A New Iterative Approach for the Synthesis of Oligo(phenyleneethynediyl) Derivatives and Its Application for the Preparation of Fullerene–Oligo(phenyleneethynediyl) Conjugates as Active Photovoltaic Materials

by **Jean-François Nierengarten***, and **Tao Gu**

Groupe de Chimie des Fullerènes et des Systèmes Conjugués, Ecole Européenne de Chimie, Polymères et
Matériaux (ECPM), Université Louis Pasteur et CNRS (UMR 7504), 25 rue Becquerel,
F-67087 Strasbourg Cedex 2
(e-mail: jfnierengarten@chimie.u-strasbg.fr)

and **Georges Hadziioannou***, **Dimitris Tsamouras**, and **Victor Krasnikov**

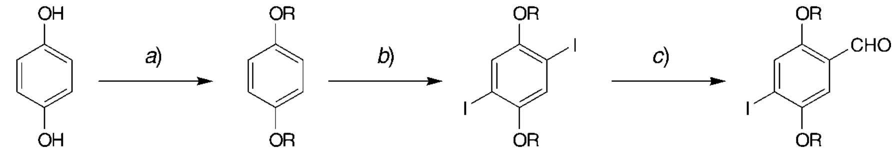
Département des Polymères, Ecole Européenne de Chimie, Polymères et Matériaux (ECPM),
Université Louis Pasteur et CNRS, 25 rue Becquerel, F-67087 Strasbourg Cedex 2
(e-mail: hadzii@ecpm.u-strasbg.fr)

Disymmetrically substituted oligo(phenyleneethynediyl) (OPE) derivatives were prepared from 2,5-bis(octyloxy)-4-[(triisopropylsilyl)ethynyl]benzaldehyde (**5**) by an iterative approach using the following reaction sequence: *i*) *Corey–Fuchs* dibromoolefination, *ii*) treatment with an excess of lithium diisopropylamide, and *iii*) a metal-catalyzed cross-coupling reaction of the resulting terminal alkyne with 2,5-diiodo-1,4-bis(octyloxy)benzene (**3**) (*Schemes 2* and *3*). Reaction of the OPE dimer **8** and trimer **13** thus obtained with *N*-methylglycine and C_{60} in refluxing toluene gave the corresponding C_{60}–OPE conjugates **16** and **17**, respectively (*Scheme 4*). On the other hand, treatment of the protected terminal alkynes **8** and **13** with Bu_4N followed by reaction of the resulting **9** and **14** with 4-iodo-*N*,*N*-dibutylaniline under *Sonogashira* conditions yielded **10** and **15**, respectively (*Schemes 2* and *3*). Subsequent treatment with *N*-methylglycine and C_{60} in refluxing toluene furnished the C_{60}–OPE derivatives **18** and **19** (*Scheme 4*). Compound **9** was also subjected to a Pd-catalyzed cross-coupling reaction with **3** to give the centrosymmetrical OPE pentamer **20** (*Scheme 5*). Subsequent reduction followed by reaction of the resulting diol **21** with acid **22** under esterification conditions led to bis-malonate **23**. Oxidative coupling of terminal alkyne **14** with the *Hay* catalyst gave bis-aldehyde **24** (*Scheme 6*). Treatment with diisobutylaluminium hydride followed by dicylcohexylcarbodiimide-mediated esterification with acid **22** gave bis-malonate **26**. Finally, treatment of bis-malonates **23** and **26** with C_{60}, I_2, and 1,8-diazabicyclco[5.4.0]undec-7-ene (DBU) in toluene afforded the bis[cyclopropafullerenes] **27** and **28**, respectively (*Scheme 7*). The C_{60} derivatives **16**–**19**, **27**, and **28** were tested as active materials in photovoltaic devices. Each C_{60}–OPE conjugate was sandwiched between poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)-covered indium tin oxide and aluminium electrodes. Interestingly, the performances of the devices prepared from the *N*,*N*-dialkylaniline-terminated derivatives **18** and **19** are significantly improved when compared to those obtained with **16**, **17**, **27**, and **28**, thus showing that the efficiency of the devices can be significantly improved by increasing the donor ability of the OPE moiety.

1. Introduction. – Following the preparation of the first photovoltaic devices from C_{60}–oligo(phenyleneethenediyl) conjugates [1], a great deal of attention has been devoted to C_{60} derivatives substituted with π-conjugated oligomers for solar-energy conversion (for a review on fullerene-(π-conjugated oligomer) dyads as active photovoltaic materials, see [2]) [3–7]. This approach using molecular dyads as the active layer in solar cells is particularly interesting since it restricts the dimension of the bicontinuous donor/acceptor network on the finest molecular level. The nanoscopic dimension of the phase separation is an advantage because the exciton diffusion length in conjugated systems is limited to that length scale [8]. In addition, another major advantage of this approach is that the behavior of a unique molecule in a photovoltaic cell allows to obtain easily structure – activity relationships for a better understanding of the photovoltaic system [2]. Actually, the molecular approach is not only an interesting model system of the devices by means of bulk heterojunction materials but it appears also as an excellent alternative to the polymeric approach. Indeed, the photosensitivity and the energy-conversion efficiency obtained with devices prepared with fullerene-(π-conjugated oligomer) dyads capable of achieving efficient and very fast photoinduced charge separation are quite promising [4]. Furthermore, this new synthetic approach also offers great versatility for design tuning of the photovoltaic system. As part of this research, we have shown that C_{60} derivatives substituted with oligo(phenyleneethyne-1,2-diyl) (OPE) subunits are interesting candidates for photovoltaic applications [6]. In this paper, we now report a full account on the synthesis of a complete series of C_{60}–OPE conjugates. In particular, we show that the OPE precursors can be efficiently prepared from a benzaldehyde derivative by an iterative approach using the following reaction sequence: *i*) *Corey* – *Fuchs* dibromoolefination [9] *ii*) treatment with an excess of lithium diisopropylamide (LDA), and *iii*) a metal-catalyzed cross-coupling reaction of the resulting terminal alkyne with a 4-iodobenzaldehyde derivative. This new iterative methodology for the synthesis of OPE derivatives is an interesting alternative to the approaches reported by *Tour* and co-workers [10] and *Ziener* and *Godt* [11]. On the one hand, compared to the strategy based on the trimethylsilyl and the 3,3-diethyltriazene functions as complementary protecting groups for terminal alkyne and aryl iodide, respectively, it avoids the use of large amounts of rather volatile carcinogenic methyl iodide [10]. On the other hand, compared to the strategy based on the bromine – iodine selectivity of the Pd-catalyzed alkyne – arene coupling, which is not always completely iodo-selective, it prevents the formation of undesirable symmetric by-products [11]. The disymmetrically substituted OPE derivatives prepared by using this new synthetic methodology have been attached to C_{60} by a 1,3-dipolar cycloaddition of the azomethine ylides (= iminium ylides) [12] generated *in situ* from the corresponding OPE aldehydes and sarcosine. Symmetrically substituted OPE derivatives bearing terminal malonate groups have also been synthesized and used for the synthesis of dumbbell-shaped bis[cyclopropafullerene] – OPE systems. Finally, we describe the preparation of photovoltaic devices from these C_{60}–OPE derivatives. Part of this work has been previously reported in preliminary communications [6].

2. Results and Discussions. – 2.1. *Synthesis.* The preparation of the key building block for the synthesis of the functionalized OPE derivatives is depicted in *Scheme 1*. Reaction of hydroquinone (**1**) with 1-bromooctane in DMF at 80° in the presence of K_2CO_3 gave **2** in 90% yield. Treatment of **2** with KIO_3 and I_2 in a mixture of AcOH, conc. H_2SO_4 solution, and H_2O at 80° [13] afforded **3** in 59% yield. Compound **4** was then obtained in 85% yield by treatment of **3** with BuLi (1 equiv.) in Et_2O at 0° followed by quenching with DMF. It is worth noting that the purification of compounds **2** – **4** was simply achieved by recrystallization, and this route allowed us to easily prepare building block **4** on a multi-gram scale.

Scheme 1



1 **2** R = C_8H_{17} **3** R = C_8H_{17} **4** R = C_8H_{17}

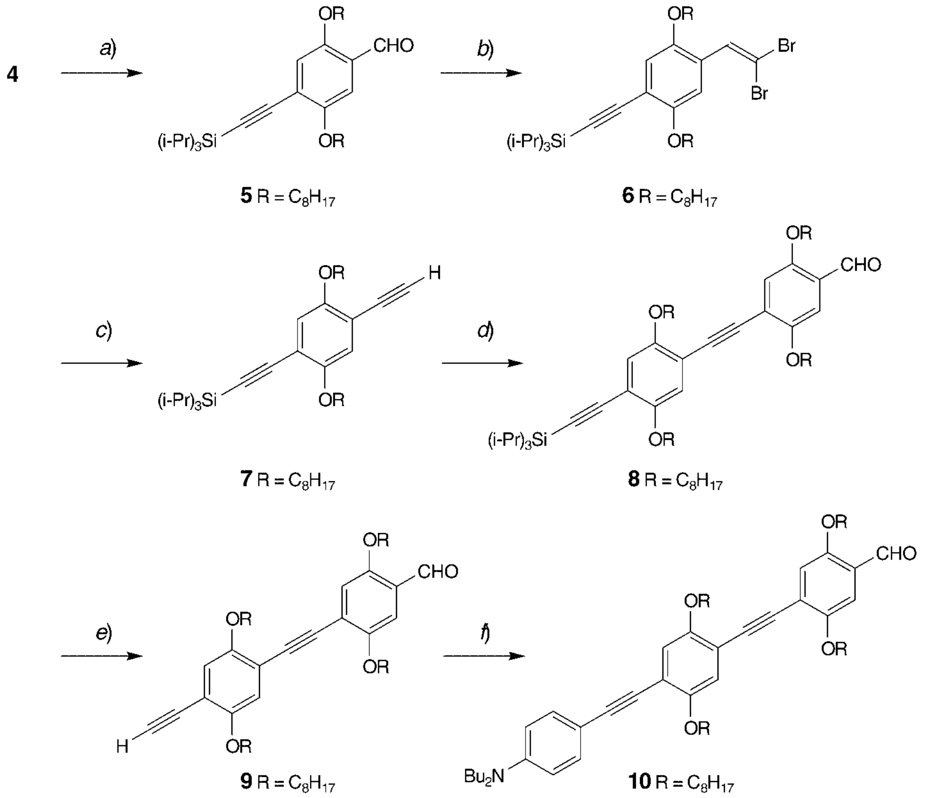
a) 1-Bromooctane, K_2CO_3, DMF, 80°, 24 h (90%). *b*) I_2, KIO_3, H_2SO_4, AcOH, 80°, 12 h (59%). *c*) BuLi (1 equiv.), Et_2O, 0°, 30 min, then DMF, 0° to r.t., 2 h (85%).

Compound **4** was subjected to a Pd-catalyzed cross-coupling reaction [14] with (triisopropylsilyl)acetylene (=ethynyltriisopropylsilane) to give **5** in 79% yield (*Scheme 2*). Subsequent treatment with $CBr_4/PPh_3/Zn$ under the conditions described by *Corey–Fuchs* [9] yielded dibromoolefine derivative **6** in a quantitative yield. Elimination of HBr and halogen-metal exchange was best achieved with an excess of LDA [15] in THF at –78°, and the resulting anion was quenched with NH_4Cl to give mono-protected bis-alkyne derivative **7** in 91% yield. The OPE dimer **8** was then obtained in 79% yield by Pd-catalyzed cross-coupling between **4** and **7**. Treatment of the terminally protected alkyne derivative **8** with tetrabutylammonium fluoride (Bu_4NF) in THF at 0° afforded **9** in 91% yield. Subsequent Pd-catalyzed cross-coupling reaction with *N*,*N*-dibutyl-4-iodoaniline under *Sonogashira* conditions then gave **10**.

