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Alternating Diacetylene Copolymer Utilizing Perfluorophenyl−Phenyl Interactions

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Abstract: The symmetric diacetylenes, 2,4-hexadiynylene dibenzoate **4** and 2,4-hexadiynylene bis(pentafluorobenzoate) **5**, as well as the unsymmetric 6-(pentafluorobenzoyloxy)hexa-2,4-diynyl benzoate **6** were prepared and investigated with respect to their reactivity toward topochemical polymerization in the crystalline state. The 1:1 cocrystal **4·5** was successfully polymerized to the corresponding poly(diacetylene) copolymer **7**, as evidenced by solid-state ^{13}C NMR and Raman spectroscopy, as well as single-crystal structure analysis of the monomer−polymer cocrystal. Thus, perfluorophenyl−phenyl interactions were utilized as complementary supramolecular synthons in the cocrystallization of two different diacetylene monomers and their unprecedented conversion into a strictly alternating diacetylene copolymer.

Introduction

The topochemical polymerization of diacetylene derivatives in the crystalline state, as first reported by Wegner et al.,[1−4] proceeds in the sense of a *trans*-stereospecific 1,4-polyaddition along a unique crystal direction and is strictly controlled by the crystal packing parameters.[5,6] If an identity period of about $d = 4.9$ Å and an inclination angle of the diacetylene axes with the packing axis of about $\phi = 45°$ are established in the monomer crystals, the molecules are placed at a distance compatible with the length of the polymer repeating unit of about 4.91 Å,[4,7] and the polymerization may proceed with only minimal packing rearrangements. In fact, crystallinity is preserved in a number of cases so that polymer single crystals are obtained.[4,7,8] The obtained poly(diacetylene)s are conjugated polymers with a macroscopic orientation of the polymer chains and interesting optoelectronic properties. While the side groups and the centers of gravity are hardly moved at all in the course of polymerization, the reacting diacetylene carbons actually experience quite a drastic displacement. This is accomplished by a shearing movement of the diacetylenes and their side groups which requires a linker that serves as a flexible hinge.[3]

The research in topochemical polymerizations has recently been reinvigorated by concepts from supramolecular chemistry and crystal engineering. For example, hydrogen bonding has been put to use in attempts to obtain topochemically polymerizable host−guest cocrystals.[9] Aromatic interactions, on the other hand, are found in a wide array of supramolecular phenomena in biology and chemistry, and their role has been increasingly appreciated and understood in supramolecular chemistry.[10] An interesting variation is the interaction of aromatic and perfluoroaromatic residues which exhibit quadrupole moments that are similar in magnitude but different in sign and are, thus, found to act as complementary supramolecular synthons similar to hydrogen bond donors and acceptors. Dougherty and Grubbs attempted to use this kind of interaction in order to promote a *cis*-stereospecific topochemical diacetylene polymerization in a cocrystal **1·2** as well as crystalline **3** (Chart 1).[11] They observed the slow formation of a low amount of an insoluble material. However, the experimental evidence for the formation of a poly(diacetylene) and its structural characterization was scarce, and the proposed pathway of polymerization remained questionable.[12]

Here, we report the synthesis and (co-) crystallization of monomers **4**,[6,13] **5**, and **6** (Chart 1), which include an ester group as a flexible linker. While attempted topochemical polymerizations of single crystalline **4**, **5**, and **6** failed, a 1:1 cocrystal **4·5** was successfully converted to the strictly alternating poly(diacetylene) copolymer **7** (Scheme 1), the structure of which

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(1) Wegner, G. *Z. Naturforsch., B* **1969**, *24*, 824.
(2) (a) Wegner, G. *Makromol. Chem.* **1971**, *145*, 85. (b) Enkelmann, V.; Leyrer, R. J.; Wegner, G. *Makromol. Chem.* **1979**, *180*, 1787.
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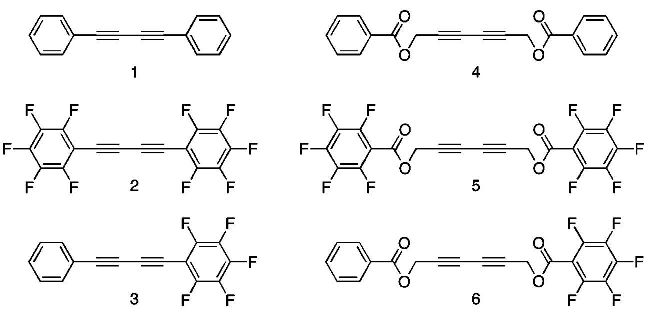
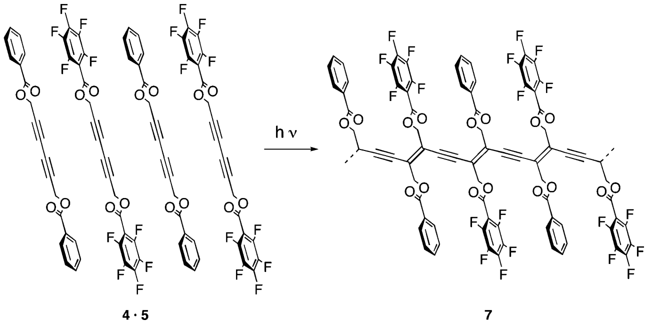
(10) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210.
(11) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Dougherty, D. A.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 248.
(12) The authors reported 18 and 16% of insoluble material in the case of **1·2** and **3**, respectively, after 18 h of irradiation with a 450 W medium-pressure Hg lamp. The authors stated that FAB MS indicated the formation of oligomers up to the hexamer. However, the postulated *cis*-stereospecific polymerization should lead to a disruption of the perfluorophenyl−phenyl interaction accompanied with a destruction of the crystals and, thus, prevent polymer formation.
(13) Hanson, A. W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 831.

