^{4}J_{\mathrm{HH}}$=2.7 Hz, 1H, $\mathrm{CH_2CH_2CC}\mathit{H}$). ^{13}C NMR (75.5 MHz, $\mathrm{C_6D_6}$): δ 153.87 ($\mathrm{COCH_3}$); 151.76 ($\mathit{C}\mathrm{OCH_3}$); 129.91 ($\mathit{C}\mathrm{CH_2CH_2CCH}$); 116.61 ($\mathit{C}\mathrm{H}$); 111.86 ($\mathit{C}\mathrm{H}$); 111.05 ($\mathit{C}\mathrm{H}$); 83.96 ($\mathrm{CCH_2CH_2}\mathit{C}\mathrm{CH}$); 68.90 ($\mathrm{CCH_2CH_2C}\mathit{C}\mathrm{H}$); 55.01 (s, $\mathrm{CO}\mathit{C}\mathrm{H_3}$); 54.96 ($\mathrm{CO}\mathit{C}\mathrm{H_3}$); 30.22 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_2{-}CCH}$); 18.98 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_2CCH}$). MS (EI, 70 eV): *m*/*z* 190 ($\mathrm{M^+}$, 68%); 151 ([$\mathrm{M^+{-}CH_2CCH}$], 100%). MS (HR, EI): $\mathrm{M^+}$ calcd: 190.0994, found: 190.0970. IR (KBr): $\tilde{\nu}$ cm^{-1} 3291 (s, $\equiv$C–H); 2116 (w, C$\equiv$C).

4-(2,5-Dimethoxy-4-methylphenyl)-but-1-yne (2b). But-1-yne **2b** was obtained from **1b** in 81% yield as a colorless unstable liquid (bp$_{0.3}$ 101–103°C; n_{D}^{20} 1.5350). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 6.73 (s, 1H, 6*H*); 6.69 (s, 1H, 3-*H)*; 3.80 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 3.78 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 2.84 (t, $^{3}J_{\mathrm{HH}}$=7.5 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CCH}$); 2.48 (td, $^{3}J_{\mathrm{HH}}$=7.5 Hz, $^{4}J_{\mathrm{HH}}$=2.6 Hz, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CCH}$); 2.23 (s, 3H, $\mathrm{CC}\mathit{H}_3$); 1.99 (t, $^{4}J_{\mathrm{HH}}$=2.6 Hz, 1H, $\mathrm{CH_2CH_2CC}\mathit{H}$). ^{13}C NMR (75.5 MHz, $\mathrm{C_6D_6}$): δ 151.69 ($\mathrm{COCH_3}$); 151.24 ($\mathit{C}\mathrm{OCH_3}$); 126.50 ($\mathit{C}\mathrm{CH_3}$); 125.00 ($\mathit{C}\mathrm{CH_2CH_2CCH}$); 113.68 ($\mathit{C}\mathrm{H}$); 112.98 ($\mathit{C}\mathrm{H}$); 84.25 ($\mathrm{CCH_2CH_2}\mathit{C}\mathrm{CH}$); 68.83 ($\mathrm{CCH_2CH_2C}\mathit{C}\mathrm{H}$); 55.27 ($\mathrm{CO}\mathit{C}\mathrm{H_3}$); 55.20 ($\mathrm{CO}\mathit{C}\mathrm{H_3}$); 30.15 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_2{-}CCH}$); 19.34 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_2CCH}$); 16.12 ($\mathrm{C}\mathit{C}\mathrm{H_3}$). MS (EI, 70 eV): *m*/*z* 204 ($\mathrm{M^+}$, 84%); 165 ([$\mathrm{M^+{-}C_3H_3}$], 100%); 135 ([$\mathrm{M^+{-}CH_2O}$], 37%). MS (HR, EI): $\mathrm{M^+}$ calcd: 204.1150, found: 204.1173. IR (KBr): $\tilde{\nu}$ cm^{-1} 3292 (s, $\equiv$C–H); 2116 (w, C$\equiv$C).

4-(2,5-Dimethoxy-3,4-dimethylphenyl)-but-1-yne (2c). But-1-yne **2c** was obtained from **1c** in 52% yield as a colorless unstable liquid (bp$_{0.16}$ 94°C; n_{D}^{20} 1.5294). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 6.62 (s, 1H, 6-*H*); 3.80 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 3.68 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 2.87 (t, $^{3}J_{\mathrm{HH}}$=7.6 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CCH}$); 2.51 (td, $^{3}J_{\mathrm{HH}}$=7.6 Hz, $^{4}J_{\mathrm{HH}}$=2.7 Hz, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CCH}$); 2.21 (s, 3H, $\mathrm{CC}\mathit{H}_3$); 2.13 (s, 3H, $\mathrm{CC}\mathit{H}_3$); 2.01 (t, $^{4}J_{\mathrm{HH}}$=2.7 Hz, 2H, $\mathrm{CH_2CH_2CC}\mathit{H}$). ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 153.56 ($\mathit{C}\mathrm{OCH_3}$); 150.29 ($\mathit{C}\mathrm{OCH_3}$); 130.76 ($\mathit{C}\mathrm{CH_3}$); 130.14 ($\mathit{C}\mathrm{CH_3}$); 124.76 ($\mathit{C}\mathrm{CH_2CH_2CCH}$); 109.28 ($\mathit{C}\mathrm{H}$); 84.30 ($\mathrm{CCH_2CH_2}\mathit{C}\mathrm{CH}$); 68.63 ($\mathrm{CCH_2CH_2C}\mathit{C}\mathrm{H}$); 60.87 ($\mathrm{CO}\mathit{C}\mathrm{H_3}$); 55.70 ($\mathrm{CO}\mathit{C}\mathrm{H_3}$); 29.55 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_2CCH}$); 19.80 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_2CCH}$); 12.74 ($\mathrm{C}\mathit{C}\mathrm{H_3}$); 11.87 ($\mathrm{C}\mathit{C}\mathrm{H_3}$). MS (EI, 70 eV): *m*/*z* 218 ($\mathrm{M^+}$, 88%); 203 ([$\mathrm{M^+{-}CH_3}$], 20%); 179 ([$\mathrm{M^+{-}C_3H_3}$], 100%). MS (HR, EI): $\mathrm{M^+}$ calcd: 218.1307, found: 218.1319. IR (NaCl): $\tilde{\nu}$ cm^{-1} 3289 (s, $\equiv$C–H); 2117 (w, C$\equiv$C).