The OPE tetramer was prepared similarly from dimer **8** by dibromoolefination according to *Corey–Fuchs* (→**11**), treatment with an excess of LDA in THF at –78° and quenching with NH_4Cl (→**12**). Pd-catalyzed cross-coupling reaction with **4** (→**13**), treatment with Bu_4NF (→**14**), and subsequent reaction with *N*,*N*-dibutyl-4-iodoaniline (*Scheme 3*). The yield of **15** was moderate since the by-product resulting from the homocoupling of **14** was systematically formed in abnormally high proportions under the conditions used in the last step. However, sufficient quantities of **15** were obtained, and no further effort was made to optimize the reaction conditions for the preparation of this OPE derivative.

The synthetic approach to prepare the C_{60}–OPE conjugates **16**–**19** relies upon the 1,3-dipolar cycloaddition of the OPE azomethine ylides (=iminium ylides) generated *in situ* from the corresponding aldehydes and *N*-methylglycine (*Scheme 4*). This methodology has been proven a powerful procedure for the functionalization of C_{60} due to its versatility and the ready availability of the starting materials [12]. Thus, reaction of aldehydes **8**, **10**, **13**, and **15** with *N*-methylglycine and C_{60} in refluxing toluene gave the corresponding fulleropyrrolidines **16**–**19** in 36–45% isolated yield after column chromatography (silica gel). The structures of the C_{60}–OPE conjugates **16**–**19** were confirmed by analytical and spectroscopic data. The ^{1}H-NMR spectra ($CDCl_3$) of **16**–**19** exhibit the expected features with the signals arising from the OPE moieties, the pyrrolidine protons (1 *AB* and 1*s*), as well as the MeN group (1*s*). The ^{13}C-NMR spectra of **16**–**19** were also in full agreement with their C_1 symmetry resulting from the presence of the asymmetric C-atom in the pyrrolidine ring. The structure of **16**–**19** was further confirmed by the FAB-MS showing the expected molecular-ion peak in all the

Scheme 2



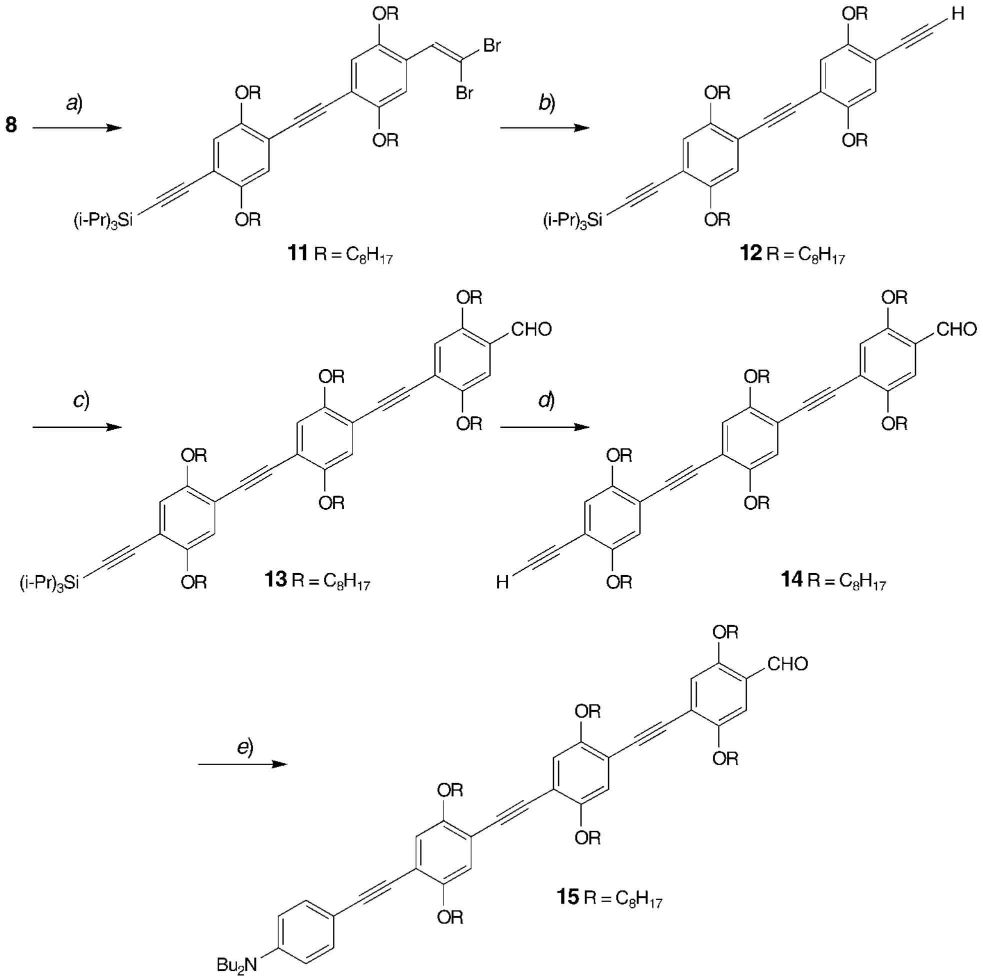
a) (Triisopropylsilyl)acetylene, [$PdCl_2(PPh_3)_2$)], CuI, Et_3N, r.t., 24 h (79%). *b*) CBr_4, PPh_3, Zn, CH_2Cl_2, 0° to r.t., 12 h (99%). *c*) LDA, THF, $< 78°$, then aq. NH_4Cl soln. (91%). *d*) **4**, [$PdCl_2(PPh_3)_2$)], CuI, Et_3N, r.t., 24 h (79%). *e*) Bu_4NF, THF, 0° (91%). *f*) *N,N*-Dibutyl-4-iodoaniline, [$PdCl_2(PPh_3)_2$)], CuI, Et_3N, 25° (66%).

cases. For all the C_{60}–OPE derivatives **16**–**19**, the UV/VIS spectrum corresponds to the sum of the spectra of their two components indicating no significant ground-state interactions between the two chromophores. Preliminary luminescence measurements show a strong quenching of the OPE fluorescence by the fullerene moiety in **16**–**19** indicating the occurrence of intramolecular photo-induced processes.

Symmetrically substituted OPE derivatives were also prepared and used for the synthesis of dumbbell-shaped bis[fullerene]–OPE systems (*Schemes 5*–*7*). In the design of these compounds, it was decided to use *Bingel*-type chemistry [16] to attach the two fullerene spheres to the conjugated system. Actually, the 1,3-dipolar cycloaddition of an azomethine ylide to C_{60} was not used because an asymmetric C-atom is generated during the cycloaddition reaction. Therefore, the use of this methodology for the preparation of π-conjugated systems bearing two fullerene spheres would yield a diastereoisomer mixture [17].

For the preparation of the first symmetrically substituted OPE derivative bearing terminal malonate groups, compound **9** was subjected to a Pd-catalyzed cross-coupling

Scheme 3

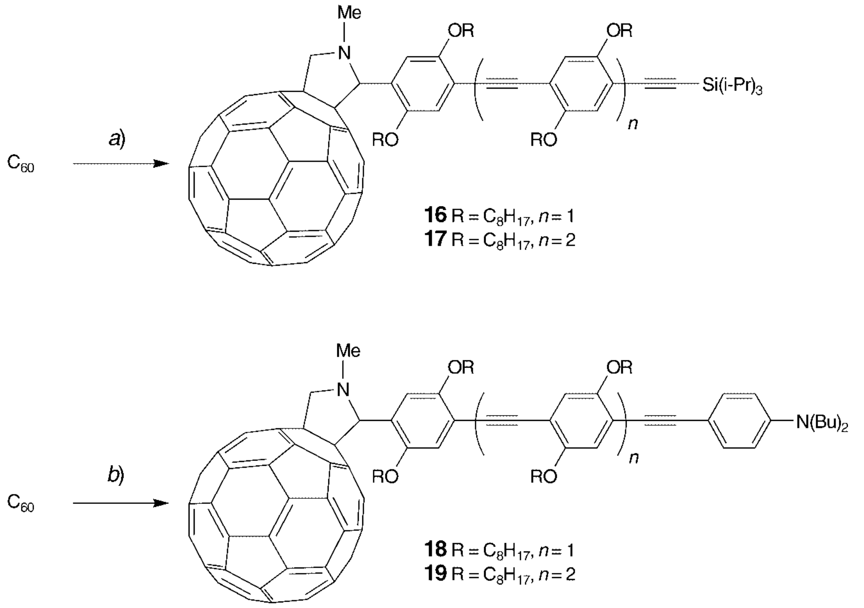


a) CBr_4, PPh_3, Zn, CH_2Cl_2, 0° to r.t., 12 h (99%). *b*) LDA, THF, −78°, then aq. NH_4Cl soln. (92%). *c*) **4**, $[PdCl_2(PPh_3)_2)]$, CuI, Et_3N, r.t., 24 h (77%). *d*) Bu_4NF, THF, 0° (92%). *e*) *N*,*N*-Dibutyl-4-iodoaniline, $[PdCl_2(PPh_3)_2)]$, CuI, Et_3N, 25° (21%).

reaction with **3** to give the centrosymmetrical OPE pentamer **20** in 79% yield. Subsequent diisobutylaluminium hydride (DIBAL-H) reduction afforded the corresponding diol **21** in 96% yield. Reaction of acid **22** with diol **21** under esterification conditions in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethylpyridin-4-amine (DMAP) led to bis-malonate **23** in 99% yield.

The second bis-malonate was prepared from bis-aldehyde **24** (*Scheme 6*) that was obtained as a by-product during the reaction of **14** with *N*,*N*-dibutyl-4-iodoaniline under *Sonogashira* conditions (see above). Compound **24** was also prepared by oxidative coupling of terminal-alkyne derivative **14** with the *Hay* catalyst [18] (CuCl,

Scheme 4

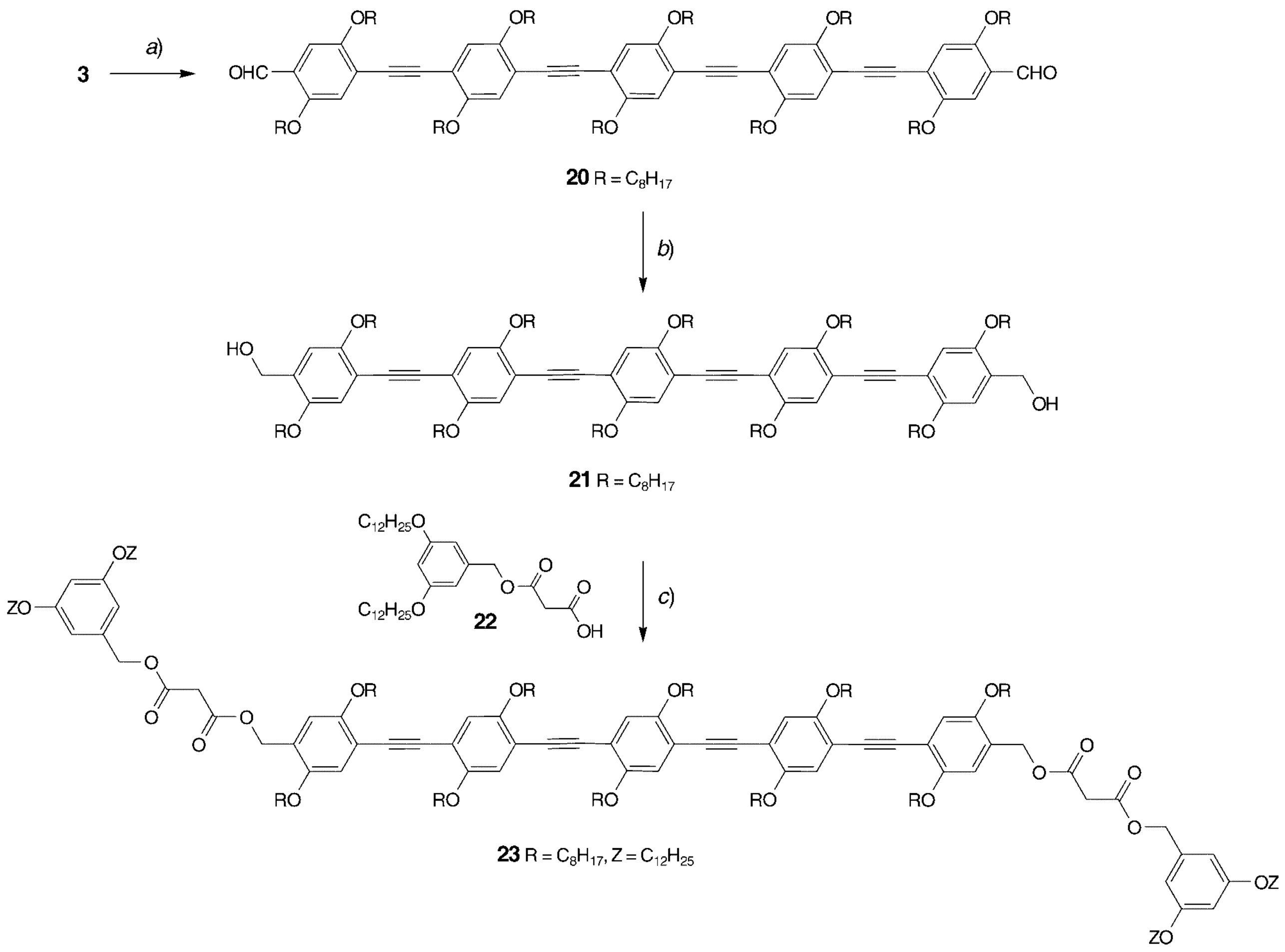


a) **8** or **13**, C_{60}, *N*-methylglycine, toluene, reflux, 16 h (**16**: 36% from **8**; **17**: 40% from **13**). *b*) **10** or **15**, C_{60}, *N*-methylglycine, toluene, reflux, 16 h (**18**: 39% from **10**; **19**: 45% from **15**).