10.1021/ja0603204 CCC: $33.50 © 2006 American Chemical Society

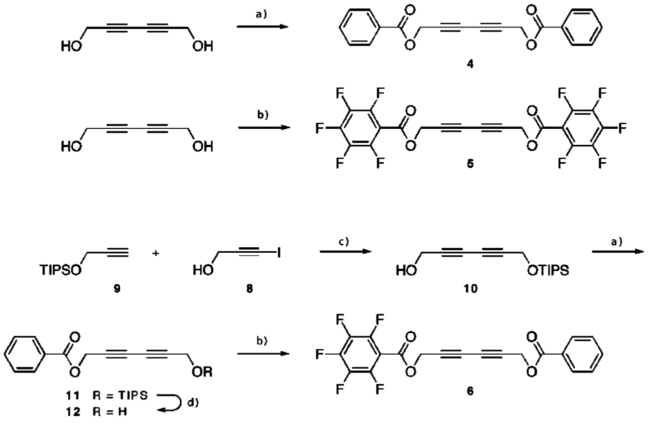
Chart 1



Scheme 1. Alternating Poly(diacetylene) Copolymer **7** by Topochemical Polymerization of Cocrystals **4·5**



Scheme 2. Synthesis of the Monomers **4**, **5**, and **6**[a]



[a] Reaction conditions: (a) PhCOCl, pyridine, DCM; (b) C_6F_5COCl, NEt_3, DCM; (c) CuCl, $NH_2OH·HCl$, *n*-$BuNH_2$, MeOH; (d) TBAF, THF, −78 °C.

was unambiguously confirmed by solid-state ^{13}C NMR spectroscopy, Raman spectroscopy, as well as X-ray structure analysis of a partially polymerized single crystal. These results are discussed in relation to the monomer crystal structures and, more particularly, the nature of the $\pi-\pi$ stacking interactions of the aromatic side groups.

Results and Discussion

Monomer Synthesis. Monomers **4** and **5** were straightforwardly synthesized by esterification of hexa-2,4-diyne-1,6-diol with benzoyl chloride and pentafluorobenzoyl chloride in 85 and 97% yield, respectively (Scheme 2). A more elaborate route had to be taken in the case of **6** because all preparation attempts via acetylene heterocoupling reactions of the corresponding propargylic and iodopropargylic esters had failed in our hands.[14] We resorted to synthesizing the unsymmetrically protected hexa-2,4-diyne-1,6-diol derivative **10** and obtained **6** in 48% yield over three steps by sequential esterification with benzoyl chloride, desilylation, and reaction with perfluorobenzoyl chloride. Single crystalline samples of **4**, **5**, and **6** as well as cocrystals **4·5** were obtained by recrystallization from DCM/hexanes in all cases.

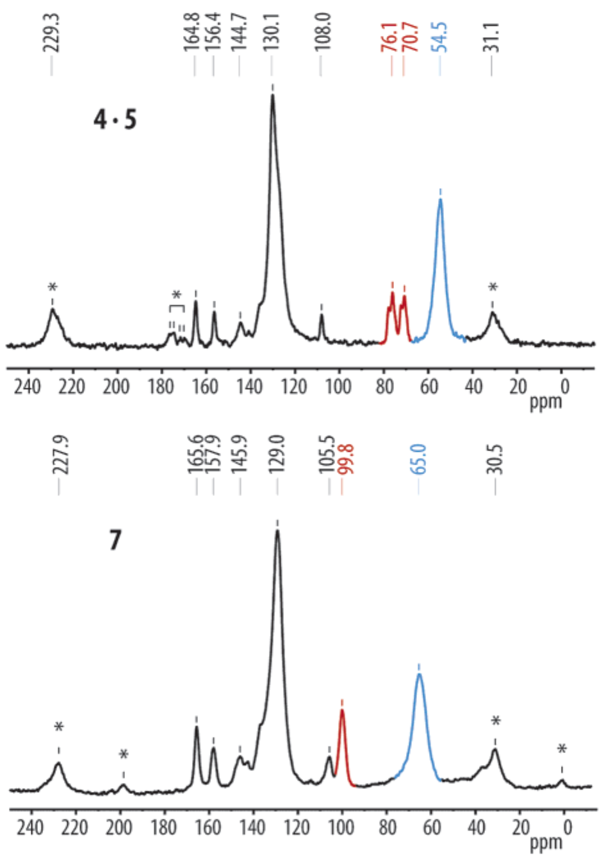


Figure 1. Solid-state ^{13}C CP-MAS NMR spectra of the cocrystal **4·5** (top) and the poly(diacetylene) copolymer **7** (bottom); spinning sidebands are marked with ∗.

Topochemical Polymerization and Polymer Characterization. UV irradiation of the cocrystals **4·5** led to the conversion into a deep red, insoluble material. After 18 h of irradiation, the pure copolymer **7** was obtained in 35% yield after extraction of residual monomer with DCM.[15]

A comparison of the solid-state CP-MAS ^{13}C NMR spectra (Figure 1) of the obtained material and the cocrystals **4·5** showed that (i) the four peaks of the acetylene carbons in **4·5** had completely disappeared; (ii) a new peak was found at $\delta = 99.8$ ppm, which would be the expected value for an acetylene group in a poly(diacetylene) backbone; and (iii) the peak of the methylene group experienced a shift from $\delta = 54.5$ to 65.0 ppm. The region where the signal of the newly formed backbone olefin groups is to be expected coincided with the large peak of the aromatic side groups.

In the Raman spectra (Figure 2) of the obtained material and the cocrystal **4·5**, the diacetylene absorption at 2260 cm^{-1} was completely replaced by the typical bands of the poly(diacetylene)

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(14) Cadiot−Chodkiewicz conditions led to a quantitative cleavage of the ester groups. Sonogashira protocols were plagued by the competing homo- and self-coupling reactions.

(15) Molecular weight determination and structural characterization of the product by solution methods was unfortunately severely hampered by its extremely poor solubility in organic solvents, including refluxing toluene, 1,2,4-trichlorobenzene, or methyl pentafluorobenzoate.