4-(2,5-Dimethoxy-3,4,6-trimethylphenyl)-but-1-yne (2d). But-1-yne **2d** was obtained from **1d** in 49% yield as a colorless unstable solid (mp 36.1°C). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 3.67 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 3.62 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{O}$); 2.88 (t, $^{3}J_{\mathrm{HH}}$=7.8 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CCH}$); 2.35 (td, $^{3}J_{\mathrm{HH}}$=7.8 Hz, $^{4}J_{\mathrm{HH}}$=2.6 Hz, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CCH}$); 2.23 (s, 3H, 6-$\mathrm{CC}\mathit{H}_3$); 2.16 (s, 6H, 3,4-$\mathrm{CC}\mathit{H}_3$); 1.98 (t, $^{4}J_{\mathrm{HH}}$=2.6 Hz, 2H, $\mathrm{CH_2CH_2CC}\mathit{H}$). ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ 152.84 ($\mathit{C}\mathrm{OCH_3}$); 152.79 ($\mathit{C}\mathrm{OCH_3}$); 130.05 ($\mathit{C}\mathrm{CH_2{-}CH_2CCH}$); 128.82 ($\mathit{C}\mathrm{CH_3}$); 127.82 ($\mathit{C}\mathrm{CH_3}$); 127.18 ($\mathit{C}\mathrm{CH_3}$); 84.26 ($\mathrm{CCH_2CH_2}\mathit{C}\mathrm{CH}$); 68.06 ($\mathrm{CCH_2CH_2C}\mathit{C}\mathrm{H}$); 60.69 ($\mathrm{CO}\mathit{C}\mathrm{H_3}$); 59.83 ($\mathrm{CO}\mathit{C}\mathrm{H_3}$); 26.61 ($\mathrm{C}\mathit{C}\mathrm{H_2{-}CH_2CCH}$); 18.89 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_2CCH}$); 12.62 ($\mathrm{C}\mathit{C}\mathrm{H_3}$); 12.50 ($\mathrm{C}\mathit{C}\mathrm{H_3}$); 11.96 (6-$\mathrm{C}\mathit{C}\mathrm{H_3}$). MS (EI, 70 eV): *m*/*z* 232 ($\mathrm{M^+}$, 65%); 217 ([$\mathrm{M^+{-}CH_3}$], 14%); 193 ([$\mathrm{M^+{-}C_3H_3}$], 100%). MS (HR, EI): M$^+$ calcd: 232.1463, found: 232.1472. IR (KBr): $\tilde{\nu}$ cm^{-1} 3307 (s, $\equiv$C–H); 2115 (w, C$\equiv$C).

4-(4-Fluoro-2,5-dimethoxyphenyl)-but-1-yne (2e). But-1-yne **2e** was obtained from **1e** in 59% yield as a colorless unstable liquid which solidifies on standing (bp$_{0.07}$ 105–107°C; mp 54°C). ^{1}H NMR (300 MHz, C_6D_6): δ 6.70 (d, $^4J_{HF}$=9.5 Hz, 1H, 6-*H*); 6.47 (d, $^3J_{HF}$=12.8 Hz, 1H, 3-*H*); 3.50 (s, 3H, CH_3O); 3.14 (s, 3H, CH_3O); 2.86 (t, $^3J_{HH}$=7.5 Hz, 2H, CH_2CH$_2$CCH); 2.45 (td, $^3J_{HH}$=7.5 Hz, $^4J_{HH}$=2.6 Hz, 2H, CH$_2$CH_2CCH); 1.88 (t, $^4J_{HH}$=2.6 Hz, 2H, CH$_2$CH$_2$CC*H*). ^{13}C NMR (75.5 MHz, C_6D_6): δ 151.96 (d, $^1J_{CF}$=244.3 Hz, *C*F); 151.45 (d, $^3J_{CF}$=7.8 Hz, 2*C*OCH$_3$); 141.14 (d, $^2J_{CF}$=10.8 Hz, 5-*C*OCH$_3$); 123.88 (d, $^4J_{CF}$=3.8 Hz, *C*CH$_2$CH$_2$CC); 116.99 (d, $^3J_{CF}$=3.0 Hz, 6*C*H); 100.41 (d, $^2J_{CF}$=22.1 Hz, 3-*C*H); 83.79 (CCH$_2$CH$_2$*C*CH); 69.05 (CCH$_2$CH$_2$C*C*H); 56.71 (CO*C*H$_3$); 55.00 (CO*C*H$_3$); 29.55 (C*C*H$_2$CH$_2$CCH); 19.06 (CCH$_2$*C*H$_2$CCH). MS (EI, 70 eV): *m/z* 208 (M$^+$, 33%); 169 ([M$^+$−C$_3$H$_3$], 100%). MS (HR, EI): M$^+$ calcd: 208.0900, found: 208.0927. IR (KBr): $\tilde{\nu}$ cm^{-1} 3287 (s, $\equiv$C–H); 2114 (w, C$\equiv$C).

4-(4-Chloro-2,5-dimethoxyphenyl)-but-1-yne (2f). But-1-yne **2f** was obtained from **1f** in 41% yield as a colorless unstable liquid which solidifies on standing (bp$_{0.17}$ 83°C; mp 54°C). ^{1}H NMR (300 MHz, C_6D_6): δ 6.80 (s, 1H, 3-*H*); 6.60 (s, 1H, 6*H*); 3.44 (s, 3H, CH_3O); 3.14 (s, 3H, CH_3O); 2.85 (t, $^3J_{HH}$=7.5 Hz, 2H, CH_2CH$_2$CCH); 2.44 (td, $^3J_{HH}$=7.5 Hz, $^4J_{HH}$=2.7 Hz, 2H, CH$_2$CH_2CCH); 1.87 (t, $^4J_{HH}$=2.7 Hz, 1H, CH$_2$CH$_2$CC*H*). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 151.55 (*C*OCH$_3$); 149.07 (*C*OCH$_3$); 128.09 (*C*CH$_2$CH$_2$CCH); 120.39 (4-*C*Cl); 115.15 (6-*C*H); 113.01 (3*C*H); 84.03 (CCH$_2$CH$_2$*C*CH); 68.83 (CCH$_2$CH$_2$C*C*H); 56.89 (CO*C*H$_3$); 55.97 (CO*C*H$_3$); 29.66 (C*C*H$_2$CH$_2$–CCH); 18.78 (CCH$_2$*C*H$_2$CCH). MS (EI, 70 eV): *m/z* 224 (M$^+$, 32%); 185 ([M$^+$−CH$_2$CCH], 100%). MS (HR, EI): M$^+$ calcd: 224.0604, found: 224.0604. IR (KBr-Film): $\tilde{\nu}$ cm^{-1} 3274 (s, $\equiv$C–H); 2111 (w, C$\equiv$C).