N,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA)) in CH_2Cl_2 in the presence of dry air. Treatment of **24** with DIBAL-H followed by DCC-mediated esterification of the resulting **25** with acid **22** gave the desired bis-malonate **26**.

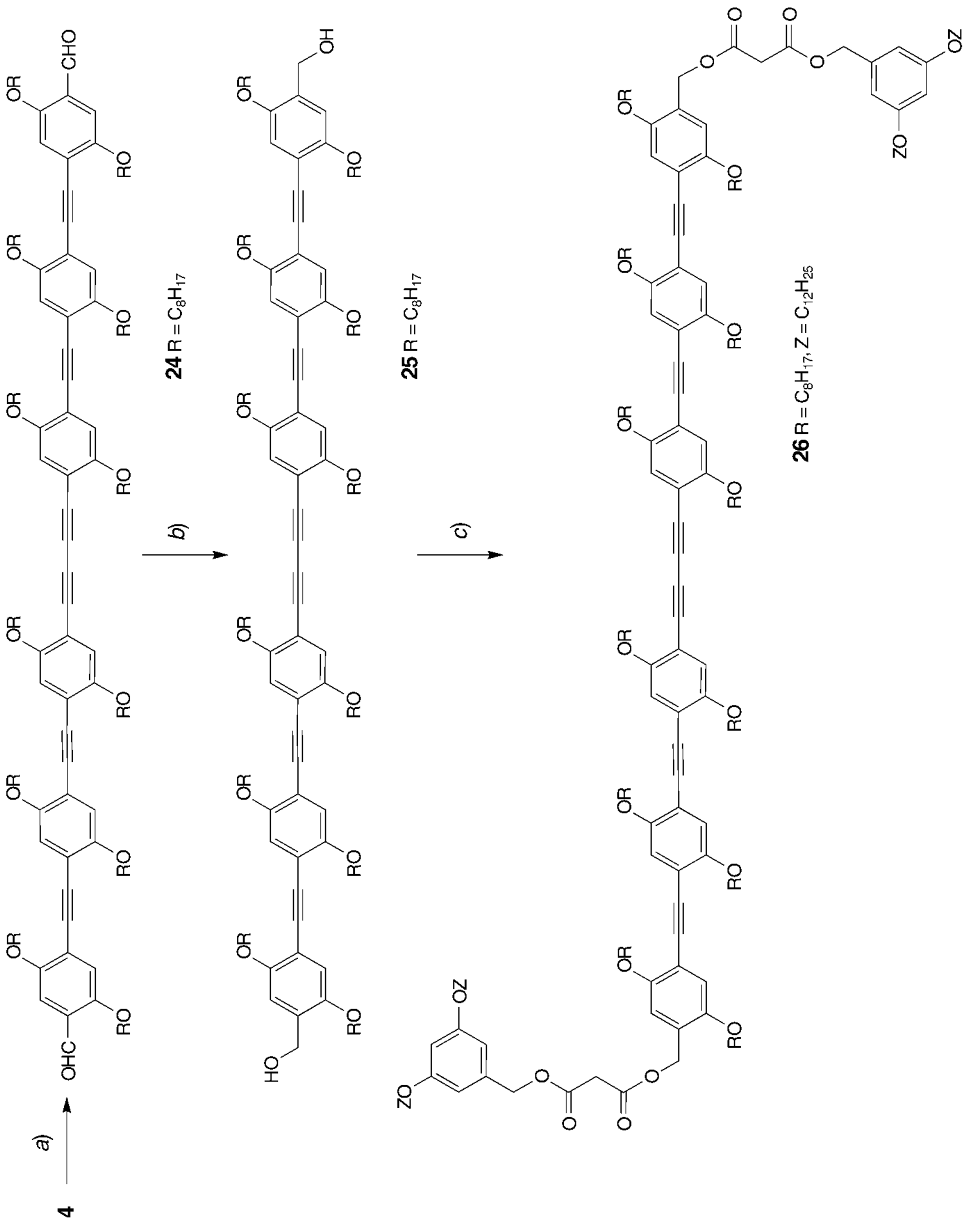
The functionalization of **23** and **26** with C_{60} is based on the *Bingel* reaction [16] (*Scheme 7*). Nucleophilic addition of a stabilized α-halocarbanion to the C_{60} core, followed by intramolecular nucleophilic substitution, leads to clean cyclopropanation of C_{60}. It has been shown that the α-halomalonate can be generated *in situ*, and direct treatment of C_{60} with malonates in the presence of I_2 [19] or CBr_4 [20] under basic conditions affords the corresponding cyclopropafullerenes in good yields. Treatment of C_{60} with bis-malonate **23**, I_2, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded bis[cyclopropafullerene] **27** in 38% yield. Similarly, reaction of **26** with C_{60} in the presence of I_2 and DBU gave the dumbbell-shaped compound **28** in 32% yield. For both bis[cyclopropafullerene] derivatives **27** and **28**, the ^1H- and ^{13}C-NMR spectra were in full agreement with their centrosymmetric structures. In addition, the structures of **27** and **28** were also confirmed by MALDI-TOF-MS showing the expected molecular-ion peaks. As seen for compounds **16** – **19**, the UV/VIS spectra of **27** and **28** correspond to the sum of the spectra of their component units indicating no significant ground-state interactions between the different chromophores. Preliminary luminescence measurements also show a strong quenching of the characteristic OPE fluorescence by the fullerene subunits in **27** and **28** indicating the occurrence of intramolecular photo-induced processes.

Scheme 5



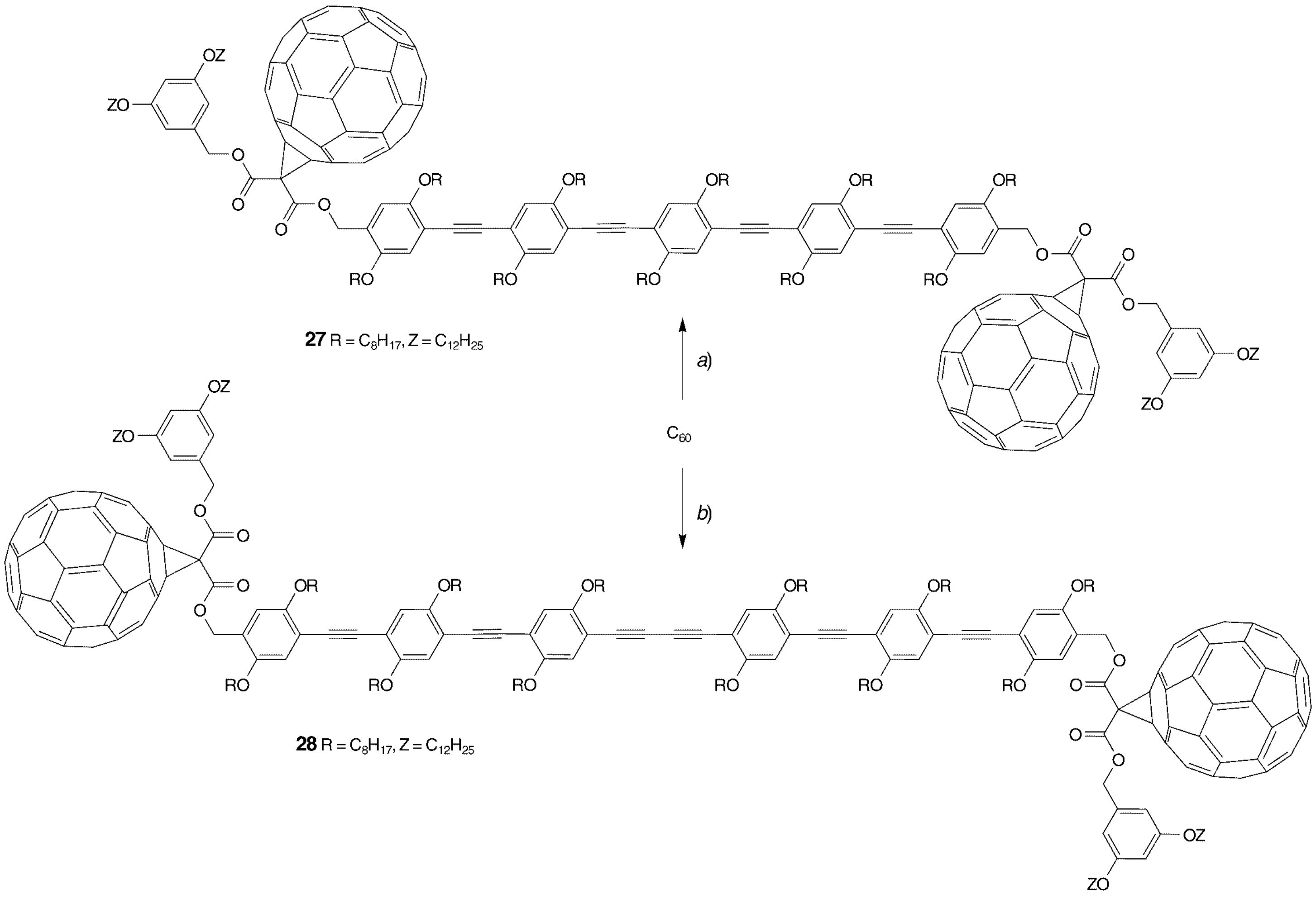
a) **9**, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, r.t., 24 h (79%). *b*) DIBAL-H, THF, 0°, 2 h (96%). *c*) DCC, DMAP, CH_2Cl_2, 0° to r.t., 14 h (99%).

Scheme 6



a) CuCl, TMEDA, dry air, CH_2Cl_2, r.t., 12 h (91%). *b*) DIBAL-H, THF, 0°, 2 h (95%). *c*) **22**, DCC, DMAP, CH_2Cl_2, 0° to r.t., 14 h (98%).

Scheme 7



27 R = C_8H_{17}, Z = $C_{12}H_{25}$

28 R = C_8H_{17}, Z = $C_{12}H_{25}$

a) **23**, C_{60}, I_2, DBU, toluene, r.t. (38%). *b*) **26**, C_{60}, I_2, DBU, toluene, r.t. (32%).

