Hexakis-Adducts of [60]Fullerene with Different Addition Patterns: Templated Synthesis, Physical Properties, and Chemical Reactivity

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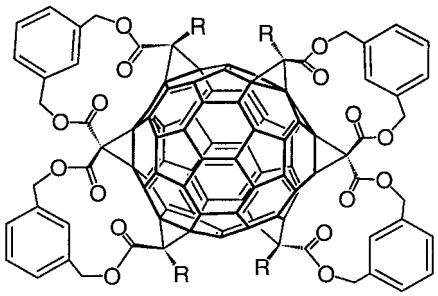
Representatives of two classes of hexakis-adducts of C_{60} were prepared by templated synthesis strategies. Compound **8** with a dipyridylmethano addend in a pseudo-octahedral addition pattern was obtained by DMA-templated addition (DMA = 9,10-dimethylanthracene; *Scheme 1*) and served as the starting material for the first supramolecular fullerene dimer **2**. Hexakis-adduct **12** also possesses a pseudo-octahedral addition pattern and was obtained by a sequence of tether-directed remote functionalization, tether removal, and regioselective bis-functionalization (*Scheme 2*). With its two diethynylmethano addends in *trans-1* position, it is a precursor for fascinating new oligomers and polymers that feature C_{60} moieties as part of the polymeric backbone (*Fig. 1*). With the residual fullerene π-electron chromophore reduced to a 'cubic cyclophane'-type sub-structure (*Fig. 4*), and for steric reasons, **8** and **12** no longer display electrophilic reactivity. As a representative of the second class of hexakis-adducts, (±)-**1**, which features six addends in a distinct helical array along an equatorial belt, was prepared by a route that involved two sequential tether-directed remote functionalization steps (*Schemes 3* and *5*). In compound (±)-**1**, π-electron conjugation between the two unsubstituted poles of the carbon sphere is maintained *via* two (*E*)-stilbene-like bridges (*Fig. 4*). As a result, (±)-**1** features very different chemical reactivity and physical properties when compared to hexakis-adducts with a pseudo-octahedral addition pattern. Its reduction under cyclic voltammetric conditions is greatly facilitated (by 570 mV), and it readily undergoes additional, electronically favored *Bingel* additions at the two sterically well-accessible central polar 6-6 bonds under formation of heptakis- and octakis-adducts, (±)-**30** and (±)-**31**, respectively (*Scheme 6*). The different extent of the residual π-electron delocalization in the fullerene sphere is also reflected in the optical properties of the two types of hexakis-adducts. Whereas **8** and **12** are bright-yellow (end-absorption around 450 nm), compound (±)-**1** is shiny-red, with an end-absorption around 600 nm. This study once more demonstrates the power of templated functionalization strategies in fullerene chemistry, providing addition patterns that are not accessible by stepwise synthetic approaches.

1. Introduction. – Among the higher adducts of buckminsterfullerene (C_{60}; for a recent example, see [1]), hexakis-adducts are increasingly attracting interest as three-dimensional scaffolds for advanced materials applications [2][3]. Among those, derivatives with a pseudo-octahedral (T_h) addition pattern have been the earliest and most widely investigated ones [4–8]. Also known is a hexakis-adduct with a D_3-symmetrical addition pattern [2]. Both types of hexakis-adducts are accessible by stepwise additions, and their addends are evenly distributed over the entire carbon sphere. In this paper, we describe the synthesis of new hexakis-adducts with the T_h-symmetrical addition pattern, which are useful modules for three-dimensional nano-scale construction.

Over the past years, tether-directed remote functionalization [7a][9] has become the method of choice for the regio- and stereoselective synthesis of multiple adducts of [60]fullerene (for recent applications of this strategy, see [8][10]). Here, we describe the application of this methodology to the preparation of hexakis-adducts of C_{60} that

are not available in stepwise-addition sequences in the absence of a template. In particular, we report the synthesis of the chiral derivative (±)-**1** by a short route that involves two sequential tether-directed remote functionalization steps (for a preliminary communication of parts of this work, see [11]). Compound (±)-**1** features a novel chiral, D_2-symmetrical addition pattern, with all addition sites aligned in a distinct helical array along an equatorial belt. We demonstrate that physical properties and chemical reactivity are strongly dependent on the nature of the addition patterns in the higher adducts (for another series of hexakis- to octakis-adducts with novel addition patterns [12], see the paper in the next issue [12a]).

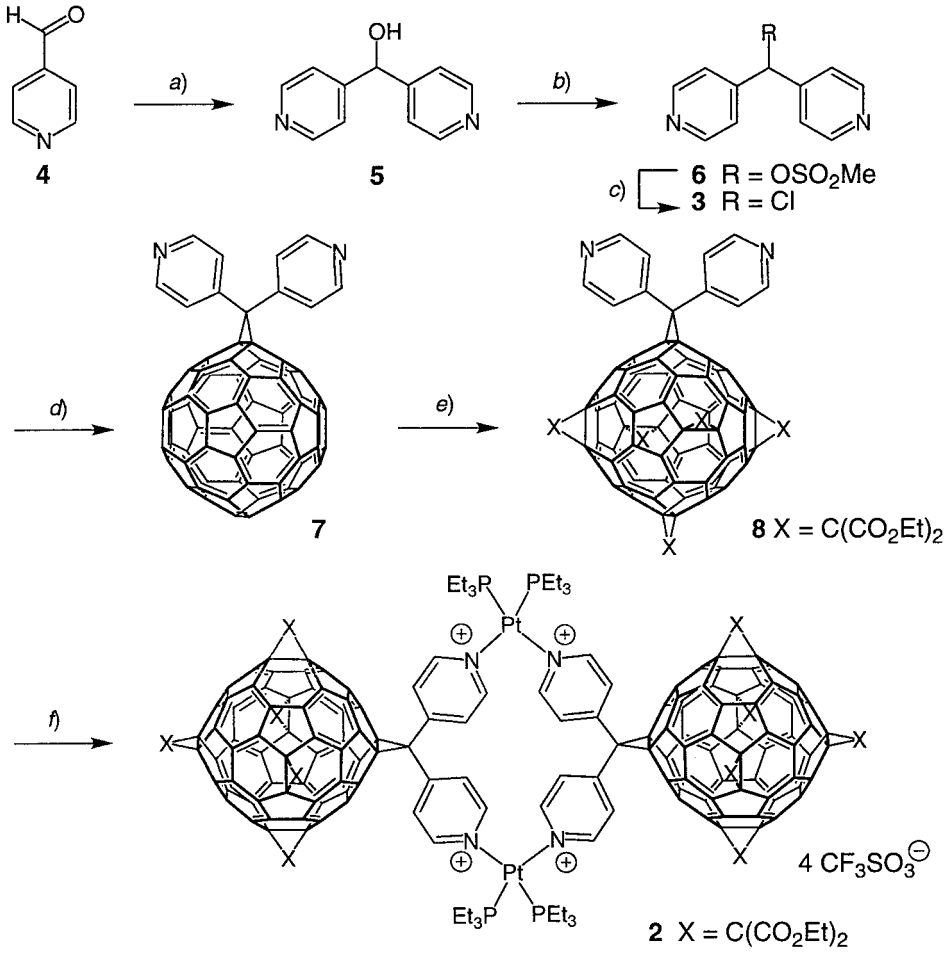


(±)-**1** R = COOEt

2. Results and Discussion. – 2.1. *A Hexakis-adduct as Precursor to a Supramolecular Fullerene Dimer*. For the synthesis of the supramolecular fullerene dimer **2** [13] by Pt^{II}-directed self-assembly (for reviews, see [14]), chlorodipyridylmethane **3** was prepared by addition of 4-lithiopyridine to pyridine-4-carbaldehyde (**4**) to give alcohol **5** [15], followed by mesylation to **6** and substitution with chloride (*Scheme 1*). Cyclopropanation under conditions of the *Bingel* reaction [16] afforded fullerene mono-adduct **7**. Attempts to complex ligand **7** with [*cis*-$Pt(PEt_3)_2(OSO_2CF_3)_2$], under preparation of a dinuclear cyclophane-type complex, led to a black, completely insoluble precipitate. To solubilize the expected complex, the yellow C_2-symmetrical hexakis-adduct **8** was prepared using the DMA-templated addition (DMA = 9,10-dimethylanthracene) of diethyl 2-bromomalonate introduced by *Hirsch* and co-workers [5b,d][7c]. The pseudo-octahedral addition pattern of **8**, with all addends in *e* (equatorial) position with respect to one another (for the naming of addition patterns, see [17]), was established by X-ray crystallography. Mixing equimolar amounts of **8** and [*cis*-$Pt(PEt_{3)2}(OSO_2CF_3)_2$] in CD_2Cl_2 provided in nearly quantitative yield the soluble tetracationic cyclophane **2** as the tetrakis-triflate salt (triflate = trifluoromethane sulfonate), for which the X-ray crystal structure was solved (for other supramolecular fullerene dimers, see [18]).