4-(4-Brom-2,5-dimethoxyphenyl)-but-1-yne (2g). But-1-yne **2g** was obtained from **1g** in 40% yield as a colorless unstable liquid which solidifies on standing (bp$_{0.02}$ 108–109°C; mp 43–45°C). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.00 (s, 1H, 3-*H*); 6.78 (s, 1H, 6*H*); 3.82 (s, 3H, CH_3O); 3.75 (s, 3H, CH_3O); 2.78 (t, $^3J_{HH}$=7.4 Hz, 2H, CH_2CH$_2$CCH); 2.43 (td, $^3J_{HH}$=7.4 Hz, $^4J_{HH}$=2.6 Hz, 2H, CH$_2$CH_2CCH); 1.94 (t, $^4J_{HH}$=2.6 Hz, 1H, CH$_2$CH$_2$CC*H*). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 151.64 (*C*OCH$_3$); 149.59 (*C*OCH$_3$); 128.70 (*C*CH$_2$CH$_2$CCH); 116.52 (3-*C*H); 114.77 (6*C*H); 109.06 (4-*C*Br); 83.77 (CCH$_2$CH$_2$*C*CH); 68.63 (CCH$_2$CH$_2$–C*C*H); 56.76 (CO*C*H$_3$); 55.80 (CO*C*H$_3$); 29.51 (C*C*H$_2$CH$_2$CCH); 18.47 (CCH$_2$*C*H$_2$CCH). MS (EI, 70 eV): *m/z* 270 ([M+2]$^+$, 58%); 268 (M$^+$, 61%); 229 ([M$^+$−CH$_2$CCH], 100%); 199 ([M$^+$−CH$_2$CCH–CH$_2$O]$^+$, 37%). MS (HR, EI): M$^+$ calcd: 268.0099, found: 268.0101. IR (KBr): $\tilde{\nu}$ cm^{-1} 3294 (s, $\equiv$C–H); 2113 (w, C$\equiv$C).

General procedure for the synthesis of octa-3,5-diynes 3a–g

To a solution of **3** (20 mmol) in 10 ml DME, a suspension of 0.594 g (6 mmol) copper(I) chloride and 1.046 g (9 mmol) tmeda in 40 ml DME was slowly added at 30–35°C. At 35–36°C, a stream of oxygen was passed through the mixture for one to two days. The reaction mixture was then poured into 300 ml water. The resulting precipitate was filtered off and recrystallized twice from the corresponding solvent (cf. mp).

1,8-Bis(2,5-dimethoxyphenyl)-octa-3,5-diyne (3a). Octa-3,5-diyne **3a** was obtained from **2a** in 34% yield as a colorless solid (mp 79–80°C; *n*-hexane). ^{1}H NMR (300 MHz, C_6D_6): δ 6.84 (d, $^4J_{HH}$=3.0 Hz, 2H, 6-H); 6.75 (dd, $^3J_{HH}$=8.8 Hz, $^4J_{HH}$=3.0 Hz, 2H, 4H); 6.54 (d, $^3J_{HH}$=8.8 Hz, 2H, 3-H); 3.50 (s, 6H, CH_3O); 3.36 (s, 6H, CH_3O); 2.88 (t, $^3J_{HH}$=7.5 Hz, 4H, CH_2CH$_2$CC); 2.49 (t, $^3J_{HH}$=7.5 Hz, 4H, CH$_2$CH_2CC). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 154.07 (*C*OCH$_3$); 151.90 (*C*OCH$_3$); 129.86 (*C*CH$_2$CC); 116.57 (3-*C*H); 112.36 (6-*C*H); 111.31 (4*C*H); 77.48 (CH$_2$CH$_2$*C*C); 67.05 (CH$_2$CH$_2$C*C*); 55.25 (CO*C*H$_3$); 55.21 (CO*C*H$_3$); 30.17 (C*C*H$_2$CH$_2$CC); 20.05 (CCH$_2$*C*H$_2$CC). MS (EI, 70 eV): *m/z* 378 (M$^+$, 26%); 151 ([C$_6$H$_3$(OCH$_3$)$_2$CH$_2$]$^+$, 100%). MS (HR, EI): M$^+$ calcd: 378.1831, found: 378.1835. IR (KBr): $\tilde{\nu}$ cm^{-1} 2149 (w, C$\equiv$C). UV/Vis (CH$_2$Cl$_2$): λ nm (ϵ) 226 (18220); 292 (10445). Anal. calcd for $C_{24}H_{26}O_4$: C 76.17%, H 6.93%; found: C 76.04%, H 7.07%.

1,8-Bis(2,5-dimethoxy-4-methylphenyl)-octa-3,5-diyne (3b). Octa-3,5-diyne **3b** was obtained from **2b** in 85% yield as colorless plates crystallizing in two modifications [mp 114.4°C (ethanol) and mp 113.4°C (methanol)]. ^{1}H NMR (500 MHz, C_6D_6): δ 6.54 (s, 2H, 6-*H*); 6.47 (s, 2H, 3-*H*); 3.44 (s, 6H, 2-CH_3O); 3.29 (s, 6H, 5CH_3O); 2.84 (t, $^3J_{HH}$=7.3 Hz, 4H, CH_2CH$_2$CC); 2.45 (t, $^3J_{HH}$=7.3 Hz, 4H, CH$_2$CH_2CC); 2.28 (s, 6H, CCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ 151.63 (*C*OCH$_3$); 151.07 (*C*OCH$_3$); 126.21 (4-*C*CH$_3$); 124.98 (*C*CH$_2$CH$_2$C$\equiv$C); 113.56 (3-*C*H); 112.76 (6*C*H); 77.45 (CH$_2$CH$_2$*C*$\equiv$C); 66.86 (CH$_2$CH$_2$C$\equiv$*C*); 55.21 (CO*C*H$_3$); 55.11 (CO*C*H$_3$); 29.86 (C*C*H$_2$CH$_2$C$\equiv$C); 20.18 (CCH$_2$*C*H$_2$C$\equiv$C); 16.24 (4-C*C*H$_3$). MS (EI, 70 eV): *m/z* 406 (M$^+$, 30%); 165 ([C$_6$H$_2$(CH$_3$)(OCH$_3$)$_2$CH$_2$]$^+$, 100%). MS (HR, EI): M$^+$ calcd: 406.2159, found: 406.2144. IR (KBr): $\tilde{\nu}$ cm^{-1} 2155 (w, C$\equiv$C). UV/Vis (CH$_2$Cl$_2$): λ nm (ϵ) 224 (18850); 292 (9957). Anal. calcd for $C_{26}H_{30}O_4$: C 76.82%, H 7.44%; found: C 76.66%, H 7.50%.