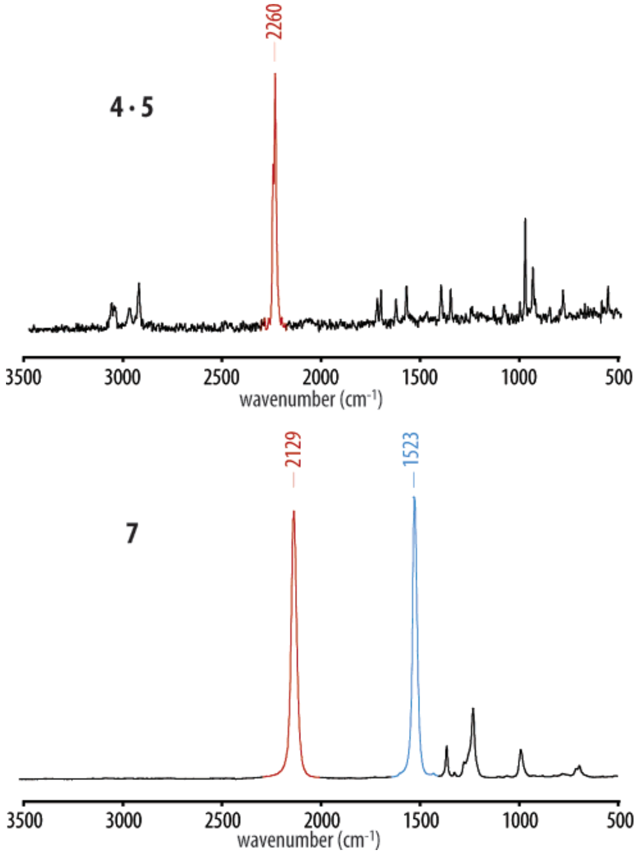

Figure 2. Raman spectra of the cocrystal **4·5** (top) and the poly(diacetylene) copolymer **7** (bottom).

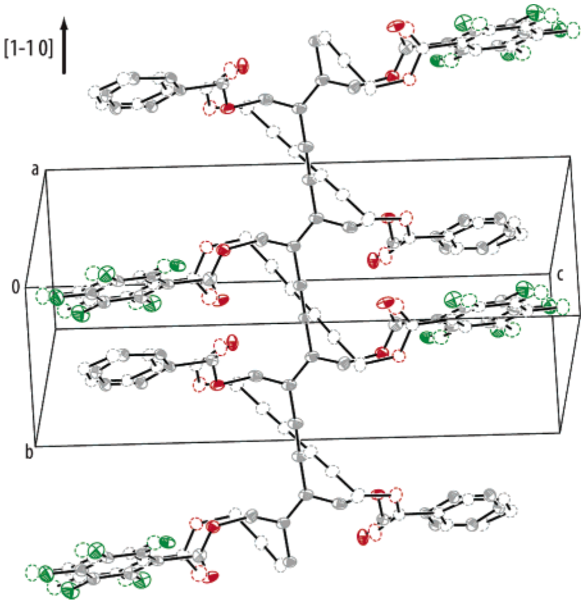

Figure 3. Crystal structure of the copolymer **7**; the disordered monomer (dashed) and polymer (solid) parts are shown as a superposition (atoms are shown as 20% thermal ellipsoids).

backbone double and triple bonds at 1523 and 2129 cm^{-1}, respectively.

Finally, the crystal structure of **4·5** after 12 h of UV irradiation could be solved as a disordered distribution of the monomers and the polymer (Figure 3). Thus, single-crystal X-ray structure analysis confirmed that the product was the strictly alternating poly(diacetylene) copolymer **7**. This result represents, to the best of our knowledge, the first unambiguously proven example of a poly(diacetylene) copolymer. It is important to remember that the topochemical diacetylene polymerization requires a crystalline order of the monomers. Therefore, the assembly of a cocrystal of two different diacetylene monomers is an indispensable prerequisite for copolymerization. The utilization of perfluorophenyl−phenyl interactions plays a crucial role in this context. The perfluorophenyl and phenyl groups serve as complementary supramolecular synthons[10] that promote a cocrystallization with an alternating placement of the two diacetylene monomers and, thus, the formation of a strictly alternating copolymer after UV irradiation.

Overall, the side groups showed a remarkable minimal displacement in the course of the polymerization (Figure 3). As expected, the ester linkages between the side groups and the diacetylene moieties serve as hinges to accommodate the shearing movement of the latter during polymerization. The polymer fiber direction was found to be the crystallographic [1 −1 0] direction, as confirmed by face indexing on the diffractometer and in agreement with morphological observations, such as the well-known mechanical anisotropy of polymer crystals.

UV irradiation of single-crystalline **4**, **5**, and **6**, on the other hand, did not seem to induce a topochemical polymerization. The materials showed an instantaneous color change from colorless to red, bright orange, and bright red, respectively, which may result from trace amounts of the polymers, but they remained virtually completely soluble even after UV irradiation of up to 3 days, both at room temperature and at temperatures of 5 °C below the substrates' melting points of 75, 68, and 72 °C, respectively. NMR, Raman, and GPC analyses confirmed that the material essentially remained the monomer in all cases. Only extensive UV irradiation of **6** led to a small amount of about 5% (w/w) of a red, intractable material which was shown to be the corresponding poly(diacetylene) by Raman spectroscopy.[16]

Monomer Crystal Structures and Polymerizability. A comparison of the single-crystal structures of **4**, **5**, and **6** as well as the cocrystals **4·5** is illustrative in order to assess the reactivity differences in topochemical polymerizations, in particular, in light of the aromatic interactions of the side groups (Table 1).

In the case of **4**,[17] the obtained structure corresponded to an isomorph which had been found to be polymerization inactive.[1,6,13] The parameters for the monomer packing were far from appropriate for a topochemical polymerization, so that the lack of reactivity does not come as a surprise. By contrast, the packing parameters in the case of **5**[17] were well in the range of the packing requirements for topochemical polymerizations, and the lack of polymerizability was, in this regard, surprising. It may, however, be a consequence of the complex side group packing. Most notably, the molecules have no center of inversion, and both the perfluorobenzoate and the methylene groups are, hence, not symmetry-related.[18] We tend to believe that this side group arrangement would not allow for an

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(16) Interestingly, the small amount of insoluble material obtained by extended irradiation of single-crystalline **6** exhibited virtually the same Raman spectrum (see Supporting Information) as the poly(diacetylene) copolymer **7**. We believe that this result may be due to the presence of a small amount of a different crystal modification with a crystal structure similar to **4·5**.

(17) See Supporting Information for figures.