This study shows the advantage of hexakis-adducts over the pristine fullerene or lower adducts in providing good solubility when incorporated into multinanometer-sized supramolecular assemblies such as **2**. We had previously taken advantage of the strongly enhanced solubility of hexakis-adducts in the preparation of soluble derivatives of carbon allotropes by fullerene-acetylene hybrid scaffolding [7b,e]. As a disadvantage, however, the fullerene hexakis-adducts in such covalent or supramolecular assemblies no longer feature desirable properties of the pure carbon spheres

Scheme 1. *Synthesis of the Supramolecular Fullerene Dimer* **2**



a) 4-Lithiopyridine, Et_2O, $-78° \rightarrow 20°$, 45 min; 53%. *b*) $MeSO_2Cl$, Et_3N, CH_2Cl_2, $-5°$, 1.5 h; 70%. *c*) $CaCl_2$, Me_2SO, 50°, 10 h; 88%. *d*) C_{60}, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), PhMe, 20°, 10 h; 32%. *e*) Diethyl 2-bromomalonate, DBU, DMA, PhMe, 20°, 5 d; 35%. *f*) [*cis*-$Pt(PEt_3)_2(OSO_2CF_3)_2$], CD_2Cl_2, 20°, 5 min; 91%.

or lower adducts, such as facile multiple one-electron reductions or efficient singlet-oxygen sensitization [19][20].

2.2. *A Novel Module for Fullerene-Acetylene Hybrid Scaffolding*. In continuation of our efforts to construct multinanometer-sized carbon-rich molecular architecture by fullerene-acetylene scaffolding [7b,c,e][21–23], we became interested in the preparation of oligomers and polymers with C_{60} moieties as part of the polymeric backbone (*Fig. 1*). For the projected synthesis of these unusual materials by oxidative acetylenic coupling [21][24], C_{60} hexakis-adducts with two bis(diethynylmethano) addends in a *trans-1* [17] relationship were required. We expected the four malonate addends on

each C-sphere to provide sufficient solubility (see discussion in *Sect. 2.1.* above) to allow full characterization of the targeted oligomers and polymers in solution.

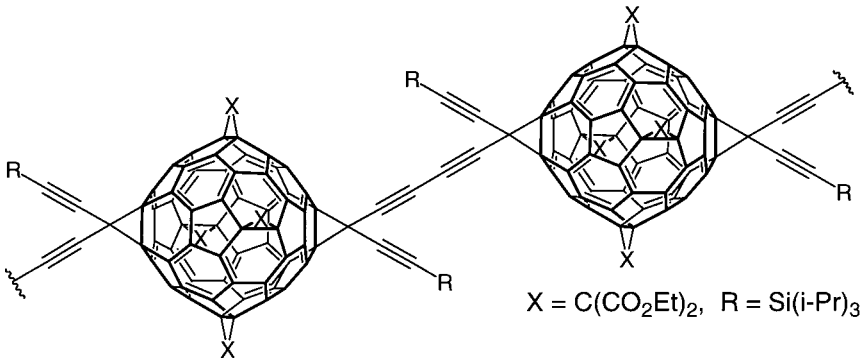


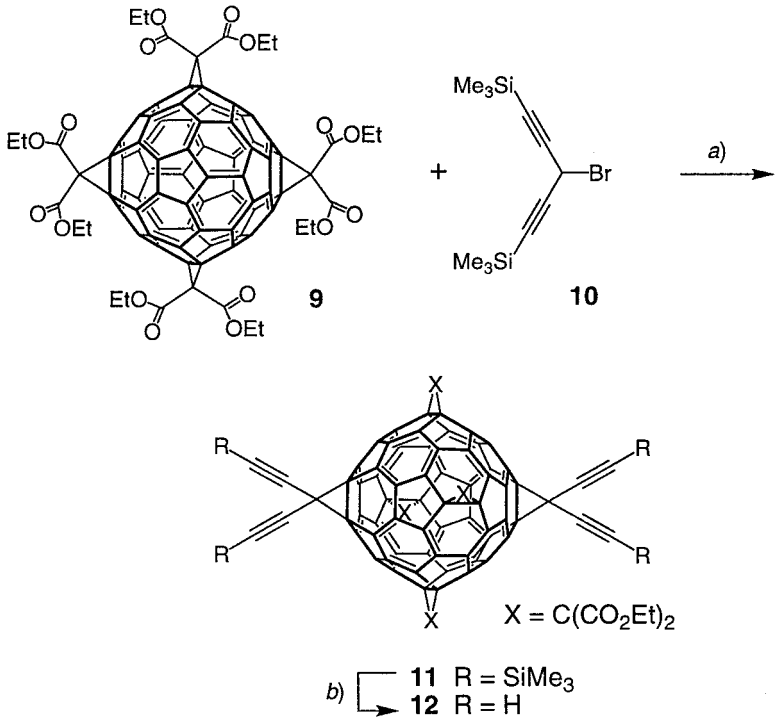
Fig. 1. *Proposed carbon-rich polymers with C_{60} hexakis-adducts as part of the polymeric backbone*

A central intermediate in the preparation of such hexakis-adducts is tetrakis-cyclopropanated **9**, which we [19a] and others [6c] had previously prepared by templated-synthesis methodology. Compound **9** features an addition pattern that cannot be established by sequential functionalization and contains two reactive polar 6-6 bonds (bonds at the intersect between two six-membered rings) – activated by the four malonate groups in *e* positions around the equator – for attachment of the bis(diethynylmethano) addends. When bis-silyl-protected 3-bromopenta-1,4-diyne **10** (20 equiv.) [7b,e] was reacted under *Bingel*-type conditions with **9** in Me_2SO in the presence of DBU (20 equiv.), a black precipitate was obtained. Extraction with organic solvents yielded only material that appeared at the baseline in analytical thin-layer chromatogram (SiO_2; CH_2Cl_2/AcOEt 19:1). These conditions had been previously applied successfully to the mono-addition of **10** to C_{60} pentakis-adducts to yield hexakis-adducts with a pseudo-octahedral addition pattern [7b,e]. Since **9** was rather insoluble in Me_2SO, the conditions were changed and the tetrakis-adduct was first dissolved in CH_2Cl_2, then Me_2SO was added until the mixture became cloudy (at a *ca.* 1:1 ratio of the two solvents) (*Scheme 2*). Upon addition of **10** (18 equiv.) and DBU (18 equiv.), the mixture rapidly turned blue, then black. Chromatographic workup (SiO_2; hexane, then hexane/CH_2Cl_2 gradients) afforded hexakis-adduct **11** in 32% yield as the only multiple adduct formed.