1,8-Bis(2,5-dimethoxy-3,4-dimethylphenyl)-octa-3,5-diyne (3c). Octa-3,5-diyne **3c** was obtained from **2c** in 81% yield as colorless light-sensitive needles (mp 130.9°C; *n*-hexane). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.58 (s, 2H, 6-*H*); 3.78 (s, 6H, CH_3O); 3.65 (s, 6H, CH_3O); 2.83 (t, $^3J_{HH}$=7.5 Hz, 4H, CH_2CH$_2$CC); 2.53 (t, $^3J_{HH}$=7.5 Hz, 4H, CH$_2$CH_2CC); 2.19 (s, 6H, CCH_3); 2.11 (s, 6H, CCH_3). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 153.42 (*C*OCH$_3$); 150.11 (*C*OCH$_3$); 130.62 (*C*CH$_3$); 129.72 (*C*CH$_3$); 124.72 (*C*CH$_2$CH$_2$CC); 109.22 (6-*C*H); 77.22 (CH$_2$CH$_2$*C*C); 65.74 (CH$_2$CH$_2$C*C*); 60.75 (CO*C*H$_3$); 55.60 (CO*C*H$_3$); 29.26 (C*C*H$_2$CH$_2$CC); 20.53 (CCH$_2$*C*H$_2$CC); 12.58 (C*C*H$_3$); 11.71 (C*C*H$_3$). MS (EI, 70 eV): *m/z* 434 (M$^+$, 28%); 179 ([C$_6$H(CH$_3$)$_2$(OCH$_3$)$_2$CH$_2$]$^+$, 100%). MS (HR, EI): M$^+$ calcd: 434.2457, found: 434.2455. IR (KBr): $\tilde{\nu}$ cm^{-1} 2146 (w, C$\equiv$C). UV/Vis (CH$_2$Cl$_2$): λ nm (ϵ) 234 (9585); 286 (5630). Anal. calcd for $C_{28}H_{34}O_4$: C 77.39%, H 7.89%; found: C 77.29%, H 7.87%.

1,8-Bis(2,5-dimethoxy-3,4,6-trimethylphenyl)-octa-3,5-diyne (3d). Octa-3,5-diyne **3d** was obtained from **2b** in 52% yield as colorless thin plates (mp 161.1°C; *n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 6H, CH_3O); 3.62 (s, 6H, CH_3O); 2.87 (t, $^3J_{HH}$=7.6 Hz, 4H, CH_2CH_2CC); 2.40 (t, $^3J_{HH}$=7.6 Hz, 4H, CH_2CH_2CC); 2.23 (s, 6H, 6-CCH_3); 2.16 (s, 6H, 4-CCH_3); 2.15 (s, 6H, 3-CCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ 153.09 ($COCH_3$); 152.99 ($COCH_3$); 130.04 (CCH_3); 129.14 (CCH_3); 128.08 (CCH_3); 127.41 (CCH_2CC); 77.56 (CH_2CH_2CC); 65.49 (CH_2CH_2CC); 60.92 ($COCH_3$); 60.08 ($COCH_3$); 26.69 (CCH_2CH_2CC); 19.96 (CCH_2CH_2CC); 12.84 (CCH_3); 12.73 (CCH_3); 12.19 (CCH_3). MS (EI, 70 eV): *m*/*z* 462 (M^+, 18%); 193 ($[C_6H(CH_3)_3(OCH_3)_2CH_2]^+$, 100%). MS (HR, EI): M^+ calcd: 462.2770, found: 462.2752. IR (KBr): $\tilde{\nu}$ cm^{-1} 2148 (w, C$\equiv$C). UV/VIS (CH_2Cl_2): λ nm (ϵ) 234 (7016); 258 (984); 274 (1651); 280 (1762). Anal. calcd for $C_{30}H_{38}O_4$: C 77.89%, H 8.28%; found: C 77.65%, H 8.29%.

1,8-Bis(4-fluoro-2,5-dimethoxyphenyl)-octa-3,5-diyne (3e). Octa-3,5-diyne **3e** was obtained from **2e** in 85% yield as colorless needles (mp 98.2°C; methanol). ^{1}H NMR (300 MHz, C_6D_6): δ 6.68 (d, $^4J_{HF}$=9.5 Hz, 1H, 6-*H*); 6.46 (d, $^3J_{HF}$=12.8 Hz, 1H, 3-*H*); 3.54 (s, 3H, CH_3O); 3.15 (s, 3H, CH_3O); 2.78 (t, $^3J_{HH}$=7.3 Hz, 2H, CH_2CH_2CC); 2.44 (t, $^3J_{HH}$=7.3 Hz, 2H, CH_2CH_2CC). ^{13}C NMR (75.5 MHz, C_6D_6): δ 152.23 (d, $^1J_{CF}$=244.5 Hz, *C*F); 151.64 (d, $^3J_{CF}$=7.8 Hz, 2$COCH_3$); 141.44 (d, $^2J_{CF}$=10.8 Hz, 5-$COCH_3$); 123.82 (d, $^4J_{CF}$=3.8 Hz, CCH_2CH_2CC); 117.14 (d, $^3J_{CF}$=3.0 Hz, 6*C*H); 100.69 (d, $^2J_{CF}$=22.1 Hz, 3-*C*H); 77.45 (CCH_2CH_2CCH); 67.13 (CCH_2CH_2CCH); 56.96 ($COCH_3$); 55.28 ($COCH_3$); 29.51 (CCH_2CH_2CCH); 20.01 (CCH_2CH_2CCH). MS (EI, 70 eV): *m*/*z* 414 (M^+, 30%); 169 ($[C_6H_2(F)(OCH_3)_2CH_2]^+$, 100%). MS (HR, EI): M^+ calcd: 414.1643, found: 414.1646. IR (KBr): $\tilde{\nu}$ cm^{-1} 2149 (br. w, C$\equiv$C). UV/Vis (CH_2Cl_2): λ nm (ϵ) 226 (15709); 288 (8422). Anal. calcd for $C_{24}H_{24}F_2O_4$: C 69.55%, H 5.84%; found: C 69.36%, H 5.85%.

1,8-Bis(4-chloro-2,5-dimethoxyphenyl)-octa-3,5-diyne (3f). Octa-3,5-diyne **3f** was obtained from **2b** in 48% yield as colorless needles (mp 151°C; benzene). ^{1}H NMR (300 MHz, C_6D_6): δ 6.68 (s, 2H, 3-*H*); 6.49 (s, 2H, 6-*H*); 3.39 (s, 6H, 2-CH_3O); 3.05 (s, 6H, 5CH_3O); 2.66 (t, $^3J_{HH}$=7.3 Hz, 4H, CH_2CH_2CC); 2.32 (t, $^3J_{HH}$=7.3 Hz, 4H, CH_2CH_2CC). ^{13}C NMR (75.5 MHz, C_6D_6): δ 151.44 ($COCH_3$); 148.69 ($COCH_3$); 127.74 (CCH_2CC); 120.42 (4-*C*Cl); 115.07 (6-*C*H); 112.83 (3*C*H); 77.20 (CH_2CH_2CC); 65.99 (CH_2CH_2CC); 56.86 (2$COCH_3$); 55.94 (5-$COCH_3$); 29.44 (CCH_2CH_2CC); 19.65 (CCH_2CH_2CC). MS (EI, 70 eV): *m*/*z* 448 ($[M+2]^+$, 9%); 446 (M^+, 13%); 185 ($[C_6H_2(Cl^{35})(OCH_3)_2CH_2]^+$, 100%). MS (HR, EI): M^+ calcd: 446.1052, found: 446.1046. IR (KBr): $\tilde{\nu}$ cm^{-1} 2160 (w, C$\equiv$C). UV/VIS (CH_2Cl_2): λ nm (ϵ) 230 (17998); 296 (10704). Anal. calcd for $C_{24}H_{24}Cl_2O_4$: C 64.44%, H 5.41%, Cl 15.85%; found: C 64.38%, H 5.37%, Cl 15.92%.