2.2. *Photovoltaic Devices.* Compounds **16**–**19**, **27**, and **28** were tested as active materials in photovoltaic devices. Each C_{60}–OPE conjugate was sandwiched between poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS)-covered indium tin oxide (ITO) and aluminium electrodes. The organic layers were prepared by spin-coating from $CHCl_3$ solutions, and observations of the surface morphology by atomic force microscopy (AFM) in the tapping mode revealed the presence of continuous and uniform films for all the compounds. In all the cases, the largest features of inhomogeneity and irregularities are smaller than 10% of the film thickness (*ca.* 100 nm) indicating the absence of pinholes. As a typical example, the surface morphology of a film prepared from compound **18** is shown in *Fig. 1.*

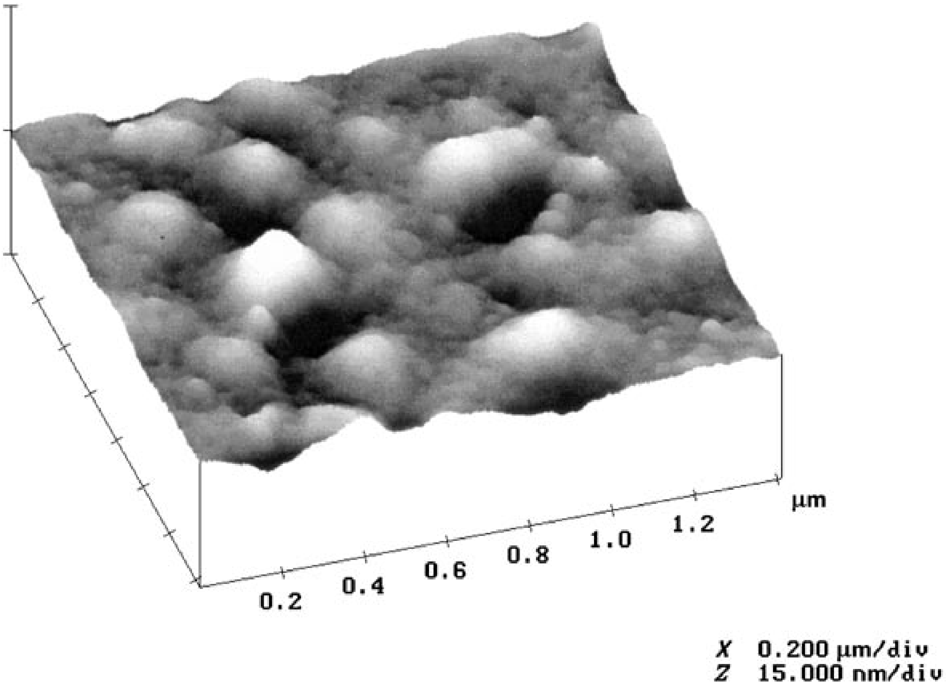


Fig. 1. *AFM Image* (1.5 μm × 1.5 μm) *showing the surface morphology of a prepared film from compound **18** with a thickness of* ca. *100 nm*

The current–voltage (*I*/*V*) characteristics of all the devices were determined in the dark and under illumination (400 nm, 1 mW/cm^2); the results are summarized in the *Table.* As typical examples, the *I*/*V* characteristics of the devices prepared from **27** and **28** are depicted in *Fig. 2.* The results obtained with compounds **16**–**19** have already been described in a previous report [6].

All the devices show clear photovoltaic behavior under illumination. Interestingly, the performances of the devices prepared from the *N*,*N*-dialkylaniline terminated derivatives **18** and **19** are significantly improved when compared to those obtained with **16**, **17**, **27**, and **28**. This can be related to the differences seen in their first oxidation

Table. *Results of the Photovoltaic Measurements for the Devices Prepared from* **16–19**, **27**, *and* **28**

	V_{OC}/V	I_{SC}/A cm^{-2}	FF[a])	T[b])/%	S_{400}/A W^{-1}	$\eta_{e,400}$[a])/%
16	0.22	$2.05 \cdot 10^{-7}$	0.27	55	$2.41 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$
17	0.58	$2.04 \cdot 10^{-7}$	0.22	27	$1.81 \cdot 10^{-4}$	$2.6 \cdot 10^{-3}$
18	0.54	$1.16 \cdot 10^{-6}$	0.32	22	$1.46 \cdot 10^{-3}$	$2.0 \cdot 10^{-2}$
19	0.59	$1.06 \cdot 10^{-6}$	0.29	39	$1.01 \cdot 10^{-3}$	$1.8 \cdot 10^{-2}$
27	0.50	$3.8 \cdot 10^{-7}$	0.33	42	$3.6 \cdot 10^{-4}$	$6.3 \cdot 10^{-3}$
28	0.42	$2.2 \cdot 10^{-7}$	0.30	44	$2.1 \cdot 10^{-4}$	$2.7 \cdot 10^{-3}$

[a]) The calculation of the overall energy-conversion efficiency η_e was done with the equation $\eta_e = (V_{OC} \cdot I_{SC} \cdot FF)/P_{INC}$ where V_{OC}, I_{SC}, FF and P_{INC} are the open-circuit potential, short-circuit current, filling factor, and incident-light power, respectively. The filling factor is given by $FF = (V_{max} \cdot I_{max})/V_{OC} \cdot I_{SC}$ where V_{max} and I_{max} are voltage and current, respectively, at the point of maximum power output. Standard intensity of light was 1 mW cm^{-2}.
[b]) T = transmission (corrected on glass, ITO, and PEDOT-PSS).

potentials [6]. Indeed, due to the increased donor ability of the OPE moiety in **18** and **19** when compared to **16**, **17**, **27**, and **28**, the energy level of their charge-separated states resulting from a photoinduced electron transfer is significantly lower in energy. Therefore, the thermodynamic driving force is more favorable, thus electron transfer which is one of the key steps for the photocurrent production must be more efficient for **18** and **19**. As a result, the power conversion efficiency of the devices is increased by one order of magnitude. As seen in the *Table*, the performances of the photovoltaic cells prepared from all the compounds are rather low. Actually, a recent study has clearly shown that an important limiting factor is the low charge-carrier mobility in the films obtained from these C_{60}–OPE conjugates [21].

3. Conclusions. – OPE Derivatives were prepared by an iterative approach from benzaldehyde derivatives by applying the following reaction sequence: *i*) *Corey–Fuchs* dibromoolefination and treatment with an excess of LDA; *ii*) metal-catalyzed cross-coupling reaction of the resulting terminal alkyne with a 4-iodobenzaldehyde derivative. The OPE building blocks prepared by using this new synthetic methodology were used for the construction of various C_{60}–OPE derivatives. These hybrid compounds were incorporated in photovoltaic devices. Importantly, analysis of the characteristics of these devices clearly revealed that the behavior of a unique molecule in a photovoltaic cell allows to obtain easily structure–activity relationships for a better understanding of the photovoltaic system. In particular, we showed that the efficiency of the devices can be significantly improved by increasing the donor ability of the OPE moiety. However, for a commercial use, the efficiency and stability of such solar cells have to be improved dramatically. For these purposes, new hybrid compounds with a stronger absorption in the VIS range and a better stability towards light are needed. In addition, the performances of the molecular photovoltaic cells are mainly limited by their low conductivity. Therefore, a critical point appears to be the orientation of the molecules within the thin film to improve the charge carrier mobility. In this respect, the use of liquid-crystalline C_{60}-(π-conjugated oligomer) conjugates could be of particular interest since such materials would spontaneously form ordered assemblies that could then be oriented and lead to high-performance thin films [22].

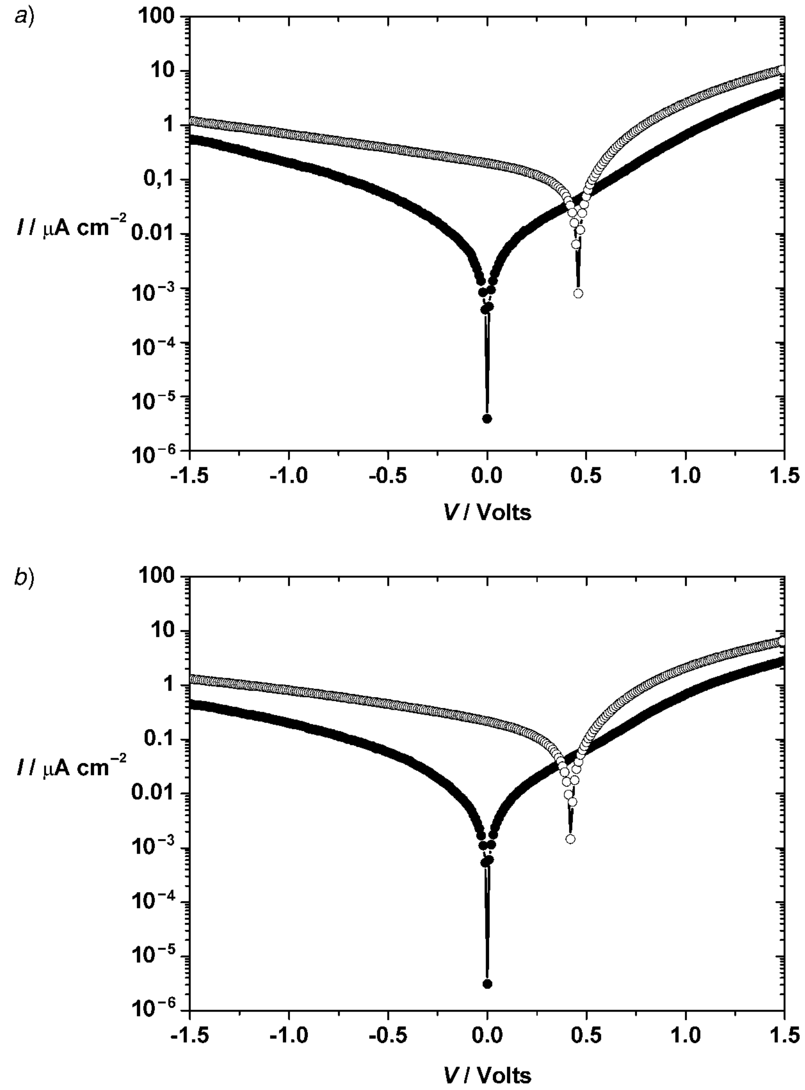


Fig. 2. I/V *Characteristics in the dark* (●) *and under illumination at 400 nm with an intensity of 1 mW cm*$^{-2}$ (○) *for* a) *ITO/PEDOT-PSS/***27***/Al and* b) *ITO/PEDOT-PSS/***28***/Al*

Experimental Part

General. Reagents and solvents were purchased as reagent grade and used without further purification. Compound **22** [23] was prepared according to the literature. All reactions were performed in standard glassware under Ar. Evaporation and concentration were done under water-aspirator pressure and drying *in vacuo* at 10^{-2} Torr. Column chromatography (CC): silica gel *60* (230–400 mesh, 0.040–0.063 mm) from *E. Merck*. TLC: glass sheets coated with silica gel *60 F*$_{254}$ from *E. Merck*; visualization by UV light. UV/VIS spectra: *Hitachi U-3000* spectrophotometer; λ_{max} in nm (ε). NMR spectra: *Bruker AC-200* (200 MHz) or *Bruker AM-400* (400 MHz); solvent peaks as reference; δ in ppm, J in Hz. FAB-MS: *ZA-HF* instrument; 4-nitrobenzyl alcohol as matrix; in *m*/*z*. MALDI-TOF-MS: *Bruker Biflex*™ mass spectrometer equipped with *Scout*™ high-resolution optics, an X-Y multi-sample probe, and a gridless reflector [24]; anthracene-1,8,9-triol(=dithranol) as matrix; in *m*/*z*. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg, France.

1,4-Bis(octyloxy)benzene (**2**). A mixture of **1** (25.0 g, 0.227 mol), K_2CO_3 (157.0 g, 1.136 mol), and 1-bromooctane (105.0 g, 0.545 mol) in DMF (300 ml) was stirred at 80° for 24 h and evaporated. The residue was taken up with Et_2O, the soln. washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue recrystallized from hexane: **2** (68.7 g, 90%). Colorless crystals. M.p. 56°. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.83 (*s*, 4 H); 3.90 (*t*, $J=6$, 4 H); 1.75 (*m*, 4 H); 1.57–1.30 (*m*, 20 H); 0.89 (*t*, $J=6$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 153.16; 115.34; 68.62; 31.80; 31.50; 29.38; 29.24; 26.05; 22.64; 14.09. Anal. calc. for $C_{22}H_{38}O_2$: C 78.99, H 11.45; found: C 78.91, H 11.43.