The yellow color of the compound – characteristic for hexakis-adducts with a pseudo-octahedral addition pattern [5–7] – was the first indication for the formation of the desired product. The ^{1}H-NMR spectrum ($CDCl_3$) showed a single Me_3Si resonance and two sets of signals for the EtO groups, indicating that the two diethynylmethano groups had been added to the two polar 6-6 bonds of **9**. In support of the D_{2h}-symmetrical structure, the ^{13}C-NMR spectrum (125.8 MHz, $CDCl_3$) contained six resonances for fullerene $^{13}C(sp^2)$-atoms and three for fullerene $^{13}C(sp^3)$-atoms. The alkynyl ^{13}C-atoms showed signals at 89.55 and 97.77 ppm. In the IR spectrum (KBr), the C≡C stretch appeared at 2167 cm^{-1}.

The MALDI-TOF-MS (matrix-assisted laser-desorption-ionization mass spectrum; matrix: dithranol = anthracene-1,8,9-triol) of **11** in the positive-ion mode displayed the

Scheme 2. *Synthesis of Tetrakis-ethynylated* **12** *for Fullerene-Acetylene Nanoscaffolding*



a) DBU, CH_2Cl_2/Me_2SO, 20°, 14 h; 32%. *b*) Anhydr. Bu_4NF on SiO_2, THF, 20°, 1.5 h; 84%.

expected molecular ion at *m/z* 1766, and peaks for its Na^+ and K^+ ion complexes. The spectrum also contained a peak at *m/z* 1560 for the loss of one and the base peak at *m/z* 1353 for the loss of the two diethynylmethano groups, with regeneration of the radical ion of the starting tetrakis-adduct $\mathbf{9}^{+\cdot}$. These data are in agreement with previous studies showing that the diethynylmethano groups are bound less tightly to the fullerene core than the malonate addends, splitting off first under MALDI-TOF-MS conditions [7b,c,e].

Removal of the four silyl protecting groups in **11** was accomplished by treatment with anhydrous Bu_4NF on SiO_2 in dry THF for 1.5 h and gave **12** as a bright-yellow solid of remarkable stability, given its four unprotected ethynyl groups. In the ^{1}H-NMR spectrum (500 MHz, $CDCl_3$), the acetylenic H-atom resonance appeared at 2.58 ppm. The MALDI-TOF-MS (THA/AHC; THA = 2′,4′,6′-trihydroxyacetophenone, AHC = ammonium hydrogencitrate) in the positive-ion mode showed the peaks for the molecular ion and for the fragments resulting from loss of one and two diethynylmethano groups, with regeneration of the tetrakis-adduct radical ion $\mathbf{9}^{+\cdot}$.

2.3. *Synthesis of a Chiral Hexakis-cyclopropanated Fullerene with All Addends Located Along an Equatorial Belt*. The preparation of hexakis-adduct **12** *via* tetrakis-adduct **9** (*Sect. 2.2* above) is a fine example of the application of templated synthesis strategies to provide access to higher adducts of C_{60} that cannot be synthesized by

stepwise additions. Using such methodology, we became interested in preparing hexakis-cyclopropanated derivatives with completely novel addition patterns, which feature the location of all addends along an equatorial belt rather than evenly distributed over the entire C-sphere. Two such addition patterns are possible: in the chiral D_2-symmetrical structure **A** (*Fig. 2*), the addition sites are aligned in a distinct helical array, whereas structure **B**, wtih a D_{3d}-symmetrical addition pattern, features a circumferential ('saturn'-like) functionalization about the equator, which dissects the residual π-electron chromophore of the fullerene into two polar halves with no direct π-electron conjugation.

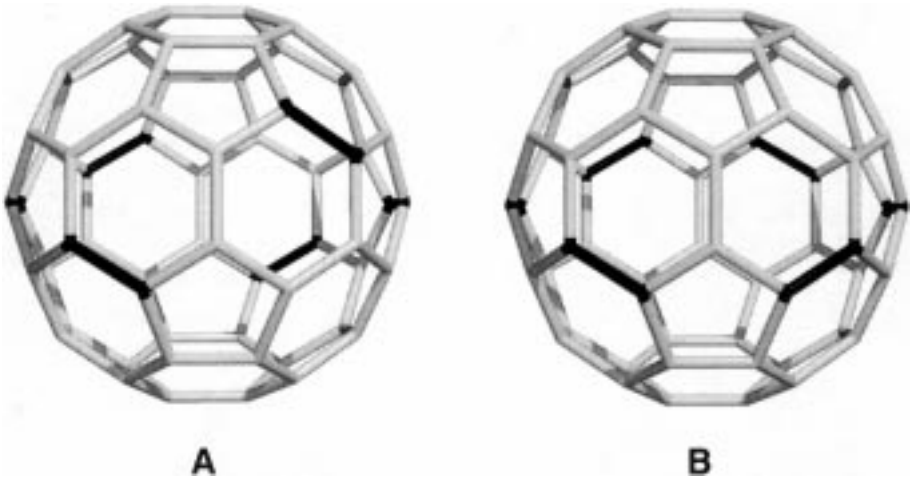
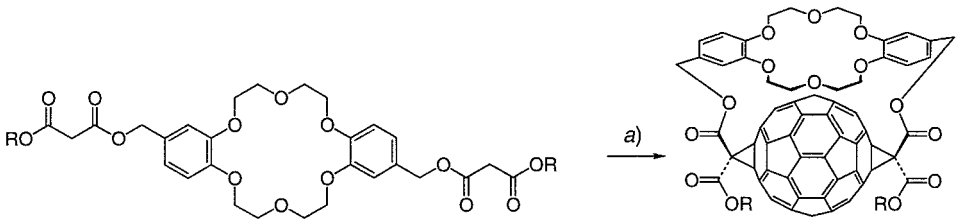


Fig. 2. *Novel hexakis-addition patterns of C_{60} with the addend sites located along an equatorial belt*

We chose a synthetic route that could potentially provide access to hexakis-adducts featuring either one of the two addition patterns **A**/**B** (*Fig. 2*) or both. A key intermediate was the fullerene-crown ether conjugate (±)-**13** with a *trans-1* addition pattern. The preparation of *trans-1* bis-adducts was a challenge for quite some time, since it required the introduction of extended tethers with a suitable degree of conformational homogeneity that span the entire fullerene sphere. We have recently showed that the *Bingel* macrocyclization of bis-malonates **14** or **15**, bridged by an *anti*-bisfunctionalized dibenzo[18]crown-6 (DB18C6) tether, which is further rigidified by K^+ ion complexation, afforded exclusively the *trans-1* derivatives (±)-**13** or (±)-**16** in $\geq$50% yield (*Scheme 3*) [25] (for other regioselective *trans-1* bisfunctionalizations, see [8][26][27]). We also demonstrated that the DB18C6 moiety in this fullerene-crown-ether conjugate is a true covalent template, which is readily removed by hydrolysis or transesterification. Here, we describe two novel applications of this tether in *Bingel* macrocyclizations, leading to *trans-1* C_{60} derivatives for further covalent and supramolecular scaffolding.

We became interested in the preparation of fullerene-crown ether conjugates that possess additional metal-ion ligating sites such as podand-like oligoether (in (±)-**17**) or pyridine (in (±)-**18**) residues. Upon coordination of a Zn^{2+}, Pt^{2+}, or Ag^+ ion to the four pyridine ligands of two molecules of (±)-**18**, we hoped to form supramolecular

Scheme 3. *Synthesis of the Fullerene-Crown Ether Conjugates* (±)-**13** *and* (±)-**16** [25b]