Table 1. Crystal Data

	4	5	6	4·5	7
formula	$C_{20}H_{14}O_4$	$C_{20}H_4F_{10}O_4$	$C_{20}H_9F_5O_4$	$C_{20}H_9F_5O_4$	$C_{20}H_9F_5O_4$
M_w	318.31	498.23	408.27	408.27	408.27
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2(1)/n$	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$
color	colorless	colorless	colorless	colorless	dark red
a (Å)	14.038(2)	21.034(2)	16.822(2)	5.9825(7)	5.974(2)
b (Å)	4.353(1)	4.9644(9)	7.1205(7)	7.576(1)	7.589(2)
c (Å)	14.864(2)	18.847(3)	15.706(2)	19.295(2)	19.199(3)
α (deg)	90.00	90.00	90.00	96.91(1)	97.47(2)
β (deg)	117.06(2)	108.89(2)	107.423(8)	91.74(1)	91.76(2)
γ (deg)	90.00	90.00	90.00	93.07(1)	92.80(2)
V (Å^3)	808.8(3)	1862.1(5)	1795.0(3)	866.4(2)	861.4(3)
radiation	CuK_α	CuK_α	CuK_α	CuK_α	CuK_α
D_{calcd} (g cm^{-3})	1.31	1.78	1.51	1.56	1.57
μ_{calcd} (mm^{-1})	0.091	0.189	0.139	0.144	0.145
F_{000}	332	984	824	412	412
T	295	295	295	295	295
Z	2	4	4	2	2
R, $R_w{}^2$	0.067, 0.210	0.0967, 0.338	0.0593, 0.194	0.0745, 0.243	0.0843, 0.304
GOF	0.94	0.99	0.940	0.948	0.923

Table 2. Diacetylene Packing Parameters and Side Group Interactions

	Diacetylene Packing Parameters				Side Group Interaction		
compound	lattice direction	diacetylene distance d[a] (Å)	inclination angle ϕ[b]	reactive carbon distance[c] (Å)	close contact distance[d] (Å)	centroid distance[e] (Å)	stacking geometry
4	[0 1 0]	4.35(1)	59°	4.02(1)	3.60(1)	4.35(1)	parallel displaced
5	[0 1 0]	4.96(1)	49°	3.79(1)	3.32(1)	4.96(1)	parallel displaced
6	[0 1 0]	7.12(1)	38°		3.45(1)	3.78(1), 3.69(1)	staggered, eclipsed [g]
4·5	[0 1 0]	7.56(1)	35°, 38° [f]		*h*	*h*	*h*
4·5	[1 1 0]	4.62(1), 4.78(1) [f]	51°, 54° [f]	3.84(1)	3.48(1)	3.82(1)	eclipsed
4·5	[1−1 0]	4.80(1), 5.10(1) [f]	46°, 53° [f]	3.79(1)	3.44(1)	3.76(1)	eclipsed

[a] Identity period *d* along the [0 1 0] axis in **4**, **5**, **6**, and **4·5**; in the case of **4·5** in the [1 1 0] and [1 −1 0] direction, the two end-to-end distances between adjacent diacetylenes **4** and **5** are given. [b] Inclination angle between the diacetylene axis and the packing axis. [c] Distance between the two reactive carbon centers in adjacent diacetylenes. [d] Shortest contact distance between two carbons in the aromatic side groups of two adjacent molecules. [e] Distance between the centroids of the aromatic rings of two adjacent molecules. [f] The diacetylene moieties of **4** and **5** are not aligned parallel with respect to one another. [g] The two groups of disordered perfluorobenzoate groups show a staggered and an eclipsed face-to-face packing, respectively [h] The perfluorophenyl−phenyl pairs stacked along the [0 1 0] axis connect adjacent monomers **4** and **5** in [1 1 0] and in [1 −1 0], respectively; therefore, they are listed in the rows below; see Figure 5.

in-plane shearing movement of the diacetylene moieties in the [0 1 0] direction. A similarly unexpected lack of reactivity has been observed in cases of molecules with twisted side groups, such as bis(2-thiophenyl) diacetylene,[19] but has, to our knowledge, not been systematically investigated to date.

The differences in reactivity between **6** and the **4·5** cocrystal came as a surprise, but they may be explained by subtle differences in the monomer packing that is dominated by the perfluorophenyl−phenyl interactions in both cases. Whereas the benzoate and perfluorobenzoate groups in **4** and **5** exhibited a typical parallel-displaced stacking mode with a short contact of around the $\pi-\pi$ stacking distance and a larger centroid distance (Table 2), the perfluorophenyl and phenyl groups in **6** and **4·5** are stacked face-to-face with only little parallel displacement. This can be seen in the relatively similar close contact and centroid distances which are both below 4 Å (Table 2). More precisely, the resulting stacking mode in the crystallographic [0 1 0] direction comes close to the expected staggered/eclipsed $\pi-\pi$ stacking in **6**[20] and eclipsed $\pi-\pi$ stacking in **4·5**. In contrast to the crystal structures of **1·2** and **3** reported in the literature,[11] however, the diacetylene moieties are not packed with an identity period similar to the perfluorophenyl−phenyl stacking distances. In the [0 1 0] direction, the diacetylene groups of adjacent monomers are placed in different layers (Figure 4A,B), leading to "tubular arrays" of the diacetylenes with an identity period along the [0 1 0] axis of $d = 7.12$ Å in the case of **6**, and a "zigzag pattern" with an identity period along the [0 1 0] axis of $d = 7.56$ Å in the case of **4·5**. Consequently, the lack of reactivity in the case of **6** is straightforwardly explained by its monomer crystal structure.[16]

Due to the slightly different packing pattern in **4·5**, however, diacetylene packing geometries appropriate for topochemical polymerizations were observed both along the crystallographic [1 1 0] and the [1 −1 0] direction (Table 2). Along both directions, the diacetylene groups of the two different monomers **4** and **5** are placed in an alternating fashion with an identity period of $d = 9.40(1)$ and 9.90(1) Å, respectively. Hence, the average monomer distance of 4.95(1) Å in the [1 −1 0] direction was in excellent agreement with the value of 4.91 Å reported for the length of the poly(diacetylene) repeating unit.[4,7] By

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(18) The perfluorobenzoate groups exist in two groups, one of which is 50%/50% disordered. The disordered perfluorobenzoate groups are almost mirror images along the *p*-C−CH_2 axis. As the disorder has virtually no influence on the placement of the diacetylene moieties, it is unlikely that they are the reason for the lack of reactivity.