2,5-Diiodo-1,4-bis(octyloxy)benzene (**3**). A soln. of **2** (40.0 g, 0.120 mol), KIO_3 (10.2 g, 0.048 mol), and I_2 (33.4 g, 0.131 mol) in AcOH (200 ml)/conc. H_2SO_4 soln. (3.6 ml)/H_2O (15 ml) was stirred at 80° for 24 h. After cooling, aq. $Na_2S_2O_3$ soln. was added until the purple color dissappeared, then the mixture was poured into H_2O (500 ml) and extracted with CH_2Cl_2. The org. layer was washed (H_2O), dried ($MgSO_4$), and evaporated. Recrystallization from hexane afforded **3** (41.68 g, 59%). Colorless crystals. M.p. 49°. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.18 (*s*, 2 H); 3.93 (*t*, $J=6$, 4 H); 1.74 (*m*, 4 H); 1.56–1.31 (*m*, 20 H); 0.90 (*t*, $J=6$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.79; 122.70; 86.27; 70.29; 31.77; 29.21; 29.11; 26.00; 22.64; 14.10. Anal. calc. for $C_{22}H_{36}I_2O_2$: C 45.07, H 6.19; found: C 45.12, H 6.31.

4-Iodo-2,5-bis(octyloxy)benzaldehyde (**4**). At 0°, 1.6M BuLi in hexane (7.5 ml, 11.94 mmol) was added dropwise to a stirred soln. of **3** (7.0 g, 11.94 mmol) in Et_2O (60 ml). The resulting mixture was stirred at 0° for 30 min, then a soln. of DMF (1.31 g, 17.92 mmol) in Et_2O (5 ml) was added dropwise. The mixture was stirred at 0° for 2 h, then sat. aq. NH_4Cl soln. was added (100 ml). The org. layer was washed (H_2O), dried ($MgSO_4$), and evaporated. Recrystallization from hexane afforded **4** (4.96 g, 85%). Colorless crystals. M.p. 71.5°. ^{1}H-NMR (200 MHz, $CDCl_3$): 10.19 (*s*, 1 H); 7.45 (*s*, 1 H); 7.18 (*s*, 1 H); 4.02 (*t*, $J=7$, 2 H); 4.00 (*t*, $J=7$, 2 H); 1.82 (*m*, 4 H); 1.59–1.29 (*m*, 20 H); 0.89 (*t*, $J=6$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.12; 155.72; 152.11; 125.11; 124.48; 108.78; 96.72; 69.86; 69.42; 31.78; 29.22; 29.09; 29.01; 26.02; 25.99; 22.64; 14.10. Anal. calc. for $C_{23}H_{37}I_2O_3$: C 44.89, H 6.06; found: C 44.88, H 5.89.

2,5-Bis(octyloxy)-4-[(triisopropylsilyl)ethynyl]benzaldehyde (**5**). $[PdCl_2(PPh_3)_2]$ (3 mol-%) and CuI (5 mol-%) were added to a stirred degassed soln. of **4** (3.40 g, 6.96 mmol) and (triisopropylsilyl)acetylene (1.27 g, 6.96 mmol) in dry Et_3N (70 ml) at r.t. The resulting mixture was stirred at r.t. for 48 h and then evaporated. The residue was taken up in CH_2Cl_2 and the org. layer washed (H_2O), dried ($MgSO_4$), and evaporated. CC (SiO_2, hexane/CH_2Cl_2 3:2) yielded **5** (3.02 g, 79%). Pale yellow crystals. M.p. 56°. ^{1}H-NMR (200 MHz, CD_2Cl_2): 7.30 (*s*, 1 H); 7.24 (*s* , 1 H); 7.06 (*s*, 1 H); 4.03 (*t*, $J=6$, 2 H); 3.98 (*t*, $J=$, 2 H); 1.80 (*m*, 4 H); 1.57–1.28 (*m*, 20 H); 1.14 (*s*, 21 H); 0.88 (*t*, $J=6$, 6 H). ^{13}C-NMR (50 MHz, CD_2Cl_2): 189.19; 155.74; 154.70; 125.40; 120.49; 118.38; 109.65; 102.79; 99.79; 69.75; 69.56; 32.28; 32.20; 29.84; 29.76; 29.70; 29.62; 29.55; 26.59; 26.41; 23.09; 23.06; 18.83; 14.27; 11.71. Anal. calc. for $C_{34}H_{58}O_3Si$: C 75.22, H 10.77; found: C 74.32, H 10.50.

{[4-(2,2-Dibromoethenyl)-2,5-bis(octyloxy)phenyl]ethynyl}triisopropylsilane (**6**). A mixture of CBr_4 (28.76 g, 86.72 mmol), PPh_3 (22.81 g, 86.72 mmol), and Zn dust (5.67 g, 86.72 mmol) in CH_2Cl_2 (300 ml) was stirred at r.t. for 24 h. The resulting suspension was then cooled to 0°, and a soln. of **5** (9.41 g, 17.34 mmol) in CH_2Cl_2 (40 ml) was added at once. The resulting mixture was slowly warmed to r.t. (over 1 h) and then stirred at r.t. for 12 h. The resulting thick suspension was filtered over SiO_2 (CH_2Cl_2) to remove the Zn salts and some of the P-contaning by-products. The resulting soln. was evaporated and the residue subjected to CC (SiO_2, hexane/CH_2Cl_2 1:1): **6** (13.0 g, 100%). Yellow liquid. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.61 (*s* , 1 H); 7.28 (*s*, 1 H); 6.89 (*s*, 1 H); 3.97 (*t*, $J=6$, 2 H); 3.93 (*t*, $J=6$, 2 H); 1.75 (*m*, 4 H); 1.56–1.30 (*m*, 20 H); 1.14 (*s*, 21 H); 0.89 (*t*, $J=6$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.00; 149.69; 132.39; 125.38; 116.84; 112.79; 102.99; 95.97; 92.28; 89.79; 69.51; 69.33; 31.86; 31.77; 29.49; 29.28; 29.23; 29.18; 26.20; 26.04; 22.67; 18.68; 14.12, 14.09; 11.34. Anal. calc. for $C_{35}H_{58}Br_2O_2Si$: C 60.16, H 8.37; found: C 60.42, H 8.30.

{[4-Ethynyl-2,5-bis(octyloxy)phenyl]ethynyl}triisopropylsilane (**7**). At −78°, 2M LDA in THF (27 ml, 54 mmol) was added dropwise to a soln. of **6** (12.11 g, 17.33 mmol) in THF (200 ml). The resulting mixture was slowly warmed to r.t. (over 3 h), then a sat. aq. NH_4Cl soln. (60 ml) was added, and the mixture diluted with hexane. The org. layer was washed (H_2O), dried ($MgSO_4$), and evaporated. CC (SiO_2, hexane/CH_2Cl_2 7:3) yielded **7** (8.49 g, 91%). Pale yellow crystals. M.p. 40°. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.91 (*s*, 2 H); 3.98 (*t*, $J=6$, 2 H); 3.93 (*t*, $J=6$, 2 H); 3.32 (*s* , 1 H); 1.75 (*m*, 4 H); 1.56–1.25 (*m*, 20 H); 1.14 (*s*, 21 H); 0.89 (*t*, $J=6$, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.12; 153.87; 117.58; 117.12; 114.59; 112.55; 102.69; 96.61; 82.09; 80.04; 69.70;

69.24; 31.86; 31.78; 29.44; 29.41; 29.29; 29.21; 29.17; 26.15; 25.90; 22.67; 18.68; 14.09; 11.34. Anal. calc. for $C_{35}H_{58}O_2Si$: C 78.00, H 10.85; found: C 77.86, H 10.57.

4-{[2,5-Bis(octyloxy)-4-[(triisopropylsilyl)ethynyl]phenyl}ethynyl}-2,5-bis(octyloxy)benzaldehyde (**8**). As described for **5**, with **4** (5.89 g, 12.06 mmol), **7** (6.50 g, 12.06 mmol), $[PdCl_2(PPh_3)_2]$ (3 mol-%), and CuI (5 mol-%) in Et_3N (150 ml). CC (SiO_2, hexane/CH_2Cl_2 7:3 → 1:1) yielded **8** (7.50 g, 79%). Yellow crystals. M.p. 53°. UV/VIS (CH_2Cl_2): 400 (33410), 306 (23650). ^1H-NMR (200 MHz, $CDCl_3$): 8.15 (*s*, 1 H); 7.32 (*s*, 1 H); 7.10 (*s*, 1 H); 6.95 (*s*, 2 H); 4.07–3.92 (*m*, 8 H); 1.75 (*m*, 8 H); 1.56–1.29 (*m*, 40 H); 1.15 (*s*, 21 H); 0.88 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.10; 155.46; 154.27; 153.49; 153.37; 124.71; 120.75; 117.77; 116.44; 114.58; 113.62; 109.95; 102.82; 96.88; 94.01; 90.66; 69.73; 69.33; 69.18; 69.11; 31.85; 31.82; 31.77; 31.56; 29.45; 29.37; 29.29; 29.20; 29.15; 26.87; 26.20; 26.18; 26.05; 25.93; 22.64; 18.67; 14.05; 11.33. Anal. calc. for $C_{58}H_{94}O_5Si$: C 77.45, H 10.53; found: C 77.38, H 10.50.

4-{[4-Ethynyl-2,5-bis(octyloxy)phenyl]ethynyl}-2,5-bis(octyloxy)benzaldehyde (**9**). At 0°, 1M Bu_4NF in THF (1.8 ml) was added to a stirred soln. of **8** (1.50 g, 1.67 mmol) in THF (100 ml) at 0°. After 1 h, several drops of H_2O were added, and the mixture was diluted with CH_2Cl_2, washed with H_2O, dried ($MgSO_4$), and evaporated. CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **9** (1.13 g, 91%). Yellow solid. M.p. 45°. UV/VIS (CH_2Cl_2): 395 (19600), 304 (14500). ^1H-NMR (200 MHz, $CDCl_3$): 8.15 (*s*, 1 H); 7.32 (*s*, 1 H); 7.10 (*s*, 1 H); 7.00 (*s*, 1 H); 6.99 (*s*, 1 H); 4.01 (*m*, 8 H); 3.36 (*s*, 1 H); 1.83 (*m*, 8 H); 1.57–1.27 (*m*, 40 H); 0.87 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.09; 155.46; 154.12; 153.56; 153.46; 124.84; 120.62; 117.92; 117.49; 117.04; 114.31; 113.21; 110.02; 93.56; 90.88; 82.55; 79.88; 69.67; 69.57; 69.37; 69.16; 31.81; 31.76; 31.56; 29.34; 29.29; 29.24; 29.19; 29.15; 26.05; 25.92; 22.62; 14.06; 14.03. Anal. calc. for $C_{49}H_{74}O_5$: C 79.20, H 10.04; found: C 79.15, H 10.15.

4-{[4-{[4-(Dibutylamino)phenyl]ethynyl}-2,5-bis(octyloxy)phenyl]ethynyl}-2,5-bis(octyloxy)benzaldehyde (**10**). As described for **5**, with **9** (665 mg, 0.895 mmol), *N,N*-dibutyl-4-iodoaniline (349 mg, 1.074 mmol), $[PdCl_2(PPh_3)_2]$ (3 mol-%), and CuI (5 mol-%) in Et_3N (30 ml). CC (SiO_2, hexane/CH_2Cl_2 3:2) gave **10** (560 mg, 66%). Yellow solid. M.p. 71°. UV/VIS (CH_2Cl_2): 421 (45400), 314 (27600). ^1H-NMR (200 MHz, $CDCl_3$): 8.15 (*s*, 1 H); 7.37 (*d*, *J* = 8, 2 H); 7.32 (*s*, 1 H); 7.11 (*s*, 1 H); 6.99 (*s*, 2 H); 6.57 (*d*, *J* = 8, 2 H); 4.04 (*m*, 8 H); 3.29 (*t*, *J* = 7.5, 4 H); 1.85 (*m*, 8 H); 1.66–1.25 (*m*, 48 H); 0.97 (*t*, *J* = 7, 6 H); 0.87 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.06; 155.48; 153.77; 153.42; 153.13; 147.96; 132.88; 124.58; 121.01; 117.37; 117.23; 116.59; 116.11; 112.22; 111.05; 109.95; 108.77; 97.18; 94.37; 90.42; 83.63; 69.59; 69.56; 69.35; 69.10; 50.63; 31.80; 31.74; 29.42; 29.29; 29.26; 29.17; 29.13; 26.10; 26.02; 25.94; 25.91; 22.66; 22.61; 20.26; 14.02; 13.93. Anal. calc. for $C_{63}H_{95}NO_5$: C 79.95, H 10.12, N 1.48; found: C 80.00, H 10.25, N 1.45.