1,8-Bis(4-bromo-2,5-dimethoxyphenyl)-octa-3,5-diyne (3g). Octa-3,5-diyne **3g** was obtained from **2g** in 74% yield as colorless crystals (mp 156°C; cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99 (s, 2H, 3-*H*); 6.76 (s, 2H, 6-*H*); 3.82 (s, 6H, CH_3O); 3.75 (s, 6H, CH_3O); 2.76 (t, $^3J_{HH}$=7.3 Hz, 4H, CH_2CH_2CC); 2.47 (t, $^3J_{HH}$=7.3 Hz, 4H, CH_2CH_2CC). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 151.50 ($COCH_3$); 149.52 ($COCH_3$); 128.31 (CCH_2CC); 115.47 (3-*C*H); 114.66 (6*C*H); 109.06 (4-*C*Br); 76.90 (CH_2CH_2CC); 65.76 (CH_2CH_2CC); 56.71 ($COCH_3$); 55.73 ($COCH_3$); 29.24 (CCH_2CH_2CC); 19.29 (CCH_2CH_2CC). MS (EI, 70 eV): *m*/*z* 538 ($[M+4]^+$, 17%); 536 ($[M+2]^+$, 34%); 534 (M^+, 18%); 229 ($[C_6H_2(Br^{79})(OCH_3)_2CH_2]^+$, 100%). MS (HR, EI): M^+ calcd: 534.0041, found: 534.0003. IR (KBr): $\tilde{\nu}$ cm^{-1} 2159 (w, C$\equiv$C). UV/Vis (CH_2Cl_2): λ nm (ϵ) 224 (29480); 296 (14157). Anal. calcd for $C_{24}H_{24}Br_2O_4$: C 53.75%, H 4.51%; found: C 53.86%, H 4.62%.

General procedure for the synthesis of octa-3,5-diynes 4a–g

To a stirred solution of **3** (300 μmol) in 40 ml acetonitrile at 25–30°C a solution of CAN (2.4 mmol) in 5 ml water was added in 1 ml portions. After stirring for 45 min, 30 ml of dichloromethane was added and the reaction mixture was then poured into 250 ml ice water. The organic phase was separated and the watery phase was extracted with dichloromethane (3×20 ml). The combined organic phases were dried over magnesium sulfate, the solvent was evaporated in vacuo, the residue dissolved in 3 ml toluene, and the resulting yellow solution was filtered through silica gel. The solvent was removed under reduced pressure and the residue was recrystallized twice from benzene or toluene.

1,8-Bis(3,6-dioxocyclohexa-1,4-dienyl)-octa-3,5-diyne (4a). Quinone **4a** was obtained from **3a** in 8% yield as yellow needles (mp 132.6–132.7°C; benzene). ^{1}H NMR (300 MHz, C_6D_6): δ 6.20 (s, 2H, 2-C*H*); 6.08 (s, 2H, 4-C*H*); 6.07 (s, 2H, 5-C*H*); 2.15 (t, $^3J_{HH}$=6.8 Hz, 4H, CH_2CH_2CC); 2.04 (t, $^3J_{HH}$=6.8 Hz, 4H, CH_2CH_2CC). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 187.34 (*C*O); 186.99 (*C*O); 146.39 (CCH_2CC); 136.64 (5-*C*H); 136.46 (2-*C*H); 133.52 (4-*C*H); 75.70 (CH_2CH_2CC); 66.73 (CH_2CH_2CC); 28.02 (CCH_2CH_2CC); 17.88 (CCH_2CH_2CC). MS (EI, 70 eV): *m*/*z* 318 (M^+, 34%); 236 ($[M^+-C_4H_2O_2]$, 54%); 123 ($[C_7H_7O_2]^+$, 100%). MS (HR, EI): M^+ calcd: 318.0892, found: 318.0866. IR (KBr): $\tilde{\nu}$ cm^{-1} 2150 (w, C$\equiv$C); 1655 (s, C$=$O) 1598 (m, C$=$C). UV/Vis (CH_2Cl_2): λ nm (ϵ) 248 (36884); 300 (2620). Anal. calcd for $C_{20}H_{14}O_4$: C 75.46%, H 4.43%; found: C 75.17%, H 4.62%.

1,8-Bis(4-methyl-3,6-dioxocyclohexa-1,4-dienyl)-octa-3,5-diyne (4b). Quinone **4b** was obtained from **3b** in 84% yield as yellow plates (mp 132–133°C; benzene). ^{1}H NMR (300 MHz, C_6D_6): δ 6.15 (s, 2H, 2-*H*); 5.98 (q, $^4J_{HH}$=1.5 Hz, 2H, 5-*H*); 1.97 (t, $^3J_{HH}$=6.8 Hz, 4H, CH_2CH_2CC); 1.89 (t, $^3J_{HH}$=6.8 Hz, 4H, CH_2CH_2CC); 1.51 (d, $^4J_{HH}$=1.5 Hz, 6H, CCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ 187.25 (*C*O); 186.79 (*C*O); 145.93 (CCH_2CC); 145.23 (4-CCH_3); 133.30 (*C*H); 133.18 (*C*H); 76.51 (CH_2CH_2CC); 67.52 (CH_2CH_2CC); 27.81 (CCH_2CH_2CC); 17.87 (CCH_2CH_2CC); 15.08 (4-CCH_3). MS (EI, 70 eV): *m*/*z* 346 (M^+, 40%); 211 ($[M^+-C_6H_2(CH_3)(O)_2CH_2]$, 45%); 137 ($[C_6H_2(CH_3)(O)_2CH_2+2H]^+$, 100%). MS (HR, EI): M^+ calcd: 346.1205, found: 346.1215. IR (KBr): $\tilde{\nu}$ cm^{-1} 2147 (w, C$\equiv$C); 1649 (vs, C$=$O) 1614 (m, C$=$C). UV/Vis (CH_2Cl_2): λ nm (ϵ) 254 (32341); 262 (27392); 280

(10704). Anal. calcd for $C_{22}H_{18}O_4$: C 76.29%, H 5.24%; found: C 75.70%, H 5.24%.