14 R = *t*-Bu
15 R = Et

(±)-**13** R = *t*-Bu
(±)-**16** R = Et

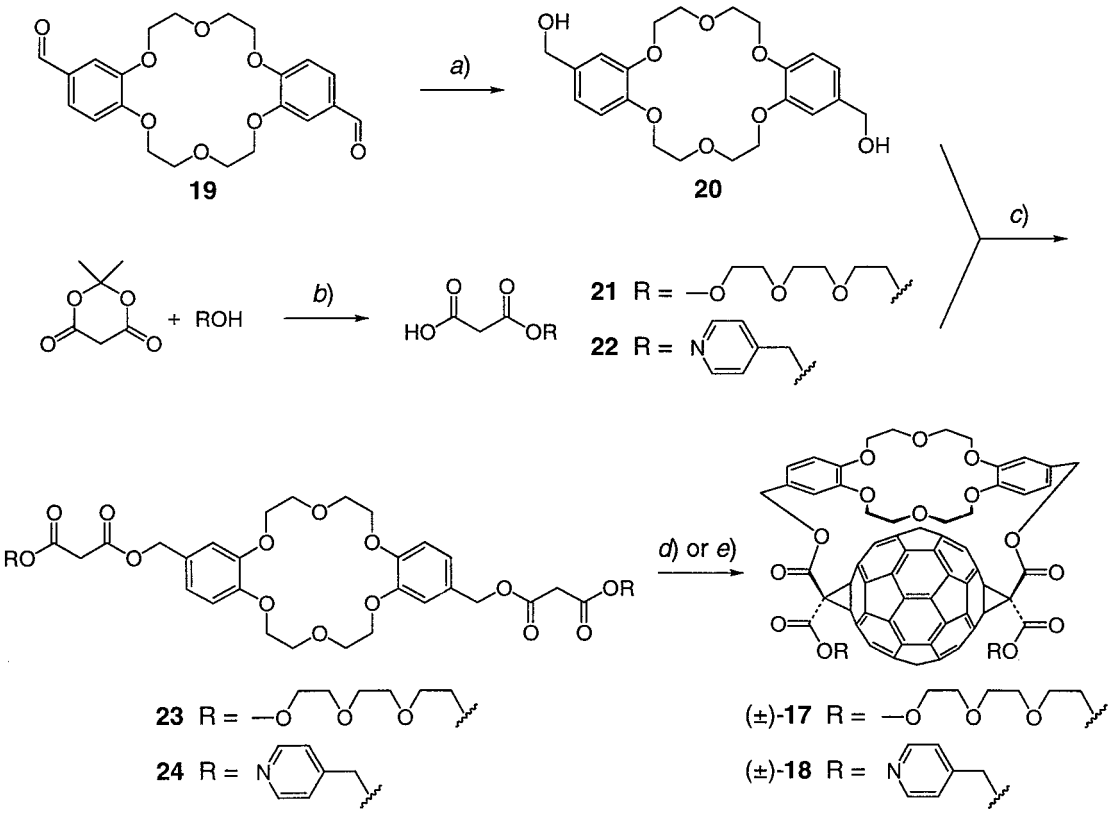
a) C_{60}, KPF_6, PhMe/MeCN, 20°; 54% ((±)-**13**), 50% ((±)-**16**).

fullerene dimers with interesting photophysical and redox properties. The synthesis of these novel construction modules started with dicarbaldehyde **19** [25], which was reduced with $NaBH_4$ in MeOH to diol **20** (*Scheme 4*). Since the isolation and purification of this highly polar molecule, which is only poorly soluble in organic solvents, proved to be difficult and tedious, it was not isolated but directly esterified as the crude product. The required malonic acid mono-esters **21** and **22** were conveniently obtained by reaction of triethyleneglycol monomethyl ether or pyridine-4-methanol with *Meldrum*'s acid (2,2-dimethyl-1,3-dioxane-4,6-dione) [28]. Esterification of crude diol **20** with **21** or **22** in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in DMF afforded the DB18C6-tethered bis-malonates **23** or **24** in good yield. *Bingel* macrocyclizations with C_{60} gave the desired crown ether conjugates (±)-**17** and (±)-**18** with high regioselectivity but in lower yields (21 and 19%, resp.), when compared to (±)-**13** and (±)-**16** (*Scheme 3*). During formation of the pyridine derivative (±)-**18**, the addition of KPF_6 led to an insoluble complex of undefined structure, thereby precluding the use of K^+ ions to further rigidify the crown ether template. Furthermore, the high polarity of the two fullerene-crown ether conjugates complicated their purification, which proceeded with loss of material. Preliminary investigations (^{1}H-NMR) provided strong evidence for the formation of supramolecular complexes by coordination of (±)-**18** to Zn^{2+} or Ag^+ ions [29]; however, X-ray crystallographic analysis will be required for an unambiguous determination of the preferred complex stoichiometry and geometry.

On the route to (±)-**1**, tetrakis(carboxylic acid) **25** was prepared by cleavage of both the crown ether template and the *tert*-butyl ester groups in (±)-**13** with toluene-4-sulfonic acid monohydrate ($TsOH \cdot H_2O$) in PhMe [25b] (*Scheme 5*). Conversion to tetrakis(acyl chloride) **26** with $(COCl)_2$ and coupling with mono-(*t*-Bu)Me_2Si-protected benzene-1,3-dimethanol [30] yielded **27**, which was deprotected with HF/pyridine to give tetraol **28**. Esterification with EtO_2CCH_2COCl led to tetrakis-malonate **29**, the precursor to (±)-**1**.

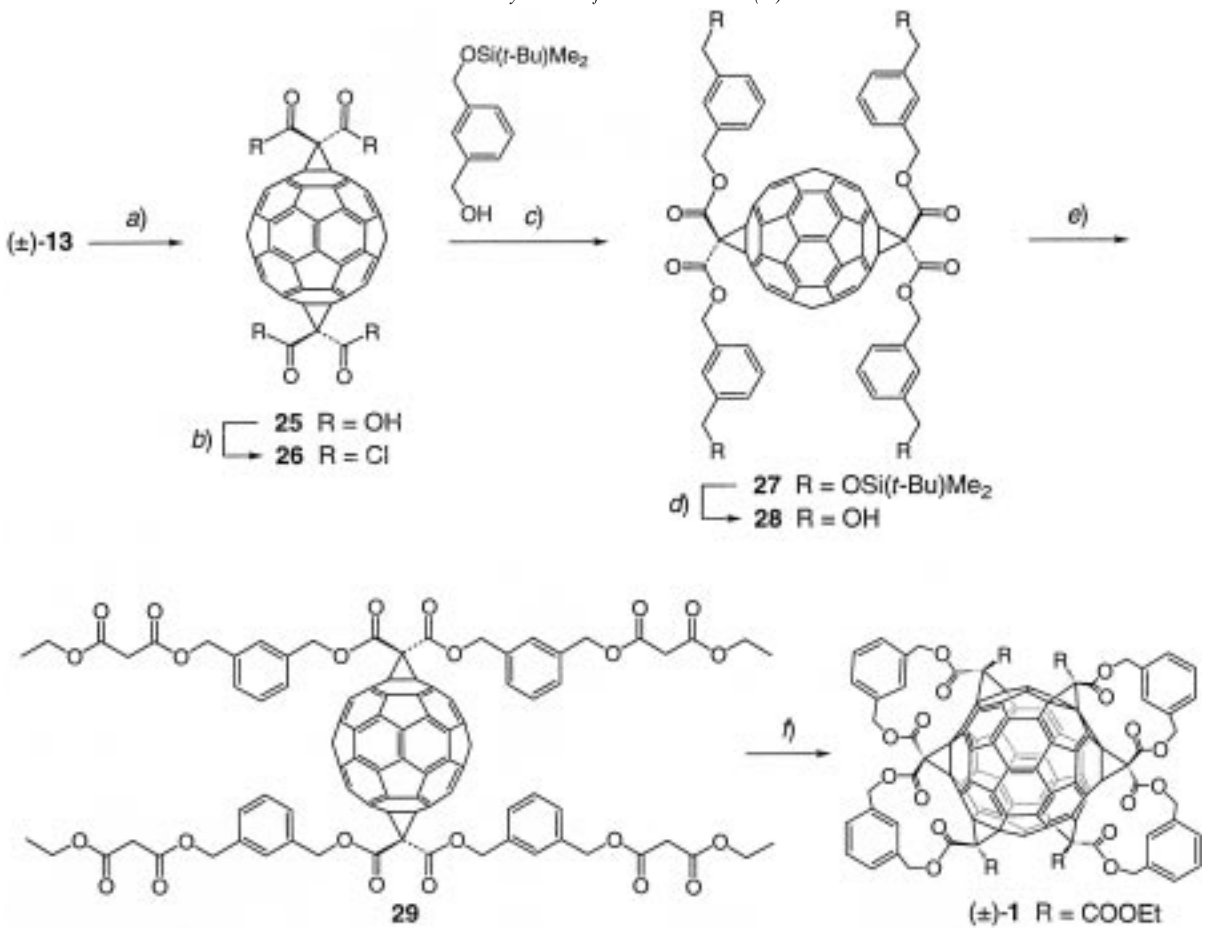
Four-fold intramolecular *Bingel* macrocyclization of **29** in PhMe/Me_2SO under high-dilution conditions followed by flash-chromatography (SiO_2-*H*; CH_2Cl_2/AcOEt 98 : 2) and further chromatographic separation of the second fraction (SiO_2-*H*; CH_2Cl_2/AcOEt 99.5 : 0.5) gave (±)-**1** as a single hexakis-adduct in 10% yield. The reaction was very sensitive to solvent composition: the reported yield was obtained only when the