(19) Sarkar, A.; Talwar, S. S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4141.

(20) The benzoate groups show a 50%/50% disorder similar to the perfluorophenyl groups in **5**. The disordered benzoate groups are almost mirror images along the *p*-C−CH_2 axis. In the two disordered cases, the perfluorophenyl and phenyl groups stack face-to-face with a small parallel displacement, coming close to an eclipsed and a staggered $\pi-\pi$ stacking, respectively.

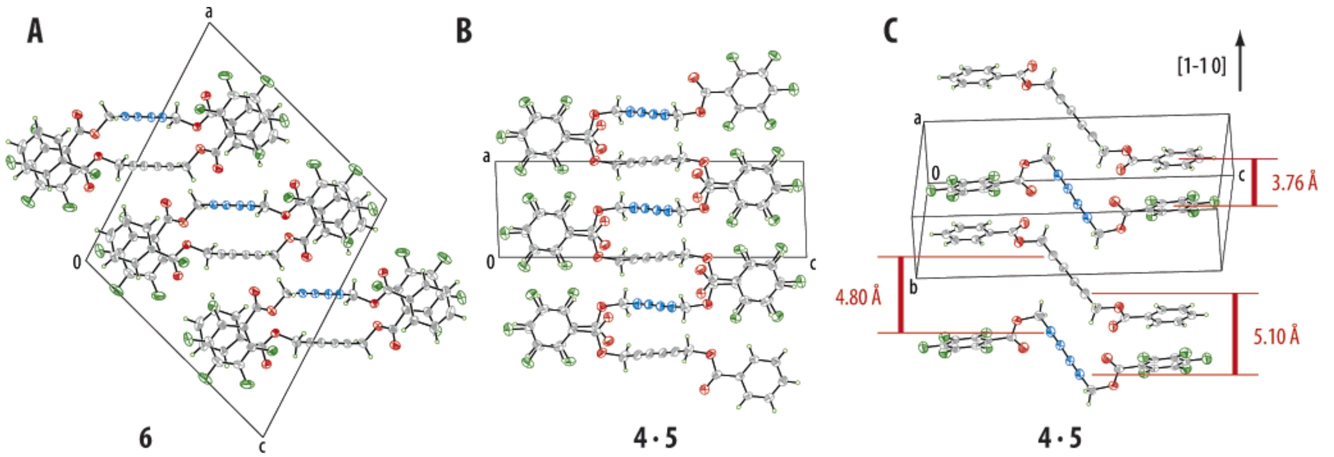

Figure 4. Comparison of the crystal structures of (A) **6** and (B,C) **4·5**; diacetylene groups of adjacent molecules **6** in (A), as well as **4** and **5** in (B) and (C) are labeled in different colors (blue and grey).

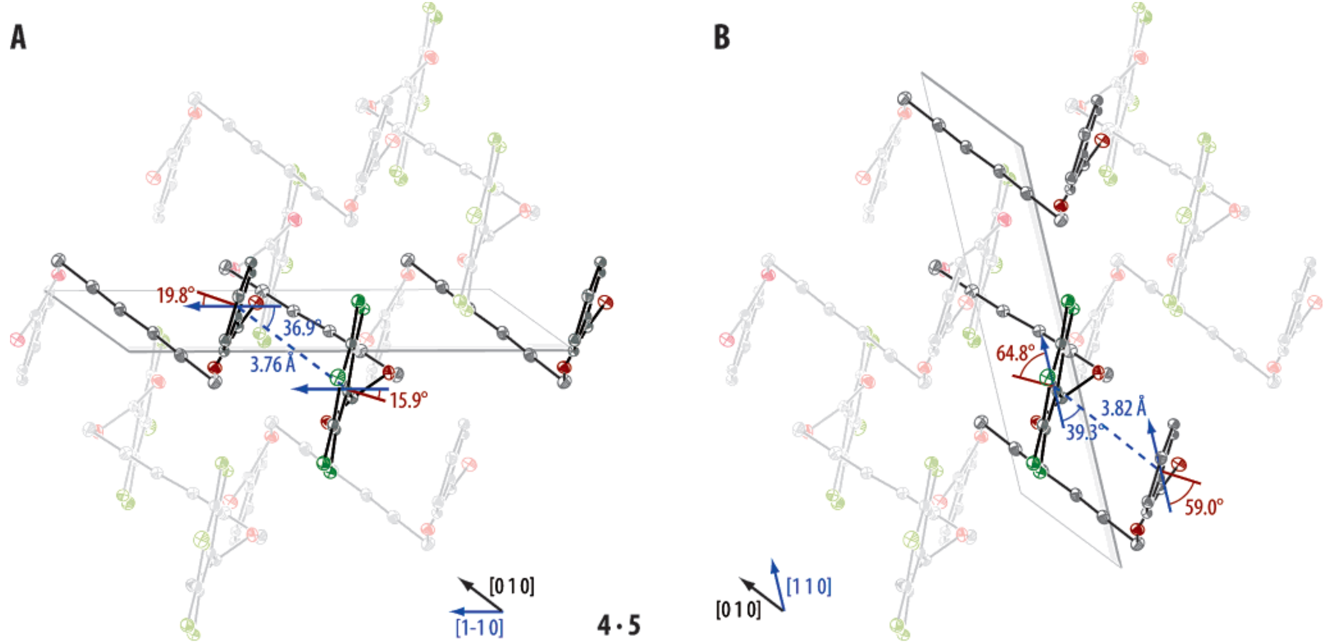

Figure 5. Perfluorophenyl−phenyl interactions in **4·5** (A) in the [1 −1 0] and (B) in [1 1 0] directions; the perfluorophenyl−phenyl stacks along the [0 1 0] axis consist of two alternating types of intimate pairs, one of which connects adjacent molecules **4** and **5** in [1 −1 0], the other one in the [1 1 0] direction.