1,8-Bis(4,5-dimethyl-3,6-dioxocyclohexa-1,4-dienyl)-octa-3,5-diyne (4c). Quinone **4c** was obtained from **3c** in 66% yield as yellow crystals (mp 88.9–89.2°C; toluene). ^1H NMR (500 MHz, $CDCl_3$): δ 6.59 (s, 2H, 2-*H*); 2.62 (t, $^3J_{HH}$=6.8 Hz, 4H, $C\mathit{H}_2CH_2CC$); 2.50 (t, $^3J_{HH}$=6.8 Hz, 4H, $CH_2C\mathit{H}_2CC$); 2.02 (s, 12H, 4-$CC\mathit{H}_3$, 5-$CC\mathit{H}_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 187.35 (*C*O); 187.17 (*C*O); 145.96 ($\mathit{C}CH_2CC$); 141.05 ($\mathit{C}CH_3$); 140.45 ($\mathit{C}CH_3$); 133.29 (*C*H); 75.98 ($CH_2CH_2\mathit{C}C$); 66.67 ($CH_2CH_2C\mathit{C}$); 28.26 ($C\mathit{C}H_2CH_2CC$); 18.05 ($CCH_2\mathit{C}H_2CC$); 12.38 ($C\mathit{C}H_3$); 12.11 ($C\mathit{C}H_3$). MS (EI, 70 eV): *m/z* 374 (M^+, 52%); 225 ($[M^+-C_6H(CH_3)_2(O)_2CH_2]$, 50%); 151 ($[C_6H(CH_3)_2(O)_2CH_2+2H]^+$, 100%). MS (HR, EI): M^+ calcd: 374.1518, found: 374.1496. IR (KBr): $\tilde{\nu}$ cm^{-1} 2148 (w, $C{\equiv}C$); 1650 (vs, $C{=}O$); 1613 (m, $C{=}C$). UV/Vis (CH_2Cl_2): λ nm (ϵ) 258 (33861); 330 (1206). Anal. calcd for $C_{24}H_{22}O_4$: C 76.99%, H 5.92%; found: C 76.73%, H 5.91%.

1,8-Bis(2,4,5-trimethyl-3,6-dioxocyclohexa-1,4-dienyl)-octa-3,5-diyne (4d). Quinone **4d** was obtained from **3d** in 85% yield as yellow light-sensitive needles (mp 122.2–122.7°C; benzene). ^1H NMR (300 MHz, C_6D_6): δ 2.36 (t, $^3J_{HH}$=6.8 Hz, 4H, $C\mathit{H}_2CH_2CC$); 2.17 (t, $^3J_{HH}$=6.8 Hz, 4H, $CH_2C\mathit{H}_2CC$); 1.84 (s, 6H, $CC\mathit{H}_3$); 1.64 (s, 12H, $CC\mathit{H}_3$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 186.87 (*C*O); 186.37 (*C*O); 141.73 ($\mathit{C}CH_2CC$); 141.25 ($\mathit{C}CH_3$); 140.45 ($\mathit{C}CH_3$); 140.08 ($\mathit{C}CH_3$); 77.00 ($CH_2CH_2\mathit{C}C$); 67.11 ($CH_2CH_2C\mathit{C}$); 25.67 ($C\mathit{C}H_2CH_2CC$); 18.77 ($CCH_2\mathit{C}H_2CC$); 12.37 ($C\mathit{C}H_3$); 12.09 ($C\mathit{C}H_3$); 11.91 ($C\mathit{C}H_3$). MS (EI, 70 eV): *m/z* 402 (M^+, 100%); 387 ($[M^+-CH_3]$, 30%); 239 ($[M^+-C_6(CH_3)_3(O)_2CH_2]$, 40%); 165 ($[C_6(CH_3)_3(O)_2CH_2+2H]^+$, 57%). MS (HR, EI): M^+ calcd: 402.1831, found: 402.1821. IR (KBr): $\tilde{\nu}$ cm^{-1} 2159 (w, $C{\equiv}C$); 1642 (vs, $C{=}O$); 1625 (w, $C{=}C$). UV/Vis (CH_2Cl_2): λ nm (ϵ) 262 (33262). Anal. calcd for $C_{26}H_{26}O_4$: C 77.59%, H 6.51%; found: C 77.46%, H 6.46%.

1,8-Bis(4-fluoro-3,6-dioxocyclohexa-1,4-dienyl)-octa-3,5-diyne (4e). Quinone **4e** was obtained from **3e** in 12% yield as yellow thin needles (mp 166.2–167.1°C; benzene). ^1H NMR (300 MHz, C_6D_6): 6.03 δ (dt, $^4J_{HF}$=8.6 Hz, $^4J_{HH}$=1.3 Hz, 2H, 2-*H*); 5.65 (d, $^3J_{HF}$=9.7 Hz, 2H, 5-*H*); 2.08 (td, $^3J_{HH}$=6.3 Hz, $^4J_{HH}$=1.3 Hz, 4H, $C\mathit{H}_2CH_2CC$); 2.00 (t, $^3J_{HH}$=6.3 Hz, 4H, $CH_2C\mathit{H}_2CC$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 186.21 (d, $^3J_{CF}$=14.0 Hz, 6-*C*O); 179.95 (d, $^2J_{CF}$=23.9 Hz, 3-*C*O); 159.38 (d, $^1J_{CF}$=292.8 Hz, 4-*C*F); 146.41 ($\mathit{C}CH_2CC$); 131.10 (d, $^3J_{CF}$=3.1 Hz, 2-*C*H); 114.67 (d, $^2J_{CF}$=8.4 Hz, 5-*C*H); 76.38 ($CH_2CH_2\mathit{C}C$); 67.56 ($CH_2CH_2C\mathit{C}$); 27.69 ($C\mathit{C}H_2CH_2CC$); 17.72 ($CCH_2\mathit{C}H_2CC$). MS (EI, 70 eV): *m/z* 354 (M^+, 6%); 215 ($[M^+-C_6H_2(F)(O)_2CH_2]$, 24%); 141 ($[C_6H_2(F)(O)_2CH_2+2H]^+$, 100%). MS (HR, FAB): M^+ calcd: 354.0704, found: 354.0730. IR (KBr): $\tilde{\nu}$ cm^{-1} 2147 (br. w, $C{\equiv}C$); 1660 (vs, $C{=}O$) 1620 (m, $C{=}C$). UV/Vis (CH_2Cl_2): λ nm (ϵ) 252 (38811); 258 (35504); 286 (3165). Anal. calcd for $C_{20}H_{12}F_2O_4$: C 67.80%, H 3.41%; found: C 68.08%, H 3.62%.