Scheme 4. *Synthesis of the Fullerene-Crown Ether Conjugates* (±)-**17** *and* (±)-**18** *Bearing Additional Metal-Ion Binding Sites*



a) $NaBH_4$, MeOH, 20°, 1 h. *b*) 110°, 4 h; 80% (**21**); 29% (**22**). *c*) DCC, DMAP, DMF, 20°, 14 h; 68% (**23** from **19**); 80% (**24** from **19**). *d*) C_{60}, DBU, I_2, KPF_6, PhMe/CH_2Cl_2/MeCN, 20°, 48 h; 21% ((±)**17**). *e*) C_{60}, DBU, I_2, PhMe/CH_2Cl_2/MeCN, 20°, 14 h; 19% ((±)-**18**).

Scheme 5. *Synthesis of Hexakis-Adduct (±)-***1**



a) TsOH · H_2O, PhMe, Δ, 12 h. *b*) $(COCl)_2$, CH_2Cl_2, Δ; 48 h. *c*) Pyridine, CH_2Cl_2, 20°, 12 h; 21% (from (±)**13**). *d*) HF · pyridine, CH_2Cl_2, 0°, 1 h; 93%. *e*) EtO_2CCH_2COCl, *N*,*N*-dimethylaniline, CH_2Cl_2, 20°, 14 h; 80%. *f*) I_2, DBU, PhMe/Me_2SO, 20°, 12 h; 10%.

reaction was started in pure PhMe, and the polarity of the solution gradually increased by addition of Me_2SO. When Me_2SO was added at the beginning of the reaction, only traces of the desired product could be isolated. In the absence of any Me_2SO, however, the increasingly substituted fullerene is too deactivated to undergo all four *Bingel* additions [7b,e].

The molecular formula of (±)-**1** was unambiguously confirmed by high-resolution MALDI-TOF-MS (matrix: 2,5-dihydroxybenzoic acid), which showed the sodium complex of the molecular ion as the parent ion at *m/z* 1875.275 (calc. for $C_{118}H_{52}NaO_{24}^+$: 1875.275). Benzene-1,3-dimethanol-tethered bis-malonates are well-known to yield regioselectively *cis-2* addition patterns on the fullerene [9][31][32]. Four-fold intramolecular *Bingel* macrocyclization with *cis-2* regioselectivity can give only – with equiprobability – two constitutionally isomeric hexakis-adducts, namely a D_2-symmetrical one with addition pattern **A** or a C_{2h}-symmetrical one with addition pattern **B** (*Fig. 2*). Whereas the symmetry of the two regioisomers cannot be unambiguously determined from their ^{1}H-NMR spectra, this can, in principle, be achieved by ^{13}C-NMR spectroscopy. In the C_{2h}-symmetrical compound, the mirror plane bisects four trigonal fullerene C-atoms, leading to a total of 22 $^{13}C(sp^2)$-resonances ($3 \times C{=}O$, $6 \times C$(aryl), $13 \times C$(fullerene)). On the other hand, the C_2-axes in the D_2-symmetrical regioisomer do not pass through any trigonal C-atoms and a total of 21 $^{13}C(sp^2)$ resonances ($3 \times C{=}O$, $6 \times C$(aryl), $12 \times C$(fullerene)) are expected. Unfortunately, the ^{13}C-NMR spectrum (125.8 MHz, $CDCl_3$; *Fig. 3*) of the isolated hexakis-adduct displayed only 20 distinct $^{13}C(sp^2)$-atom resonances due to accidental isochrony; hence, it was not useful for assigning symmetry and molecular constitution.

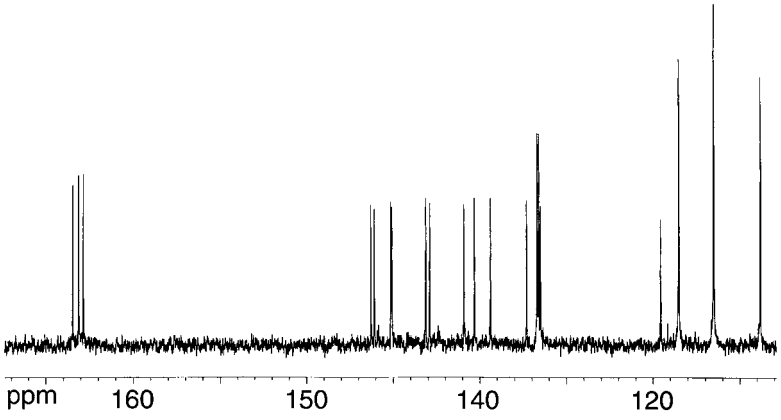


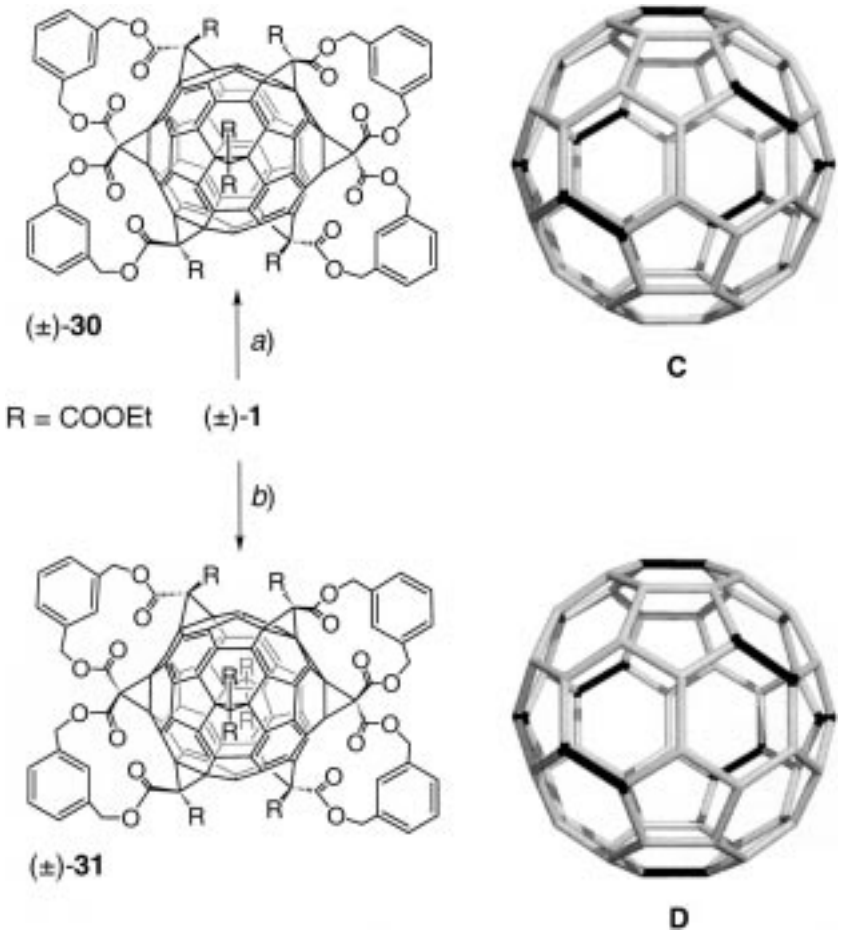
Fig. 3. *$^{13}C(sp^2)$-Region in the ^{13}C-NMR spectrum* (125.8 MHz, $CDCl_3$) *of (±)-***1**

Fortunately, an X-ray crystal-structure analysis of the isolated hexakis-adduct was obtained. The molecular structure revealed the distinct helical nature of addition pattern **A** and allowed an unambiguous assignment of structure (±)-**1** to this compound (for details on the X-ray crystal structure, see the preliminary communication [11]). Distortion of the C_{60} sphere in (±)-**1** due to the belt of six fused cyclopropane rings was found to be small, and its overall shape closely resembles that determined previously for bis-adduct (±)-**13** [25b].