contrast, the average distance of 4.70(1) Å in the [1 1 0] direction seemed less favorable. This may be one reason the polymerization exclusively proceeded in the [1 −1 0] direction. Remarkably, the diacetylene groups of **4** and **5** are not aligned exactly parallel, so that the distance between them is 5.10 Å on one end and only 4.80 Å on the other one (Figure 4C). A similar effect is also observed in the [1 1 0] direction, but is less pronounced (Table 2). In other words, the reactive diacetylene carbon centers appear to approach each other in the monomer crystal structure so that the polymer is, to a certain degree, already "preformed". Finally, a careful structural analysis led us to believe that the complex side group interactions may play a role in this context. The phenyl and perfluorophenyl groups formed stacks with an almost perfectly eclipsed face-to-face packing and only minimal parallel displacement as well as inclination along the [0 1 0] axis. The stacks consisted of two alternating types of perfluorophenyl−phenyl pairs, one of which (type A) has a centroid distance of 3.76 Å, the other one (type B) of 3.82 Å. These two types of intimate phenyl/perfluorophenyl pairs "connected" adjacent monomers **4** and **5** in the [1 −1 0] (type A) and the [1 1 0] (type B) directions, respectively (Figure 5). Hence, the observed polymerization in the [1 −1 0] direction appeared to coincide with the slightly more optimal type of perfluorophenyl−phenyl pair. More importantly, the inclination angles of the centroid−centroid vectors with the respective axes were found to be relatively similar, that is, 36.9° for type A and [1 −1 0] versus 39.3° for type B and [1 1 0]. However, the normal vectors on the phenyl (perfluorophenyl) rings were tilted only 19.8° (15.9°) against the [1 −1 0], but 59.0° (64.8°) against the [1 1 0] axis. As a result, the polymerization proceeded almost perpendicular to the planes of the aromatic side groups which it would not in the [1 1 0] direction. In this regard, it almost looks like the perfluorophenyl−phenyl interaction does not only promote the alternating placement of two different monomers **4** and **5** but also determines the polymerization direction in that it helps to "stitch together" the copolymer.

Conclusions

In conclusion, we prepared the symmetric 2,4-hexadiynylene dibenzoate **4** and 2,4-hexadiynylene bis(pentafluorobenzoate) **5**, as well as the unsymmetric 6-(pentafluorobenzoyloxy)hexa-2,4-diynyl benzoate **6**. While **4**, **5**, and **6** were unreactive, a 1:1 cocrystal **4·5** underwent topochemical polymerization under UV irradiation. A detailed comparison of the monomer and polymer crystal structures revealed that the perfluorophenyl and phenyl side groups qualified as reliable complementary supramolecular synthons.[10] They helped to assemble a cocrystal with an alternating placement of the two different diacetylene monomers. The topochemical polymerization of this cocrystal led to the unprecedented formation of a strictly alternating poly(diacetylene) copolymer **7**. We believe that perfluorophenyl−phenyl interactions may also be a powerful supramolecular motif to promote the self-assembly of, for example, oligo(ethylene oxide) equipped diacetylenes in (aqueous) solution. The topochemical polymerization within such self-assembled aggregates may provide a new platform for an atom-efficient, initiator- and catalyst-free preparation of soluble and functional conjugated polymers for use in optoelectronic applications in the future.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out in dried Schlenk glassware in an inert N_2 atmosphere. All reagents were purchased as reagent grade from commercial sources and used without further purification. Solvents were purchased as reagent grade and distilled once prior to use. Anhydrous solvents were freshly distilled and stored over molecular sieves prior to use. DCM was dried over CaH_2, freshly distilled, and stored over molecular sieves prior to use. 2,4-Hexadiyne-1,6-diol was obtained from commercial sources.

UV Polymerization. The (powdered) crystalline samples of compounds **4**, **5**, **6**, and **4·5** were placed on a Petri dish and irradiated for time periods between 15 min and several hours using a 250 W Ga-doped low-pressure Hg flood lamp.

Crystal Structure Analysis. For **4**, **5**, **6**, and **4·5**, routine X-ray data collection and reduction was performed at an Oxford Xcalibur CCD diffractometer.[21] The structures were solved and refined with standard SHELX procedures.[22] To determine the crystal structure of the polymer/monomer crystal **4·5** after UV irradiation, selected irradiated crystals were mounted on a CAD4 diffractometer. The unit cell was determined to be nearly the same as that for the nonirradiated **4·5** crystals (Table 1), but the reflections' angular width was doubled and their shape was less regular. A full data set was obtained with a measurement on an OXFORD XCALIBUR CCD diffractometer. The structure solution with direct methods (SHELXS) showed essentially the monomer structure with some additional peaks, but anisotropic refinement produced unreasonable ellipsoids and poor agreement. Therefore, the **4·5** monomer structure model was used as the input with isotropic displacement parameters. The maxima of a subsequent difference Fourier synthesis could straightforwardly be interpreted as the polymer partial structure. The quality of the data and the model allowed a constrained anisotropic refinement (SHELX DELU constraints) of a disordered distribution with 74% monomer and 26% polymer in the crystal. To obtain an acceptable data/parameter ratio, the perfluorophenyl and phenyl residues were refined in rigid body mode with idealized geometry. Because of the low occupancy of the polymer and the high correlation parameters between the monomer and polymer partial structures, the interatomic distances of the polymer backbone were constrained to literature values.

Solution Phase and Solid-State ^{13}C NMR Measurements. The peaks of the aromatic carbon atoms and the carbonyl carbon atom of the pentafluorophenyl residues were not visible in conventional high-resolution ^{13}C NMR spectra. However, they could be determined via 2D ^{19}F−^{13}C HMQC NMR spectroscopy, and their values have been included in the peak listings. Solid-state CP-MAS ^{13}C NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer at a rotational frequency of 12.5 kHz.