1,8-Bis(4-chloro-3,6-dioxocyclohexa-1,4-dienyl)-octa-3,5-diyne (4f). Quinone **4f** was obtained from **3f** in 38% yield as yellow needles (mp 132–133°C; benzene). ^1H NMR (300 MHz, $CDCl_3$): δ 6.98 (s, 2H, 5-*H*); 6.78 (s, 2H, 2-*H*); 2.63 (t, $^3J_{HH}$=6.5 Hz, 4H, $C\mathit{H}_2CH_2CC$); 2.51 (t, $^3J_{HH}$=6.5 Hz, 4H, $CH_2C\mathit{H}_2CC$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 184.56 (*C*O); 179.18 (*C*O); 146.92 ($\mathit{C}CH_2CC$); 143.88 (4-*C*Cl); 133.46 (*C*H); 132.54 (*C*H); 75.41 ($CH_2CH_2\mathit{C}C$); 66.77 ($CH_2CH_2C\mathit{C}$); 27.65 ($C\mathit{C}H_2CH_2CC$); 17.73 ($CCH_2\mathit{C}H_2CC$). MS (EI, 70 eV): *m/z* 386 (M^+, 16%); 231 ($[M^+-C_6H_2(Cl^{35})(O)_2CH_2]$, 44%); 157 ($[C_6H_2(Cl^{35})(O)_2CH_2+2H]^+$, 100%). MS (HR, EI): M^+ calcd: 386.0113, found: 386.0131. IR (KBr): $\tilde{\nu}$ cm^{-1} 2149 (w, $C{\equiv}C$); 1666 (vs, $C{=}O$) 1596 (m, $C{=}C$). UV/Vis (CH_2Cl_2):λ nm (ϵ) 260 (33775); 264 (33775); 292 (5308). Anal. calcd for $(C_{20}H_{12}Cl_2O_4)_2\cdots C_6H_5CH_3$: C 65.14%, H 3.72%, Cl 16.36%; found: C 65.02%, H 3.94%, Cl 15.91%.

1,8-Bis(4-bromo-3,6-dioxocyclohexa-1,4-dienyl)-octa-3,5-diyne (4g). Quinone **4g** was obtained from **3g** in 17% yield as yellow needles (mp 141.8°C; benzene). ^1H NMR (300 MHz, C_6D_6): δ 6.51 (s, 2H, 5-*H*); 6.06 (s, 2H, 2-*H*); 1.96 (t, $^3J_{HH}$=6.5 Hz, 4H, $C\mathit{H}_2CH_2CC$); 1.88 (t, $^3J_{HH}$=6.5 Hz, 4H, $CH_2C\mathit{H}_2CC$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 183.83 (*C*O); 178.73 (*C*O); 146.08 ($\mathit{C}CH_2CC$); 137.85 (5-*C*H); 137.07 (4-*C*Br); 132.24 (2-*C*H); 76.39 ($CH_2CH_2\mathit{C}C$); 67.54 ($CH_2CH_2C\mathit{C}$); 27.69 ($C\mathit{C}H_2CH_2CC$); 17.58 ($CCH_2\mathit{C}H_2CC$). MS (EI, 70 eV): *m/z* 478 ($[M+4]^+$, 8%); 476 ($[M+2]^+$, 17%); 474 (M^+, 13%); 275 ($[M^+-C_6H_2(Br^{79})(O)_2CH_2]$, 33%); 157 ($[C_6H_2(Br^{79})(O)_2CH_2+2H]^+$, 63%); 78 ($[C_6H_6]^+$, 100%). MS (HR, EI): M^+ calcd: 386.0113, found: 386.0131. IR (KBr): $\tilde{\nu}$ cm^{-1} 2157 (w, $C{\equiv}C$); 1667 (vs, $C{=}O$) 1590 (m, $C{=}C$). UV/Vis (CH_2Cl_2): λ nm (ϵ) 268 (20250). Anal. calcd for $C_{20}H_{12}Br_2O_4$: C 50.45%, H 2.54%, Br 33.57%; found: C 50.32%, H 2.78%, Br 33.13%.

all-*E*-Poly{1,2-bis[2-(2,5-dimethoxy-3,4-dimethylphenyl)-ethyl]-but-1-en-3-ynylene} (5). A crystalline sample of 57.2 mg (131.3 μmol) **3c** was irradiated with UV light ($\lambda \geq 254$ nm) for 40 h at 15°C. To remove unreacted monomer, the orange solid was extracted with boiling THF for 3 h and then dried in vacuo to yield 21.1 mg (37%) of **5** as a orange-bronze solid (mp >320°C). MS (FD): *m/z* 1736 [$(C_{28}H_{34}O_4)_4^+$, <1%], 1302 [$(C_{28}H_{34}O_4)_3^+$, 1%], 868 [$(C_{28}H_{34}O_4)_2^+$, 8%], 434 ($C_{26}H_{26}O_4^+$, 100%). IR (KBr): $\tilde{\nu}$ cm^{-1} 2990 (m); 2940 (m); 2864 (m); 2834 (m); 2146 (w, $C{\equiv}C$); 1624 (w); 1585 (w); 1484 (m); 1468 (s); 1409 (s); 1379 (w); 1342 (w); 1317 (m); 1254 (m); 1230 (vs); 1189 (s); 1119 (s); 1093 (s); 1018 (m); 841 (m); 689 (m). Raman (solid): $\tilde{\nu}$ cm $^{-1}$ 2109 (s, $C{\equiv}C$); 1489 (m, $C{=}C$).

all-*E*-Poly{1,2-bis[2-(2,4,5-trimethyl-3,6-dioxocyclohexa-1,4-dienyl)-ethyl]-but-1-en-3-ynylene} (6). A finely powdered sample of 60.3 mg (149.2 μmol) **4d** was irradiated with UV light ($\lambda \geq 254$ nm) for 3 h at 15°C. To remove unreacted monomer, the intensive-blue solid was extracted with ethyl acetate for 2 h and then dried in vacuo to yield 18.1 mg (30%) of **6** as a red solid (mp >320°C). MS (FD): *m/z* 1608 [$(C_{26}H_{26}O_4)_4^+$, <1%], 1206 [$(C_{26}H_{26}O_4)_3^+$, <1%], 804 [$(C_{26}H_{26}O_4)_2^+$, 4%], 402 ($C_{26}H_{26}O_4^+$, 100%). IR (KBr): $\tilde{\nu}$ cm^{-1} 2941 (w); 2855 (w); 2161 (w, $C{\equiv}C$); 1643 (vs, $C{=}O$); 1625 (w, $C{=}C$); 1549 (w); 1428 (m); 1406 (w); 1375 (m); 1353 (w); 1326 (w);

Table 3. Crystal data and structure refinement for α-**3b**, β-**3b**, **3c**, **3e** and **3f**