{[4-{[4-(2,2-Dibromoethenyl)-2,5-bis(octyloxy)phenyl]ethynyl}-2,5-bis(octyloxy)phenyl]ethynyl}triisopropylsilane (**11**). As described for **6**, with CBr_4 (7.58 g, 22.85 mmol), PPh_3 (6.01 g, 22.85 mmol), Zn dust (1.50 g, 22.85 mmol), and **8** (4.11 g, 4.57 mmol) in CH_2Cl_2 (200 ml). CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **11** (5.14 g, 99%). Yellow solid. ^1H-NMR (200 MHz, $CDCl_3$): 7.64 (*s*, 1 H); 7.37 (*s*, 1 H); 6.97 (*s*, 1 H); 6.95 (*s*, 1 H); 6.94 (*s*, 1 H); 4.07–3.90 (*m*, 8 H); 1.90–1.77 (*m*, 8 H); 1.56–1.29 (*m*, 40 H); 1.15 (*s*, 21 H); 0.89–0.83 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.30; 153.18; 153.12; 149.94; 132.15; 125.19; 117.85; 116.33; 116.19; 114.32; 113.89; 113.44; 102.99; 96.35; 92.25; 91.26; 91.10; 89.65; 69.75; 69.14; 69.11; 31.83; 31.77; 31.56; 29.45; 29.39; 29.28; 29.21; 29.17; 26.87; 26.18; 26.04; 25.99; 25.94; 22.64; 18.67; 14.09; 14.05; 11.33. Anal. calc. for $C_{59}H_{94}Br_2O_4Si$: C 67.15, H 8.98; found: C 67.34, H 8.95.

{[4-{[4-Ethynyl-2,5-bis(octyloxy)phenyl]ethynyl}-2,5-bis(octyloxy)phenyl]ethynyl}triisopropylsilane (**12**). As described for **7**, with **11** (4.82 g, 4.567 mmol), and 2M LDA in THF (11.42 ml) in dry THF (50 ml). CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **12** (3.78 g, 92%). Yellow solid. M.p. 50–51°. UV/VIS (CH_2Cl_2): 378 (37300), 309 (34000). ^1H-NMR (200 MHz, $CDCl_3$): 6.99 (*s*, 1 H); 6.97 (*s*, 1 H); 6.94 (*s*, 2 H); 4.05–3.92 (*m*, 8 H); 3.35 (*s*, 1 H); 1.87–1.71 (*m*, 8 H); 1.57–1.26 (*m*, 40 H); 1.15 (*s*, 21 H); 0.89–0.83 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.33; 154.14; 153.29; 153.25; 117.93; 117.87; 116.91; 116.43; 114.96; 114.23; 114.04; 112.52; 103.01; 96.46; 91.63; 91.01; 82.28; 80.04; 69.80; 69.70; 69.53; 69.16; 31.90; 31.85; 31.82; 29.50; 29.42; 29.34; 29.25; 29.18; 28.86; 25.99; 25.94; 22.67; 18.70; 14.09; 11.37. Anal. calc. for $C_{59}H_{94}O_4Si$: C 79.14, H 10.58; found: C 79.16, H 10.92.

4-{[4-{[2,5-Bis(octyloxy)-4-[(triisopropylsilyl)ethynyl]phenyl}ethynyl}-2,5-bis(octyloxy)phenyl]ethynyl}-2,5-bis(octyloxy)benzaldehyde (**13**). As described for **5**, with **12** (2.0 g, 2.233 mmol) and **4** (1.09 g, 2.23 mmol) in Et_3N (30 ml). CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **13** (2.18 g, 77 %). Yellow crystals. M.p. 66°. UV/VIS (CH_2Cl_2) : 412 (51000), 318 (29200). ^1H-NMR (200 MHz, $CDCl_3$): 8.14 (*s*, 1 H); 7.32 (*s*, 1 H); 7.11 (*s*, 1 H); 7.01 (*s*, 2 H); 6.94 (*s*, 2 H); 4.09–3.92 (*m*, 12 H); 1.88–1.74 (*m*, 12 H); 1.56–1.27 (*m*, 60 H); 1.15 (*s*, 21 H); 0.89–0.83 (*m*, 18 H). ^{13}C-NMR (50 MHz, CD_2Cl_2): 155.46; 154.30; 153.66; 153.50; 153.45; 153.23; 124.74; 120.79; 117.87; 117.43; 117.29; 117.13; 116.44; 114.99; 114.21; 114.07; 113.56; 109.98; 102.96; 96.51; 93.99; 91.92; 91.15; 90.86;

69.78; 69.65; 69.57; 69.35; 69.13; 31.85; 31.82; 31.77; 31.56; 29.45; 29.37; 29.31; 29.20; 29.15; 26.87; 26.18; 26.05; 25.99; 25.94; 22.64; 18.67; 14.04; 11.34. Anal. calc. for $C_{82}H_{130}O_7Si$: C 78.41, H 10.43; found: C 78.69, H 10.74.

4-{{4-{[4-Ethynyl-2,5-bis(octyloxy)phenyl]ethynyl}-2,5-bis(octyloxy)phenyl}ethynyl}-2,5-bis(octyloxy)benzaldehyde (**14**). As described for **9**, with **13** (1.40 g, 1.11 mmol) and 1M Bu_4N in THF (1.2 ml) in THF (100 ml). CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **14** (1.13 g, 92%). Yellow solid. M.p. 73°. UV/VIS (CH_2Cl_2): 408 (51300), 318 (28200), 273 (18300). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.15 (*s*, 1 H); 7.32 (*s*, 1 H); 7.11 (*s*, 1 H); 7.02 (*s*, 2 H); 6.99 (*s*, 1 H); 6.98 (*s*, 1 H); 4.03 (*m*, 12 H); 3.35 (*s*, 1 H); 1.82 (*m*, 12 H); 1.56 – 1.26 (*m*, 60 H); 0.86 (*m*, 18 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.07; 155.45; 154.09; 153.63; 153.49; 153.45; 153.26; 124.74; 120.72; 117.90; 117.43; 117.26; 117.16; 116.94; 114.79; 113.68; 112.61; 109.97; 93.91; 91.49; 91.37; 90.90; 82.31; 79.96; 69.62; 69.59; 69.53; 69.33; 69.13; 31.80; 31.75; 29.37; 29.33; 29.26; 29.18; 29.12; 25.96; 25.90; 22.61; 14.02. Anal. calc. for $C_{73}H_{110}O_7$: C 79.73, H 10.08; found: C 79.97, H 10.26.

4-{{4-{{4-{[4-(Dibutylamino)phenyl]ethynyl}-2,5-bis(octyloxy)phenyl}ethynyl}-2,5-bis(octyloxy)phenyl}ethynyl}-2,5-bis(octyloxy)benzaldehyde (**15**). As described for **5**, with **14** (700 mg, 0.64 mmol), *N,N*-dibutyl-4-iodoaniline (253 mg, 0.76 mmol), $[PdCl_2(PPh_3)_2]$ (3 mol-%), and CuI (5 mol-%) in Et_3N (30 ml). CC (SiO_2, hexane/CH_2Cl_2 3:2) gave **15** (180 mg, 21%). Yellow solid. M.p. 64°. UV/VIS (CH_2Cl_2): 424 (90800), 322 (40800). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.14 (*s*, 1 H); 7.37 (*d*, *J* = 8, 2 H); 7.32 (*s*, 1 H); 7.11 (*s*, 1 H); 7.02 – 6.99 (*m*, 4 H); 6.57 (*d*, *J* = 8, 2 H); 4.03 (*m*, 12 H); 3.29 (*t*, *J* = 7, 4 H); 1.84 (*m*, 12 H); 1.57 – 1.28 (*m*, 68 H); 0.96 (*t*, *J* = 7, 6 H); 0.87 (*m*, 18 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.01; 155.43; 153.63; 153.58; 153.45; 153.34; 153.13; 147.90; 132.83; 124.68; 120.80; 117.39; 117.29; 117.16; 117.10; 116.60; 115.52; 113.32; 112.74; 111.03; 109.93; 108.85; 96.85; 94.05; 92.19; 90.85; 90.77; 83.67; 69.64; 69.56; 69.32; 69.08; 50.62; 31.80; 31.72; 29.42; 29.36; 29.28; 29.15; 29.10; 26.09; 26.01; 25.96; 25.88; 22.64; 22.61; 20.25; 14.02; 13.91. Anal. calc. for $C_{87}H_{130}NO_7$: C 80.26, H 10.06, N 1.08; found: C 79.68, H 10.19, N 1.06.

*5′-{4-{{2,5-Bis(octyloxy)-4-[(triisopropylsilyl)ethynyl]phenyl}ethynyl}-2,5-bis(octyloxy)phenyl}-1′,5′-dihydro-1′-methyl-2′*H*-[5,6]fullereno-C$_{60}$-*I$_h$*-[1,9-*c*]imidazole* (**16**). A mixture of **8** (350 mg, 0.389 mmol), C_{60} (308 mg, 0.428 mmol), and *N*-methylglycine (208 mg, 2.334 mmol) in toluene (300 ml) was refluxed for 16 h. After cooling, the mixture was filtered and evaporated. CC (SiO_2, toluene/hexane 4:1) gave **16** (230 mg, 36%). Brown solid. M.p. 124°. UV/VIS (CH_2Cl_2): 303 (64100), 329 (47000), 363 (49900), 430 (48700), 702 (220). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.58 (*s* , 1 H); 7.03 (*s*, 1 H); 6.93 (*s*, 1 H); 6.92 (*s*, 1 H); 5.54 (*s*, 1 H); 4.98 (*d*, *J* = 9, 1 H); 4.32 (*d*, *J* = 9, 1 H); 4.18 – 3.67 (*m*, 8 H); 2.83 (*s*, 3 H); 1.86 – 1.73 (*m*, 8 H); 1.58 – 1.28 (*m*, 40 H); 1.14 (*s*, 21 H); 0.88 – 0.84 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 156.57; 154.97; 154.27; 154.03; 154.00; 153.71; 153.12; 151.43; 147.25; 146.69; 146.57; 146.22; 146.18; 146.14; 146.06; 146.02; 145.90; 145.68; 145.52; 145.41; 145.25; 145.19; 145.07; 144.56; 144.50; 144.42; 144.29; 143.00; 142.95; 142.63; 142.59; 142.51; 142.23; 142.20; 142.09; 142.04; 141.91; 141.69; 141.58; 140.13; 140.08; 139.65; 139.39; 136.39; 136.20; 136.07; 134.53; 127.12; 117.77; 116.41; 116.14; 114.72; 114.32; 113.75; 113.33; 102.99; 96.35; 91.33; 90.42; 76.48; 75.59; 69.97; 69.73; 69.19; 69.13; 68.58; 40.13; 31.88; 31.85; 31.82; 29.50; 29.45; 29.37; 29.28; 26.18; 26.04; 26.01; 25.91; 22.74; 22.67; 18.68; 14.18; 14.12; 14.09; 11.34. FAB-MS: 1647.7 (M^+, $C_{120}H_{99}NO_4Si^+$; calc. 1647.2). Anal. calc. for $C_{120}H_{99}NO_4Si$: C 87.50, H 6.06; found: C 87.69, H 6.19.