2.4. *Physical Properties and Chemical Reactivity of (±)-***1**: *Preparation of Unique Heptakis- and Octakis-adducts.* In (±)-**1**, π-electron conjugation between the two unsubstituted poles is maintained *via* two (*E*)-stilbene-like bridges (*Fig. 4*). As a result of this retained, extended conjugation, the compound is red-colored with an end-absorption extending to 600 nm. This contrasts sharply with the light-yellow color (end-absorption around 450 nm) of hexakis-adducts with pseudo-octahedral addition patterns such as **8** or **11**, wherein the residual π-electron chromophore is reduced to a benzenoid 'cubic cyclophane'-type substructure (*Fig. 4*) [19].

This difference in the extension of the residual conjugated π-electron chromophore leads to profound differences in the chemical reactivity of the various types of hexakis-adducts. We had previously shown by cyclic voltammetry (CV) on a glassy carbon

Scheme 6. *Synthesis of Heptakis-Adduct (±)-***30** *and Octakis-Adduct (±)-***31**



a) $(EtOOC)_2CHBr$ (2 equiv.), DBU, PhMe/Me_2SO 1:1, 20°, 12 h; *ca.* 40%. *b*) $(EtOOC)_2CHBr$ (20 equiv.), DBU, PhMe/Me_2SO 1:1, 20°, 12 h; *ca.* 80%. Also shown are the addition patterns (black bonds) **C** (in (±)-**30**) and **D** (in (±)-**31**). The indicated yields have high uncertainty due to the small quantities of material used.

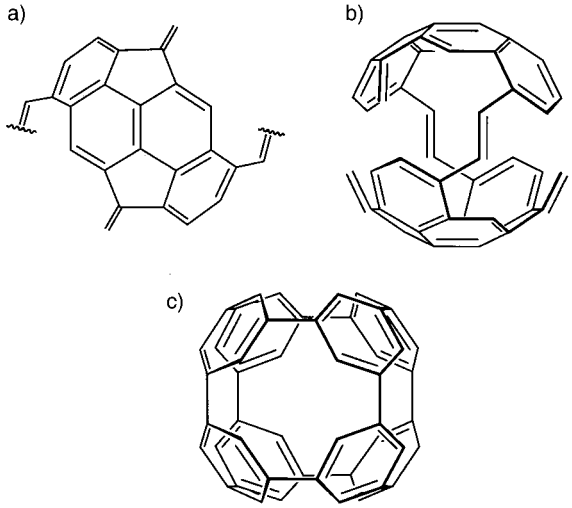


Fig. 4. *Residual π-electron chromophores in different hexakis-adducts. a*) View on one of the two unfunctionalized poles and *b*) on the (*E*)-stilbene-like moiety, which maintains π-electron conjugation between the two hemispheres in (±)-**1**. *c*) In pseudo-octahedral hexakis-adducts such as **8** or **11**, the residual conjugated π-electron chromophore is reduced to a benzenoid 'cubic cyclophane'-type substructure.

electrode that a hexakis-adduct with a pseudo-octahedral addition pattern as in **8** and **11** undergoes one fullerene-centered irreversible reduction step at −1.87 V (*vs.* the ferrocene/ferricinium couple Fc/Fc^+) in CH_2Cl_2 (+0.1M Bu_4NPF_6) [19]. In sharp contrast, (±)-**1** underwent, under the same experimental conditions, an irreversible reduction at −1.3 V, *i.e.*, at a potential that is shifted anodically by 570 mV [33]. This greatly facilitated reduction is clearly due to the retained extended π-electron delocalization (see *Fig. 4*,*a* and *b*) in the novel hexakis-adduct with the addends located along the equatorial belt. Interestingly, the first fullerene-centered oxidation step occurs at similar potential (+0.99 V in the pseudo-octahedral hexakis-adduct and +0.95 V in (±)-**1**) [19b].

Pseudo-octahedrally functionalized hexakis-adducts such as **8** and **11** possess low electrophilic reactivity and do not undergo any additional cyclopropanations. Introduction of an additional addend would disrupt the local aromaticity of one of the eight benzene rings in the residual 'cubic cyclophane'-type π-chromophore. Furthermore, a new addend would necessarily be located directly adjacent to an addend already in place, in a *cis-1* relationship [17], which causes severe steric repulsion. In sharp contrast, (±)-**1** readily undergoes further additions at the central 6-6 bond of each pole, avoiding steric overcrowding and not disrupting the aromaticity of isolated benzene rings. A *Bingel* reaction with diethyl 2-bromomalonate (2 equiv.) in PhMe/Me_2SO 1:1 in the presence of DBU afforded heptakis-adduct (±)-**30**, featuring the novel addition pattern **C**, as a single new product together with some starting material (*Scheme 6*). Addition of a 20-fold excess of the same reagent to (±)-**1** produced, by double *Bingel* addition, the octakis-adduct (±)-**31**, with addition pattern **D**, along with traces of (±)-**30**.

The high-resolution MALDI mass spectra (matrix: DHB) displayed as the parent ions the sodium complexes of the molecular ions ((±)-**30**): *m/z* 2033.331 (calc. for $C_{125}H_{62}NaO_{28}^{+}$: 2033.332); (±)-**31**): *m/z* 2191.388 (calc. for $C_{132}H_{72}NaO_{32}^{+}$: 2191.390)). Unambiguous proof for the proposed addition patterns was provided by ^{1}H-NMR spectroscopy (300 MHz, $CHCl_3$). The spectrum of (±)-**30** corresponds to a C_2-symmetrical compound, with four *AB* systems for four different benzylic CH_2 groups, whereas the spectrum of (±)-**31** displays only two such *AB* systems, in agreement with its higher, D_2 symmetry. Addition patterns of this symmetry can only be obtained starting from (±)-**1** by mono- and bis-cyclopropanation at the central polar 6-6 bonds. Attack at these specific bonds is favored since they are the least sterically hindered ones and have an (electronically activating) *e*-relationship to the *trans-1*-arranged malonate addends introduced during the synthesis of (±)-**29** (*Scheme 5*).

Since the two (*E*)-stilbene-type C=C bonds (*Fig. 4,b*) still maintain the π-electron conjugation between the two chromophoric hemispheres in (±)-**30** and (±)-**31**, the hypsochromic shift upon passing from hexakis-adduct (±)-**1** (λ_{max} 576 nm), to heptakis-adduct (±)-**30** (λ_{max} 556 nm, sh), and to octakis-adduct (±)-**31** (λ_{max} 551 nm) is relatively small (*Fig. 5*), and solutions of the latter still display an orange-yellow color. In comparison, the longest-wavelength absorption maximum in the yellow hexakis-adduct **11** with the residual benzenoid 'cubic cyclophane'-type chromophore (*Fig. 4,c*) appears at 448 nm. This example clearly illustrates that the electronic properties of higher adducts of C_{60} strongly vary with the nature of the addition pattern [31b].