	α-**3b**	β-**3b**	**3c**	**3e**	**3f**
Empirical formula	$C_{26}H_{30}O_4$	$C_{26}H_{30}O_4$	$C_{28}H_{34}O_4$	$C_{24}H_{24}F_2O_4$	$C_{24}H_{24}Cl_2O_4$
Molecular mass [g mol^{-1}]	406.5	406.5	434.6	414.4	447.3
Solvent	Ethanol	Methanol	*n*-hexane/benzene (10:1)	[D_6]-benzene	Toluene
Crystal size [mm]	0.5×0.25×0.05	0.3×0.2×0.05	0.4×0.4×0.4	0.4×0.4×0.4	0.5×0.4×0.3
Crystal color	Colorless	Colorless	Colorless	Yellow	Light yellow
Crystal shape	Plate	Plate	Needle	Plate	Prism
Crystal system	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Cell dimensions					
a [Å]	15.560(2)	9.2318(4)	5.023(1)	4.498(1)	9.244(2)
b [Å]	7.795(1)	10.7979(4)	35.63(1)	9.665(1)	10.503(1)
c [Å]	9.323(1)	11.3607(5)	6.655(2)	12.133(2)	11.443(2)
α [°]	90	81.665(2)	90	102.74(1)	80.55(1)
β [°]	90.73(1)	81.083(2)	92.45(2)	99.11(1)	82.02(3)
γ [°]	90	87.657(2)	90	90.86(1)	89.31(1)
V [Å^3]	1130.7(2)	1106.78(8)	1190.2(6)	507.3(2)	1085.2(3)
D_{calcd} [10^3×kg m^{-3}]	1.19	1.22	1.21	1.4	1.37
Z	2	2	2	1	2
$F(000)$	436	436	468	218	468
T [K]	193	108	193	208	193
hkl range (min/max)	0/20, 0/10, −12/12	−12/11, −14/14, −14/15	0/6, 0/46, −8/8	0/5, −12/12, −15/15	−12/12, −13/13, 0/15
$(\sin\theta\ \lambda^{-1})_{max}$ [Å^{-1}]	0.66	0.67	0.66	0.66	0.66
μ [mm^{-1}]	0.08	0.08	0.08	0.1	0.33
No. of reflns. Colld.	2802	10411	3172	2721	5467
No. of indep. Reflns.	2710	5393	2875	2417	5209
No. of reflns. Observed	1661	4018	2389	1537	4278
R_{int}	0.049	0.075	0.022	0.039	0.016
Refined parameters	139	391	149	184	359
$(\Delta\ \sigma^{-1})_{max}$	<0.01	<0.001	<0.01	<0.01	<0.002
R [$I > 2\sigma(I)$]	0.097	0.051	0.058	0.044	0.041
R_{w2}	0.264	0.126	0.184	0.107	0.118
S (gof) on F^2	1.19	1.04	1.16	1.07	1.03
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ [e Å^{-3}]	0.57/−0.41	0.29/−0.21	0.31/−0.32	0.23/−0.24	0.95/−0.28

Table 4. Crystal data and structure refinement for **4f** and **5**

	4f···benzene	**5**
Empirical formula	$C_{20}H_{12}Cl_2O_4\cdots C_6H_6$	$[C_{28}H_{34}O_4]_n$
Molecular mass [g mol^{-1}]	387.2	$[434.6]_n$
Solvent	Benzene	*n*-hexane / benzene (10:1)
Crystal size [mm]	0.3×0.2×0.02	0.4×0.4×0.4
Crystal color	Orange	Orange
Crystal shape	Plate	Needle
Crystal system	$C2/c$	$P2_1/c$
Cell dimensions		
a [Å]	23.126(4)	4.940(1)
b [Å]	9.388(1)	35.67(5)
c [Å]	11.023(1)	6.733(4)
α [°]	90	90
β [°]	114.62(2)	92.52(3)
γ [°]	90	90
V [Å^3]	2175.6(5)	1185(2)
D_{calcd} [10^3×kg m^{-3}]	1.18	1.22
Z	4	2
$F(000)$	792	468
T [K]	192	193
*hkl*range (min/max)	0/30, 0/12, −14/13	0/6, 0/47, −8/8
$(\sin\theta\ \lambda^{-})_{max}$ [Å^{-1}]	0.66	0.66
μ [mm^{-1}]	0.32	0.08
No. of reflns. Colld.	2688	3151
No. of indep. Reflns.	2627	2850
No. of reflns. observed	1237	1939
R_{int}	0.119	0.203
Refined parameters	146	193
$(\Delta\sigma^{-1})_{max}$	<0.01	<0.004
R [$I>2\sigma(I)$]	0.12	0.137
R_{w2}	0.206	0.415
S (gof) on F^2	1.09	1.97
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ [e Å^{-3}]	0.54/−0.52	0.76/−0.62

1306 (m); 1262 (m); 1216 (w); 1183 (w); 1111 (w); 1072 (m); 1028 (m); 863 (m); 829 (w); 814 (w); 795 (w); 756 (w); 716 (m); 619 (w). Raman (solid): $\tilde{\nu}$ cm^{-1} 2087 (s, C≡C); 1466 (m, C═C).

Crystal structure determinations

Crystal data of α-**3b**, β-**3b**, **3c**, **3e**, **3f**, **4f** and **5** are presented in Tables 3 and 4, respectively. Selected bond distances and angles are given in Tables 1 and 2. Data collection was performed on an Enraf-Nonius CAD4 diffractometer for α-**3b**,β-**3c**, **3e**, **3f**, **4f** and **5** or a Nonius-Kappa CCD diffractometer for β-**3b** (Mo-$K\alpha$ radiation, graphite monochromator, $\omega-2\theta$ scan with θ=2–28°). Differentiation of centric and acentric space groups with the same systematic extinctions were done by the statistic $N(Z)$-test.[42] Intensities were corrected for absorption effects in the case of **3f** (numerical[43]) and **4f** (semi empirical[44]). The structures were solved by direct methods (SHELXS-97[45]) and refined by full-matrix least-squares methods based on F^2 (SHELXL-97[45] and SHELXL-93,[29] respectively). All non-hydrogen atoms were refined using anisotropic temperature factors. For α-**3b**, **3c**, **4f** and **5** the hydrogen atoms were inserted in calculated positions. All hydrogen atoms of β-**3b**, **3e** and **3f** were refined using isotropic temperature factors. Further details on the structure determinations are given in Tables 3 and 4, respectively.[11]

The R-factors of **4f** and **5** are relatively large. In the case of **4f** disorder effects on the included benzene are responsible for disturbing the crystalline order. A single crystal of **5** consists of a mixture of only 18% of the polymer **5** and 82% of the monomer **3c**. The refinement was performed with a combination of both structures with the corresponding occupancy factors.

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