*5′-{4-{{4-{{2,5-Bis(octyloxy)-4-[(triisopropylsilyl)ethynyl]phenyl}ethynyl}-2,5-bis(octyloxy)phenyl}ethynyl}-2,5-bis(octyloxy)phenyl}-1′,5′-dihydro-1′-methyl-2′*H*-[5,6]fullereno-C$_{60}$-*I$_h$*-[1,9-*c*]imidazole* (**17**). As described for **16**, with **13** (400 mg, 0.318 mmol), C_{60} (252 mg, 0.350 mmol), and *N*-methylglycine (170 mg, 1.91 mmol) in toluene (250 ml). CC (SiO_2, toluene/hexane 1:1) gave **17** (260 mg, 40%). Brown solid. M.p. 108°. UV/VIS (CH_2Cl_2): 392 (70900), 326 (54600), 311 (67300). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.59 (*s*, 1 H); 7.04 (*s*, 1 H); 6.99 (*s*, 2 H); 6.93 (*s*, 2 H); 5.55 (*s*, 1 H); 4.98 (*d*, *J* = 9, 1 H); 4.32 (*d*, *J* = 9, 1 H); 4.15 – 3.72 (*m*, 12 H); 2.84 (*s*, 3 H); 1.86 – 1.71 (*m*, 12 H); 1.57 – 1.28 (*m*, 60 H); 1.15 (*s*, 21 H); 0.89 – 0.85 (*m*, 18 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 156.50; 154.92; 154.28; 153.96; 153.61; 153.39; 153.15; 151.41; 147.18; 146.61; 146.53; 146.11; 146.06; 146.02; 145.84; 145.62; 145.46; 145.33; 145.20; 145.12; 145.01; 144.50; 144.44; 144.34; 144.24; 142.94; 142.90; 142.57; 142.52; 142.44; 142.19; 142.14; 142.03; 141.98; 141.85; 141.63; 141.53; 140.08; 140.05; 139.60; 139.35; 136.33; 136.17; 135.99; 134.49; 127.12; 117.87; 117.19; 117.08; 117.05; 116.38; 116.22; 116.16; 114.75; 114.35; 114.24; 114.11; 113.86; 113.38; 102.99; 96.37; 91.57; 91.53; 91.34; 90.42; 76.45; 75.59; 75.54; 69.94; 69.77; 69.57; 69.14; 69.11; 68.54; 40.08; 31.85; 31.82; 29.44; 29.39; 29.34; 29.26; 26.17; 25.98; 25.93; 22.70; 22.64; 18.67; 14.17; 14.10; 14.05; 11.33. FAB-MS: 2003.9 (M^+, $C_{144}H_{135}O_6NSi^+$; calc. 2003.7). Anal. calc. for $C_{144}H_{135}NO_6Si$: C 86.32, H 6.79, N 0.70; found: C 86.58, H 6.87, N 0.71.

N,N*-Dibutyl-4-{{4-{{4-(1′,5′-dihydro-1′-methyl-2′*H*-[5,6]fullereno-C$_{60}$-*I$_h$*-[1,9-*c*]imidazol-5′-yl)-2,5-bis(octyloxy)phenyl}ethynyl}-2,5-bis(octyloxy)phenyl}ethynyl}benzenamine* (**18**). As described for **16**, with **10** (330 mg, 0.35 mmol), C_{60} (276 mg, 0.38 mmol), and *N*-methylglycine (186 mg, 2.09 mmol) in toluene (300 ml). CC (SiO_2, hexane/CH_2Cl_2 3:7) gave **18** (230 mg, 39%). Dark brown solid. M.p. 134°. UV/VIS (CH_2Cl_2): 393 (85200), 328

(58800), 298 (71900). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.58 (*s*, 1 H); 7.36 (*d*, $J = 8$, 2 H); 7.04 (*s*, 1 H); 6.96 (*s*, 2 H); 6.56 (*d*, $J = 8$, 2 H); 5.54 (*s*, 1 H), 4.98 (*d*, $J = 9$, 1 H); 4.32 (*d*, $J = 9$, 1 H); 4.15–3.67 (*m*, 8 H); 3.28 (*t*, $J = 7$, 4 H); 2.84 (*s*, 3 H); 1.80 (*m*, 8 H); 1.66–1.27 (*m*, 48 H); 0.96 (*t*, $J = 7$, 6 H); 0.89 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 156.53; 154.95; 154.03; 153.92; 153.64; 153.47; 153.10; 151.39; 147.84; 147.18; 146.62; 146.54; 146.14; 146.11; 146.06; 146.03; 146.00; 145.94; 145.84; 145.62; 145.46; 145.36; 145.19; 145.11; 145.01; 144.52; 144.44; 144.36; 144.24; 142.94; 142.89; 142.55; 142.52; 142.44; 142.19; 142.14; 142.09; 142.06; 142.03; 141.98; 141.85; 141.64; 141.60; 141.53; 140.08; 140.03; 139.60; 139.33; 136.35; 136.15; 136.01; 134.48; 132.83; 126.90; 117.16; 116.57; 116.14; 115.22; 114.80; 113.59; 112.95; 111.03; 108.93; 96.69; 91.02; 90.66; 83.70; 76.47; 75.57; 69.97; 69.72; 69.53; 69.16; 68.54; 50.62; 40.07; 31.85; 31.80; 31.53; 29.47; 29.42; 29.33; 29.25; 26.85; 26.09; 25.99; 25.90; 22.70; 22.64; 20.26; 14.15; 14.09; 14.05; 13.94. FAB-MS: 1694.1 (M^+, $C_{125}H_{100}N_2O_4^+$; calc. 1694.2). Anal. calc. for $C_{125}H_{100}N_2O_4$: C 88.62, H 5.95, N 1.65; found: C 88.35, H 6.25, N 1.69.

N,N-*Dibutyl-4-{{4-{{4-{{4-(1′,5′-dihydro-1′-methyl-2′*H*-[5,6]fullereno-*C_{60}-I$_h$*-[1,9-*c*]imidazol-5′-yl)-2,5-bis(octyloxy)phenyl}ethynyl}-2,5-bis(octyloxy)phenyl}ethynyl}-2,5-bis(octyloxy)phenyl}ethynyl}benzenamine* (**19**). As described for **16**, with **15** (140 mg, 0.11 mmol), C_{60} (86 mg, 0.12 mmol), and *N*-methylglycine (58 mg, 0.651 mmol) in toluene (100 ml). CC (SiO_2, hexane/CH_2Cl_2 3:7) gave **19** (101 mg, 45%). Dark brown solid. M.p. 70°. UV/VIS (CH_2Cl_2): 702 (370), 404 (96300), 309 (72500). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.59 (*s*, 1 H); 7.37 (*d*, $J = 8$, 2 H); 7.04 (*s*, 1 H); 6.99 (*s*, 2 H); 6.98 (*s*, 2 H); 6.57 (*d*, $J = 8$, 2 H); 5.55 (*s*, 1 H); 4.98 (*d*, $J = 9$, 1 H); 4.32 (*d*, $J = 9$, 1 H); 4.15–3.67 (*m*, 12 H); 3.29 (*t*, $J = 7$, 4 H); 2.84 (*s*, 3 H); 1.82 (*m*, 12 H); 1.56–1.26 (*m*, 48 H); 0.96 (*t*, $J = 7$, 6 H); 0.86 (*m*, 18 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 156.55; 154.95; 154.03; 153.98; 153.68; 153.55; 153.39; 153.36; 153.15; 151.43; 147.90; 147.21; 146.65; 146.56; 146.18; 146.14; 146.10; 146.06; 146.02; 145.98; 145.87; 145.65; 145.49; 145.38; 145.22; 145.17; 145.14; 145.09; 145.04; 144.53; 144.47; 144.39; 144.31; 144.26; 142.97; 142.92; 142.60; 142.55; 142.47; 142.22; 142.17; 142.12; 142.09; 142.06; 142.01; 141.88; 141.68; 141.64; 141.55; 140.11; 140.06; 139.63; 139.36; 136.36; 136.19; 136.03; 134.51; 132.87; 132.74; 127.11; 117.19; 117.10; 116.68; 116.17; 115.38; 114.82; 114.35; 114.05; 113.43; 112.95; 111.05; 108.91; 96.78; 91.79; 91.45; 91.04; 90.46; 83.71; 76.48; 75.59; 69.97; 69.73; 69.61; 69.54; 69.18; 68.57; 50.65; 40.10; 31.86; 31.82; 29.44; 29.31; 29.28; 29.21; 26.10; 25.98; 25.94; 22.70; 22.62; 20.28; 14.17; 14.10; 14.07; 13.96. FAB-MS: 2051.1 ($[M + H]^+$, $C_{149}H_{136}N_2O_6^+$; calc. 2050.7). Anal. calc. for $C_{149}H_{135}O_6N_2$: C 87.31, H 6.64, N 1.37; found: C 86.99, H 6.62, N 1.33.

4,4′-{[2,5-Bis(octyloxy)-1,4-phenylene]bis{ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl}}bis[2,5-bis(octyloxy)benzaldehyde] (**20**). As described for **5**, with **9** (330 mg, 0.443 mmol), **3** (130 mg, 0.222 mmol), [$PdCl_2(PPh_3)_2$)] (3 mol-%), and CuI (5 mol-%) in Et_3N (20 ml). CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **20** (320 mg, 79%). Orange solid. M.p. 126°. UV/VIS (CH_2Cl_2): 432 (89100), 323 (34100). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.14 (*s*, 2 H); 7.33 (*s*, 2 H); 7.11 (*s*, 2 H); 7.02 (*s*, 6 H); 4.04 (*m*, 20 H); 1.85 (*m*, 20 H); 1.56–1.19 (*m*, 100 H); 0.87 (*m*, 30 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.07; 155.45; 153.64; 153.49; 153.44; 124.74; 117.43; 117.18; 114.93; 114.26; 113.62; 109.98; 93.96; 91.84; 91.45; 90.90; 69.62; 69.35; 69.13; 31.80; 31.75; 29.37; 29.29; 29.18; 29.13; 26.04; 25.98; 25.90; 22.62; 14.04. Anal. calc. for $C_{120}H_{182}O_{12}$: C 79.33, H 10.10; found: C 79.21, H 10.05.

4,4′-{[2,5-Bis(octyloxy)-1,4-phenylene]bis{ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl}}bis[2,5-bis(octyloxy)benzenemethanol] (**21**). At 0°, 1M of DIBAL-H (0.5 ml) was added to a soln. of **20** (300 mg, 0.165 mmol) in THF (40 ml). After 2 h, a few drops of H_2O were added, the mixture was then diluted with CH_2Cl_2 and filtered. The soln. was dried ($MgSO_4$), filtered, and evaporated. CC (SiO_2, CH_2Cl_2) gave **21** (290 mg, 96%). Yellow solid. M.p. 124°. UV/VIS (CH_2Cl_2): 412 (86600), 318 (33500). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.01 (*s*, 6 H); 6.98 (*s*, 2 H); 6.89 (*s*, 2 H); 4.68 (*d*, $J = 6$, 4 H); 4.03 (*m*, 20 H); 2.36 (*t*, $J = 6$, 2 H); 1.83 (*m*, 20 H); 1.57–1.26 (*m*, 100 H); 0.87 (*m*, 30 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 153.90; 153.44; 153.41; 153.36; 150.21; 130.95; 117.18; 115.52; 114.48; 114.24; 113.99; 113.60; 112.44; 91.57; 91.53; 91.39; 89.86; 69.83; 69.59; 68.49; 61.83; 31.80; 31.74; 29.36; 29.28; 29.18; 26.09; 25.94; 22.61; 14.01. Anal. calc. for $C_{120}H_{186}O_{12}$: C 79.16, H 10.30; found: C 79.06, H 10.43.