2,4-Hexadiynylene dibenzoate 4. 2,4-Hexadiyne-1,6-diol (0.44 g, 4 mmol, 1 equiv) and benzoyl chloride (0.93 mL, 8 mmol, 2 equiv) were dissolved in dry DCM. The solution was cooled to 0 °C, and pyridine (1.3 mL, 16 mmol, 4 equiv) was added slowly. The mixture was allowed to warm to room temperature and stirred for 4 h. After aqueous workup, the crude product was purified by column chromatography (silica gel, DCM/hexanes 1:25); 1.08 g (85%) of **4** was obtained as colorless crystals. Crystals appropriate for X-ray analysis were prepared by slow addition of hexanes to a 15% w/w solution of **4** in DCM until opalescence occurred and subsequent slow evaporation of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (m, 4H, PhH_o), 7.59 (m, 2H, PhH_p), 7.45 (m, 4H, PhH_m), 5.00 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4 ($C{=}O$), 133.3, 129.7, 129.0, 128.3 (Ph), 73.7, 70.4 ($C{\equiv}C$), 52.6 (CH_2). Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46%; H, 4.43%; O, 20.10%. Found: C, 74.94%; H, 4.50%; O, 19.91%. HRMS (EI) *m/z* calcd for $C_{20}H_{14}O_4$ ($[M]^+$): 318.0892. Found: 318.0886. Mp: 73−75 °C; 74.8 °C (DSC). $R_f = 0.85$ (DCM).

2,4-Hexadiynylene bis(pentafluorobenzoate) 5. 2,4-Hexadiyne-1,6-diol (0.44 g, 4 mmol, 1 equiv) and pentafluorobenzoyl chloride (1.15 mL, 8 mmol, 2 equiv) were dissolved in dry DCM. The solution was cooled to 0 °C, and triethylamine (2.23 mL, 16 mmol, 4 equiv) was added. The mixture was allowed to warm to room temperature and stirred overnight. After aqueous workup, the organic solution was concentrated in vacuo; 1.93 g (97%) of pure **5** was obtained as slightly yellow crystals. Colorless crystals appropriate for X-ray analysis were prepared by slow addition of hexanes to a 20% w/w solution of **5** in DCM until opalescence occurred and subsequent slow evaporation of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.04 (s, 4H, CH_2). ^{19}F NMR (188 MHz, $CDCl_3$): δ −137.2 (m, 4F), −147.2 (m, 2F), −160.1 (m, 4F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2 ($C{=}O$),[23] 145.7,[23] 143.7,[23] 137.7,[23] 106.9[23] (C_6F_5), 72.7, 71.2 ($C{\equiv}C$), 54.0 (CH_2). Anal. Calcd for $C_{20}H_4F_{10}O_4$: C, 48.21%; H, 0.81%; F, 38.13%; O, 12.85%. Found: C, 48.36%; H, 0.71%; F, 37.95%. HRMS (EI) *m/z* calcd for $C_{20}H_4F_{10}O_4$ ($[M]^+$): 497.9950. Found: 497.9944. Mp: 65−68 °C; 67.8 °C (DSC). $R_f = 0.88$ (DCM).

Cocrystallization of 4 and 5. Cocrystals of **4** and **5** for X-ray analysis were obtained as colorless platelets by addition of hexanes to a 20% w/w solution of a 1:1 mixture of **4** and **5** in DCM until opalescence occurred and subsequent slow evaporation of the solvent. Anal. Calcd for $C_{40}H_{18}F_{10}O_8$: C, 58.84%; H, 2.22%; F, 23.27%; O, 15.68%. Found: C, 58.96%; H, 2.35%; F, 23.46%. Mp: 60−79 °C (color change to red upon onset of melting); 61.5 °C (DSC).

3-Iodoprop-2-yn-1-ol 8. A solution of propargyl alcohol (5.8 mL, 100 mmol, 1 equiv) in 100 mL of methanol was added slowly to a solution of potassium hydroxide (14 g, 250 mmol, 2.5 equiv) in 20 mL of H_2O at 0 °C. The mixture was stirred for an additional 10 min. Then, iodine (27 g, 110 mmol, 1.1 equiv) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred for 3 h before it was extracted with diethyl ether. The combined organic phases were washed with $Na_2S_2O_3$ and brine. Upon concentration of the solution in vacuo, 14.58 g (80%) of pure **8** was obtained in the form of yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.39 (s, 2H, CH_2), 3.18 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 92.4 ($C{\equiv}CI$), 52.1 (CH_2), 2.8($C{\equiv}CI$). Anal. Calcd for C_3H_3IO: C, 19.80%; H,

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(21) http://www.oxford-diffraction.com/crysalis.htm.

(22) Sheldrick, G. *SHELXS/L-97*, Program for the Solution/Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

(23) Determined from ^{19}F−^{13}C HMQC spectra.

1.66%; O, 8.79%; I, 69.74%. Found: C, 19.86%; H, 1.68%; O, 8.93%; I, 69.70%. HRMS (EI) *m*/*z* calcd for C_3H_3IO ($[M]^+$): 181.9229. Found: 181.9229.

Triisopropyl(prop-2-ynyloxy)silane 9. Propargyl alcohol (1.12 g, 20 mmol, 1 equiv) and imidazole (1.63 g, 24 mmol, 1.2 equiv) were dissolved in dry DCM. Then, triisopropylsilyl chloride (3.84 g, 20 mmol, 1 equiv) was added slowly at 0 °C. The mixture was allowed to stir for 2 h at room temperature and diluted with DCM. After aqueous workup, 4.16 g (98%) of the crude product was obtained as a slightly yellow liquid and used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.37 (s, 2H, CH_2), 2.37 (s, 1H, $C{\equiv}CH$), 1. 08 (m, 21H, CH_3, $CHMe_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 82.3 ($\mathit{C}{\equiv}CH$), 72.5 ($C{\equiv}\mathit{C}H$), 51.6 (CH_2), 17.8 (CH_3), 11.9 ($CHMe_2$).