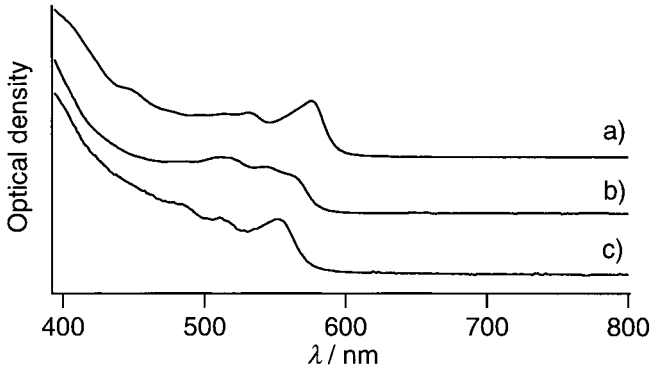


Fig. 5. *Qualitative comparison of the absorption spectra* (CH_2Cl_2, 20°) *of* a) *hexakis-adduct (±)*-**1**, b) *heptakis-adduct (±)*-**30**, *and* c) *octakis-adduct (±)*-**31**. The molar extinction coefficients of (±)-**30** and (±)-**31** were not determined due to the small quantity of material.

3. Conclusions. – Representatives of two classes of hexakis-adducts of C_{60} are described in this paper. Compounds **8** and **11** feature a pseudo-octahedral addition pattern characterized by a residual benzenoid π-chromophore of the carbon sphere and vanishing electrophilic reactivity for electronic and steric reasons. The optical end-absorption of these bright-yellow compounds appears around 450 nm, in agreement with the limited π-electron delocalization in the residual fullerene chromophore. They represent interesting building blocks for supramolecular (**8**) and covalent (**11**) fullerene-based nanoscaffolding. With the construction of molecular square **2** from **8**,

the first example of a supramolecular fullerene dimer was obtained. On the other hand, the properties of hexakis-adduct (±)-**1**, with six addends in a distinct helical array along an equatorial belt, strongly differ from those of hexakis-adducts featuring a pseudo-octahedral addition pattern (for a recent report on another higher adduct of C_{60} with all addends placed along an equatorial belt, see [34]). Compound (±)-**1** features an addition pattern (**A** in *Fig. 2*) in which π-electron conjugation between the two unsubstituted polar regions is maintained *via* two (*E*)-stilbene-like bridges. As a result, its reduction under CV conditions is greatly facilitated (anodic potential shift of 570 mV) when compared to **8** or **11**, and its optical end-absorption occurs around 600 nm. It readily undergoes further sterically and electronically favored *Bingel* additions at the two central polar 6-6 bonds under formation of heptakis- and octakis-adducts, (±)-**30** and (±)-**31**, respectively. Since the (*E*)-stilbene-like π-electron conjugation is maintained in the latter higher adducts, their longest-wavelength absorption bands appear near 550 nm, lending them an orange-yellow color. This study once more demonstrates the power of templated functionalization strategies in fullerene chemistry, providing addition patterns that are not accessible by stepwise synthetic approaches.

We were unable to isolate the regioisomer of (±)-**1** with addition pattern **B** (*Fig. 2*) although molecular-modeling calculations [35] predicted only little energetic difference between the two compounds. There may, however, exist differential steric interactions between adjacent EtOCO groups in the transition states of the two final cyclopropanation steps. The geometric relationship between two adjacent ethyl malonate addends in (±)-**1** is *cis-3*, whereas it is *cis-2* in the regioisomer (*Fig. 2*), and the closer proximity of adjacent EtOCO groups in the latter could render its formation unfavorable. We intend to test this hypothesis with an analog of **29** that contains four smaller, terminal methyl-malonate residues, which we expect to yield hexakis-adducts with both **A** and **B** addition patterns. The pronounced helical nature of the inherently chiral addition pattern **A** in (±)-**1** promises interesting chiroptical properties [36]. Therefore, in the continuation of this work, we intend to introduce chiral tethers instead of the benzene-1,3-dimethanol moieties in **29** to prepare optically active derivatives of (±)-**1** in a diastereoselective way [9][31][36b].

This work was supported by the *Swiss National Science Foundation*. We thank Dr. *Carlo Thilgen* (ETH-Zürich) for assistance with the nomenclature.

Experimental Part

General. Reagents and solvents were purchased reagent grade and used without further purification. C_{60} (99.5%) was purchased from *Southern Chemical Group*. CH_2Cl_2 was dried over CaH_2. Compounds **5** [15], **9** [19a], and (±)-**13** and **19** [25] were prepared according to literature procedures. All reactions were performed in standard glassware under an inert atmosphere of Ar. Evaporation and concentration *in vacuo* was performed at water-aspirator pressure, and compounds were dried at 10^{-2} Torr. TLC: *Alugram SIL G/UV*$_{254}$, *Macherey-Nagel*, visualization by UV light at 254 or 366 nm. Column (CC) and flash chromatography (FC): SiO_2-*H*, 5–40 μm, *Fluka*; SiO_2 *60*, 0.04–0.063 mm, *Fluka*; SiO_2 *60*, 0.063–0.2 mm, *Merck*. FC: elution at pressures between 0.1 and 0.5 bar. M.p.: *Büchi B-540* apparatus, uncorrected. UV/VIS Spectra (λ_{max} in nm (ε [1 mol^{-1} cm^{-1}])): *Varian Cary 5* spectrometer. IR Spectra (cm^{-1}): *Perkin-Elmer 1600-FTIR*. NMR Spectra: *Bruker AM-500* and *Varian Gemini-300* or *-200* at 300 K, with solvent peaks as reference. MS: *m*/*z* (% relative intensity). EI-MS: *VG TRIBRID* spectrometer at 70 eV; ESI-MS: *Finnigan TSQ-7000* spectrometer; FAB-MS: *VG ZAB-2SEQ* instrument; 3-nitrobenzyl alcohol as matrix; MALDI-TOF-MS: *Bruker REFLEX* spectrometer, matrices: 2.5-

dihydroxybenzoic acid (DHB); 2,4,6-trihydroxyacetophenone/ammonium hydrogencitrate (THA/AHC); anthracene-1,8,9-triol (dithranol); HR-ESI-FT-MS: *7T-Finnigan Newstar FT/MS system*, MeOH as solvent and poly(methyl methacrylate) as the internal reference; HR-MALDI-FT-MS: *Ion Spec Ultima FT-ICR* mass spectrometer with DHB as a matrix. For MALDI, FAB, and ESI mass spectra of all fullerene derivatives, the experimentally observed highest peak in the molecular-ion cluster is reported, followed, in parentheses, by the isotopic molecular formula corresponding to the calculated most-intense peak in the cluster. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich.

Di(pyridin-4-yl)methyl Methanesulfonate (**6**). To **5** (0.50 g, 2.69 mmol) and Et_3N (1.09 g, 10.74 mmol) in CH_2Cl_2 (20 ml), $MeSO_2Cl$ (0.61 g, 5.37 mmol) in CH_2Cl_2 (2 ml) was added dropwise at $-5°$. The suspension was stirred at $-5°$ for 1 h, then more $MeSO_2Cl$ (0.147 g, 1.289 mmol) was added. After 30 min, the mixture was poured on ice, extracted with Et_2O (2×75 ml), and the org. phase was dried ($MgSO_4$). CC (SiO_2; CH_2Cl_2/MeOH 98:2 → 96:4) gave **6** (0.49 g, 70%). Red oil, which slowly crystallized. M.p. 80°. IR (KBr): 2998*w*, 2922*w*, 1595*m*, 1564*w*, 1415*s*, 1359*s*, 1320*m*, 1287*w*, 1223*w*, 1172*s*, 981*m*, 956*s*, 887*m*, 855*s*, 815*m*, 740*w*, 646*w*, 604*s*, 565*m*, 529*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.89 (*s*, 3 H); 6.51 (*s*, 1 H); 7.21–7.24 (*m*, 4 H); 8.57–8.60 (*m*, 4 H). ^{13}C-NMR (50.3 MHz, CD_3OD): 39.03; 79.79; 121.14; 145.28; 150.27. EI-MS: 264 (M^+). Anal. calc. for $C_{12}H_{12}N_2O_3S$ (264.30): C 54.53, H 4.58, N 10.60, S 12.13; found: C 54.45, H 4.70, N 10.59, S 11.97.