Propanedioic Acid [2,5-Bis(octyloxy)-1,4-phenylene]bis{ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]methylene} Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Ester (**23**). DCC (22 mg, 0.105 mmol) was added to a stirred soln. of **21** (160 mg, 0.088 mmol), **22** (109 mg, 0.193 mmol), and DMAP (4.3 mg, 0.035 mmol) in CH_2Cl_2 (50 ml) at 0°. After 1 h, the mixture was allowed to slowly warm to r.t. (within 1 h), then stirred for 12 h, filtered, and evaporated. CC (SiO_2, CH_2Cl_2/hexane 4:1) gave **23** (251 mg, 98%). Yellow glassy product. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.02–6.92 (*m*, 8 H); 6.47–6.40 (*m*, 8 H); 5.24–5.03 (*m*, 8 H); 4.03–3.88 (*m*, 28 H); 3.52–3.43 (*m*, 4 H); 1.79 (*m*, 28 H); 1.59–1.27 (*m*, 172 H); 0.87 (*m*, 42 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.16; 166.08; 160.36; 153.69; 153.41; 150.25; 137.11; 132.23; 132.02; 131.40; 131.33; 128.48; 128.24; 125.24; 117.15; 115.82; 114.39; 114.24; 114.08; 113.51; 106.14; 100.98; 91.52; 91.41; 90.13;

69.75; 69.54; 68.68; 67.90; 67.05; 66.16; 65.58; 62.42; 41.41; 31.83; 31.78; 29.58; 29.55; 29.34; 29.26; 29.15; 25.96; 22.59; 14.01.

4,4′-{But-1,3-diyne-1,4-diylbis{[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl}}bis[2,5-bis(octyloxy)benzaldehyde] (**24**). CuCl (100 mg, 1.01 mmol) and TMEDA (1 ml, 6.60 mmol) were added to a soln. of **14** (176 mg, 0.160 mmol) in CH_2Cl_2 (70 ml). The resulting mixture was vigorously stirred for 12 h in the presence of dry air, then filtered over a short SiO_2 plug (CH_2Cl_2) and evaporated. CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **24** (160 mg, 91%). Yellow solid. M.p. 113°. UV/VIS (CH_2Cl_2): 440 (134000), 324 (50000). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.15 (*s*, 2 H); 7.33 (*s*, 2 H); 7.11 (*s*, 2 H); 7.02 (*s*, 4 H); 7.00 (*s*, 4 H); 4.03(*m*, 24 H); 1.83 (*m*, 24 H); 1.56 – 1.27 (*m*, 120 H); 0.87 (*m*, 36 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 189.06; 155.45; 154.94; 153.64; 153.49; 153.29; 124.78; 120.72; 117.80; 117.43; 117.27; 117.18; 116.99; 115.28; 114.75; 113.78; 112.58; 110.00; 93.93; 92.04; 91.63; 90.96; 79.56; 79.34; 69.64; 69.35; 69.13; 31.80; 31.74; 29.37; 29.33; 29.28; 29.21; 29.17; 29.12; 25.96; 25.91; 22.62; 14.02. Anal. calc. for $C_{146}H_{218}O_{14}$: C 79.81, H 10.00; found: C 79.42, H 10.10.

4,4′-{But-1,3-diyne-1,4-diylbis{[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl}}bis[2,5-bis(octyloxy)benzenemethanol] (**25**). As described for **21**, with **24** (200 mg, 0.091 mmol) and 1M DIBAL-H in hexane (0.3 ml) in THF (20 ml). CC (SiO_2, CH_2Cl_2) gave **25** (190 mg, 95%). Orange solid. M.p. 112°. UV/VIS (CH_2Cl_2): 427 (106000), 315 (42000). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.02 – 6.98 (*m*, 10 H); 6.90 (*s*, 2 H); 4.68 (*d*, $J = 6$, 4 H); 4.02 (*m*, 24 H); 2.37 (*t*, $J = 6$, 2 H); 1.83 (*m*, 24 H); 1.59 – 1.18 (*m*, 120 H); 0.87 (*m*, 36 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 154.94; 153.95; 153.53; 153.39; 150.29; 130.97; 117.83; 117.27; 116.99; 115.58; 115.44; 114.71; 113.83; 113.73; 112.52; 112.46; 92.22; 91.66; 91.18; 89.86; 79.56; 79.29; 69.89; 69.65; 68.54; 61.98; 31.82; 31.77; 29.37; 29.29; 29.21; 26.12; 25.96; 22.62; 14.04. Anal. calc. for $C_{120}H_{186}O_{12}$: C 79.66, H 9.25; found: C 79.47, H 9.24.

Propanedioic Acid But-1,3-diyne-1,4-diylbis[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]methylene} Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Ester (**26**). As described for **23**, with **25** (130 mg, 0.059 mmol), **22** (73 mg, 0.130 mmol), DCC (30 mg, 0.145 mmol), and DMAP (2.89 mg, 0.024 mmol) in CH_2Cl_2 (50 ml). CC (SiO_2, CH_2Cl_2) gave **25** (194 mg, 100%). Orange glassy product. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.01 – 6.91 (*m*, 10 H); 6.47 – 6.40 (*m*, 8 H); 5.24 – 5.02 (*m*, 8 H); 4.01 – 3.88 (*m*, 32 H); 3.51 – 3.49 (*m*, 4 H); 1.79 (*m*, 32 H); 1.57 – 1.26 (*m*, 156 H); 0.87 (*m*, 48 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.24; 166.14; 160.41; 154.92; 153.72; 153.52; 153.42; 150.31; 137.14; 125.30; 117.82; 117.23; 116.96; 115.90; 115.41; 114.61; 114.27; 113.91; 113.52; 112.44; 106.23; 101.04; 100.85; 92.20; 91.52; 91.21; 90.13; 79.55; 79.29; 69.83; 69.62; 68.76; 67.98; 67.13; 66.22; 62.49; 41.46; 31.86; 31.80; 29.57; 29.36; 29.29; 29.20; 29.12; 25.99; 25.91; 22.62; 14.05.

*3′*H-*Cyclopropa[1,9][5,6]fullerene-C_{60}-*I$_h$*-3′,3′-dicarboxylic Acid [2,5-Bis(octyloxy)-1,4-phenylene]bis{ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]methylene} Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Ester* (**27**). A soln. of **23** (250 mg, 0.086 mmol), C_{60} (136 mg, 0.189 mmol), DBU (0.1 ml, 0.695 mmol), and I_2 (54.5 mg, 0.215 mmol) in toluene (300 ml) was stirred for 6 h at r.t., then filtered over a short SiO_2 plug (CH_2Cl_2), and evaporated. CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **27** (145 mg, 38%). Brown solid. M.p. 95°. UV/VIS (CH_2Cl_2): 324 (99800), 411 (95400), 688 (200). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.05 (*s*, 2 H); 7.03 (*s*, 2 H); 7.02 (*s*, 2 H); 7.00 (*s*, 2 H); 6.97 (*s*, 2 H); 6.59 (*s*, 2 H); 6.58 (*s*, 2 H); 6.40 (*t*, $J = 2$, 2 H); 5.58 (*s*, 4 H); 5.43 (*s*, 4 H); 4.05 – 3.87 (*m*, 28 H); 1.84 (*m*, 20 H); 1.73 (*m*, 8 H); 1.55 – 1.26 (*m*, 172 H); 0.89 (*m*, 42 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 163.42; 160.45; 153.67; 153.45; 153.41; 150.61; 145.13; 145.10; 145.05; 145.02; 144.96; 144.80; 144.59; 144.46; 144.40; 143.74; 142.91; 142.85; 142.10; 141.83; 141.75; 140.79; 140.76; 139.26; 138.70; 136.50; 124.53; 117.23; 115.95; 114.87; 114.34; 114.26; 114.22; 114.17; 106.84; 101.62; 91.54; 91.49; 91.33; 90.51; 71.42; 69.86; 69.62; 68.86; 68.06; 64.16; 51.90; 31.89; 31.83; 29.67; 29.61; 29.38; 29.34; 29.30; 29.26; 26.08; 26.05; 25.98; 25.95; 22.63; 14.09; 14.06. MALDI-TOF-MS: 4347.9 (M^+, $C_{308}H_{294}O_{22}^+$; calc. 4347.7). Anal. calc. for $C_{308}H_{294}O_{22}$: C 85.08, H 6.82; found: C 84.85, H 6.99.

*3′*H-*Cyclopropa[1,9][5,6]fullerene-C_{60}-*I$_h$*-3′,3′-dicarboxylic Acid But-1,3-diyne-1,4-diylbis{[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]ethyne-2,1-diyl[2,5-bis(octyloxy)-4,1-phenylene]methylene} Bis{[3,5-bis(dodecyloxy)phenyl]methyl} Ester* (**28**). As described for **27**, with **26** (194 mg, 0.059 mmol), C_{60} (94 mg, 0.130 mmol), I_2 (38mg, 0.147 mmol), and DBU (0.1 ml, 0.695 mmol) in toluene (200 ml). CC (SiO_2, hexane/CH_2Cl_2 1:1) gave **28** (90 mg, 32%). Brown solid. UV/VIS (CH_2Cl_2): 426 (12600), 320 (11500), 257 (27900). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.05 – 6.97 (*m*, 12 H); 6.58 – 6.39 (*m*, 6 H); 5.58 (*s*, 4 H); 5.43 (*s*, 4 H); 4.01 – 3.85 (*m*, 32 H); 1.81 (*m*, 32 H); 1.58 – 1.26 (*m*, 156 H); 0.88 (*m*, 48 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 163.46; 163.43; 160.46; 154.94; 153.68; 153.53; 153.42; 153.26; 150.63; 145.14; 145.09; 145.03; 144.96; 144.80; 144.60; 144.47; 144.40; 143.75; 142.92; 142.86; 142.11; 141.84; 141.76; 140.80; 140.77; 139.27; 138.71; 136.51; 130.86; 128.80; 124.58; 117.83; 117.31; 117.23; 117.00; 116.00; 115.41; 114.93; 114.55; 114.21; 113.99;

112.47; 106.87; 101.65; 92.20; 91.42; 91.28; 90.50; 79.58; 79.33; 71.46; 69.89; 69.67; 68.87; 68.07; 64.21; 53.39; 31.91; 31.83; 29.68; 29.63; 29.41; 29.36; 29.23; 26.10; 26.05; 26.01; 25.98; 25.93; 22.66; 14.12; 14.07. MALDI-TOF-MS: 4728.5 (M^+, $C_{334}H_{330}O_{24}^+$; calc. 4728.3). Anal. calc. for $C_{334}H_{330}O_{24}$: C 84.84, H 7.03; found: C 84.52, H 7.31.

Photovoltaic Devices. The substrates utilized were always 20 × 20 mm ITO-coated glass slices. In all cases and prior to film deposition, substrates were cleaned ultrasonically by repeating at least twice a procedure including successive washing steps with 35% H_2O_2 soln./ammonia/H_2O solution 1:1:5 (*v*/*v*), EtOH, and acetone. Just before application of the active layer, every substrate was spin-coated by a layer of PEDOT-PSS (*Baytron P*, *Bayer AG*) as a hole injection/transport layer resulting in a thickness of *ca.* 70 nm, as measured by a *Dektak-3130* surface profiler. Subsequently they were left to dry at 10^{-6} Torr for several hours at an elevated temperature. Active-layer films were fabricated by spin-coasting (*ca.* 1000 rpm) from 2% (*w*/*w*) $CHCl_3$ solns. (thickness *ca.* 100 nm as measured by a *Dektak-3130* surface profiler). Finally, Al electrodes were vapor-deposited at a dynamic vacuum around $3 \cdot 10^{-7}$ Torr on the top of the structure, with a deposition rate of 0.4 nm/s, to a thickness of 100 nm. *I*/*V* curves were measured with a *Keithley-236*-source measure unit, while an *Oriel-60100* xenon lamp and a *CVI-Digikrom-120* monochromator provided illumination through the ITO side. In forward bias, the ITO electrode was wired as the anode. The impedance spectroscopy was carried out with a *Solartron-SI1260* impedance/gain phase analyzer. A standard calibrated silicon photodiode was used to record the action photovoltaic spectra. All measurements were performed in a glovebox under N_2.

Morphology Characterization. The compounds were spin-coated from 2% (*w*/*w*) $CHCl_3$ solns. on cleaved mica and examined by AFM by using a *Digital Nanoscope III*. Silicon cantilevers were used to acquire topography images in the tapping mode at r.t. under ambient conditions.

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