6-(Triisopropylsilyloxy)hexa-2,4-diyn-1-ol 10. CuCl (0.062 g, 0.6 mmol, 0.06 equiv) was dissolved in a mixture of 10 mL of methanol and 10 mL of *n*-butylamine. Then, triisopropyl(prop-2-ynyloxy)silane **9** (2.12 g, 10 mmol, 1 equiv) was added at 0 °C, followed by the dropwise addition of 3-iodoprop-2-yn-1-ol **8** (1.82 g, 10 mmol, 1 equiv). Whenever the reaction mixture turned to green, a few crystals of $NH_2OH{\cdot}HCl$ were added. After stirring for 1 h at 0 °C and for another 3 h at room temperature, the reaction mixture was filtered through a pad of silica gel. After aqueous workup, the crude product was purified by column chromatography (silica gel, EtOAc/hexanes 1:3); 1.5 g (56%) of pure **10** was obtained as a brownish liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.44 (s, 2H, CH_2), 4.32 (s, 2H, CH_2), 3.23 (b, 1H, OH), 1.07 (m, 21H, CH_3 and $CHMe_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.8, 77.0, 69.6, 68.7 ($C{\equiv}C$), 52.2, 50.1 (CH_2), 17.8 (CH_3), 11.8 ($CHMe_2$). Anal. Calcd for $C_{15}H_{26}O_2Si$: C, 67.61%; H, 9.84%; O, 12.01%; Si, 10.54%. Found: C, 67.49%; H, 9.86%. HRMS (EI) *m*/*z* calcd for $C_{15}H_{26}O_2Si$ ($[M]^+$): 266.1702. Found: 266.1701. $R_f = 0.38$ (EtOAc/hexanes 1:3).

6-(Triisopropylsilyloxy)hexa-2,4-diynyl benzoate 11. A solution of 6-(triisopropylsilyloxy)hexa-2,4-diyn-1-ol **10** (1.06 g, 4 mmol, 1 equiv) and benzoyl chloride (0.46 mL, 4 mmol, 1 equiv) in dry DCM was cooled to 0 °C, and pyridine (0.65 mL, 8 mmol, 2 equiv) was added slowly. The mixture was allowed to warm to room temperature and stirred for 4 h. After aqueous workup, the crude product was purified by column chromatography (silica gel, DCM/hexanes 1:25); 1.04 g (70%) of pure **11** was obtained as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (m, 2H, PhH_o), 7.59 (m, 1H, PhH_p), 7.46 (m, 2H, PhH_m), 5.01 (s, 2H, CH_2), 4.47 (s, 2H, CH_2), 1.10 (m, 21H, CH_3, $CHMe_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6 ($C{=}O$), 133.3, 129.8, 129.2, 128.4 (Ph), 78.6, 72.5, 71.0, 68.4 ($C{\equiv}C$), 52.8, 52.2 (CH_2), 17.8 (CH_3), 11.9 ($CHMe_2$). $R_f = 0.35$ (EtOAc/hexanes 1:15).

6-Hydroxyhexa-2,4-diynyl benzoate 12. A solution of 6-(triisopropylsilyloxy)hexa-2,4-diynyl benzoate **11** (1.42 g, 3.8 mmol, 1 equiv) in THF was cooled to −78 °C, and tetrabutylammonium fluoride (4.6 mL, 1.2 equiv, 1.0 M solution in THF) was added via a syringe. The reaction was stirred for 2 h at −78 °C and then diluted with Et_2O. After aqueous workup, the crude product was purified by column chromatography (silica gel, EtOAc/hexanes 1:2); 0.65 g (79%) of pure **12** was obtained as a brown syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (m, 2H, PhH_o), 7.56 (m, 1H, PhH_p), 7.43 (m, 2H, PhH_m), 4.98 (s, 2H, CH_2), 4.33 (s, 2H, CH_2), 3.46 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.7 ($C{=}O$), 133.3, 129.6, 128.8, 128.3 (Ph), 78.3, 72.9, 70.6, 68.9 ($C{\equiv}C$), 52.8, 50.8 (CH_2). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89%; H, 4.70%; O, 22.41%. Found: C, 72.78%; H, 4.76%; O, 22.30%. HRMS (EI) *m*/*z* calcd for $C_{13}H_{10}O_3$ ($[M]^+$): 214.0630. Found: 214.0622. $R_f = 0.26$ (EtOAc/hexanes 1:2).

6-(Pentafluorobenzoyloxy)hexa-2,4-diynyl benzoate 6. A solution of 6-hydroxyhexa-2,4-diynyl benzoate **12** (0.65 g, 3 mmol, 1 equiv) and pentafluorobenzoyl chloride (0.43 mL, 3 mmol, 1 equiv) in dry DCM was cooled to 0 °C, and triethylamine (1 mL, 7 mmol, 2.3 equiv) was added slowly. The mixture was allowed to warm to room temperature and stirred for 5 h. After aqueous workup and column chromatography (silica gel, DCM), 1.06 g (87%) of pure **6** was obtained as bright yellow crystals. Colorless crystals appropriate for X-ray analysis were prepared by slow addition of hexanes to a 20% w/w solution of **5** in DCM until opalescence occurred and subsequent slow evaporation of the solvent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (m, 2H, PhH_o), 7.58 (m, 1H, PhH_p), 7.46 (m, 2H, PhH_m), 5.05 (s, 2H, CH_2), 5.01 (s, 2H, CH_2). ^{19}F NMR (188 MHz, $CDCl_3$): δ −137.1 (m, 2F), −147.2 (m, 1F), −160.0 (m, 2F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 158.2[23] ($C{=}O$), 145.7[23] (C_6F_5), 143.6[23] (C_6F_5), 137.7[23] (C_6F_5), 133.4, 129.7, 129.0, 128.4 (Ph), 107.0[23] (C_6F_5), 74.5, 72.0, 71.4, 70.0 ($C{\equiv}C$), 54.0, 52.5 (CH_2). Anal. Calcd for $C_{20}H_9F_5O_4$: C, 58.84%; H, 2.22%; F, 23.27%; O, 15.68%. Found: C, 58.71%; H, 2.28%; F, 23.10%. HRMS (EI) *m*/*z* calcd for $C_{20}H_9F_5O_4$ ($[M]^+$): 408.0421. Found: 408.0412. Mp: 70−72 °C; 71.80 °C (DSC). $R_f = 0.70$ (DCM).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **4**, **5**, **6**, **8**, **9**, **10**, **11**, and **12**; ^{19}F and ^{19}F−^{13}C HMQC NMR spectra of **5** and **6**. Raman spectra of **6** before and after UV irradiation; ORTEP representations, crystal structure illustrations, and complete crystallographic data (CIF) of **4**, **5**, **6**, and **4·5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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