Chlorodi(pyridin-4-yl)methane (**3**). $CaCl_2$ (2.66 g, 14.18 mmol) was added to **6** (0.25 g, 0.95 mmol) in Me_2SO (15 ml) at 20°, and the suspension was heated for 10 h to 50°, then poured into CH_2Cl_2 (50 ml) and H_2O (200 ml). The org. phase was washed with H_2O (100 ml) and dried ($MgSO_4$). CC (SiO_2; CH_2Cl_2/MeOH 98:2 → 96:4) gave **3** (0.17 g, 88%). Colorless powder, which rapidly decomposed at 20° and was directly used without further purification. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.93 (*s*, 1 H); 7.26–7.29 (*m*, 4 H); 8.59–8.62 (*m*, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 59.99; 121.87; 147.49; 150.03. EI-MS: 204 (44, M^+), 169 (100, $[M-Cl]^+$).

*3′,3′-Di(pyridin-4-yl)-3′*H*-cyclopropa[1,9](C$_{60}$-I$_h$)[5,6]fullerene* (**7**). To C_{60} (0.35 g, 0.49 mmol) and **3** (0.13 g, 0.64 mmol) in PhMe (300 ml), DBU (74 mg, 0.49 mmol) was added dropwise under N_2, and the mixture was stirred for 7 h at 20°. More DBU (50 mg, 0.33 mmol) was added, and the mixture was stirred for 3 h, then filtered through a plug (SiO_2; PhMe, then CH_2Cl_2/MeOH 9:1). CC (SiO_2; CH_2Cl_2/MeOH 96.5:3.5) gave pure **7** (0.14 g, 32%). Black crystals. M.p. >280°. IR (KBr): 2965*w*, 2922*w*, 1726*m*, 1631*m*, 1536*w*, 1467*m*, 1261*w*, 1119*s*, 801*w*, 675*w*, 616*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.02–8.05 (*m*, 4 H); 8.78–8.81 (*m*, 4 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 54.76; 76.62; 125.72; 138.16; 141.14; 141.99; 142.12; 143.02; 143.06; 143.10; 143.79; 144.46; 144.51; 144.79; 144.92; 145.24; 145.29; 146.02; 146.30; 150.59. FAB-MS: 889 (5, MH^+); 720 (100, C_{60}^+). HR-FAB-MS: 889.0821 (MH^+, $C_{71}H_9N_2^+$; calc. 889.0766).

*Decaethyl 3‴″,3‴″″-Di(pyridin-4-yl)-3′*H*,3″*H*,3‴*H*,3⁗*H*,3⁗″*H*,3⁗″″-hexacyclopropa[1,9:16,17:21,40:30,31:44,45:52,60](C$_{60}$-I$_h$)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3⁗,3⁗,3⁗″,3⁗″,3⁗″″-decacarboxylate* (**8**). A soln. of **7** (105 mg, 0.12 mmol) in PhMe (150 ml) was purged with N_2 for 30 min, and DMA (243 mg, 1.18 mmol) was added. After stirring for 2 h, diethyl 2-bromomalonate (226 mg, 0.95 mmol) and DBU (180 mg, 1.18 mmol) were added, and the mixture was stirred under N_2 at 20° for 5 d. Plug filtration (SiO_2; CH_2Cl_2, then CH_2Cl_2/MeOH 9:1) followed by CC (SiO_2-*H*; AcOEt/hexane/MeOH 5:5:1) gave **8** (70 mg, 35%). Yellow solid, which was recrystallized from AcOEt/CH_2Cl_2/PhH/hexane for X-ray crystallography. M.p. >270°. UV/VIS (CH_2Cl_2): 272 (68900), 282 (71900), 318 (44700), 336 (37300), 389 (sh, 5100), 433 (sh, 1400), 449 (sh, 900), 539 (150). IR (KBr): 2978*w*, 2922*w*, 1745*s*, 1633*w*, 1588*w*, 1361*w*, 1294*w*, 1261*s*, 1222*s*, 1078*w*, 1016*w*, 713*w*, 529*w*, 528*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.29 (*t*, $J=7.1$, 12 H); 1.32 (*t*, $J=7.1$, 6 H); 1.34 (*t*, $J=7.1$, 6 H); 1.40 (*t*, $J=7.1$, 6 H); 4.30 (*q*, $J=7.1$, 4 H); 4.31 (*q*, $J=7.1$, 4 H); 4.33 (*q*, $J=7.1$, 4 H); 4.35 (*q*, $J=7.1$, 4 H); 4.42 (*q*, $J=7.1$, 4 H); 7.70 (*dd*, $J=4.5$, 1.6, 4 H); 8.58 (*dd*, $J=4.5$, 1.6, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.00; 14.02; 14.04; 14.09; 45.44; 45.47; 45.67; 47.82; 62.87; 62.90; 62.91; 69.09; 69.24; 69.41; 69.46; 73.37; 125.32; 141.07; 141.18; 141.19; 141.22; 141.51; 142.15; 144.95; 145.53; 145.59; 145.66; 145.69; 145.76; 146.83; 150.23; 163.68; 163.76; 163.91. FAB-MS: 1680 (100, MH^+). X-Ray Analysis: see [13]. For full experimental protocols of the synthesis and characterization of **2**, including X-ray, see [13].

*Octaethyl 3‴,3‴,3⁗,3⁗,3⁗″″-Tetrakis[(trimethylsilyl)ethynyl]-3′*H*,3″*H*,3‴*H*,3⁗*H*,3⁗″*H*,3⁗″″*H*-hexacyclopropa[1,9:16,17:21,40:30,31:44,45:52,60](C$_{60}$-I$_h$)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3⁗,3⁗,3⁗″,3⁗″-octacarboxylate* (**11**). To **9** (12.0 mg, 8.87 μmol) and **10** (45.8 mg, 0.160 mmol) in deoxygenated CH_2Cl_2 (1 ml), deoxygenated Me_2SO (1 ml) was added to give a cloudy mixture. DBU (24.3 mg, 0.160 mmol) was added portionwise over 1 min, and the mixture immediately became dark blue and turned black after 10 min. After 14 h, the mixture was diluted with PhMe, washed with sat. aq. NaCl soln. (3×), and dried ($MgSO_4$). Evaporation *in vacuo* and FC (SiO_2; hexane, then hexane/CH_2Cl_2 gradient 1:1 → 1:4) afforded **11** (5 mg, 32%). Bright-yellow solid. TLC (SiO_2; hexane/CH_2Cl_2 1:1): R_f 0.11. M.p. >250°. UV/VIS (CH_2Cl_2): 281 (94300), 319 (sh, 60600), 337 (54400), 390 (sh, 16600), 435 (sh, 3400), 448 (sh, 1750). IR (KBr): 2978*m*, 2956*m*, 2900*w*, 2167*m*, 1744*s*, 1628*w*, 1467*m*, 1444*w*,

1394*w*, 1367*m*, 1250*s*, 1217*s*, 1161*m*, 1094*m*, 1078*m*, 1033*m*, 917*w*, 844*s*, 761*m*, 728*m*, 717*m*, 644*w*, 572*w*, 539*m*, 524*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.18 (*s*, 36 H); 1.29 (*t*, *J* = 7.1, 12 H); 1.34 (*t*, *J* = 7.1, 12 H); 4.33 (*q*, *J* = 7.1, 8 H); 4.36 (*q*, *J* = 7.1, 8 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): −0.09; 14.01; 14.06; 45.36; 45.50; 62.70; 62.84; 69.13; 69.30; 73.41; 89.55; 97.77; 141.17; 141.51; 141.59; 145.81; 145.91; 145.96; 163.68; 163.84. MALDI-TOF-MS (dithranol): 1804 (25, $[M+K]^+$), 1789 (34, $[M+Na]^+$), 1766 (35, M^+,$^{13}C^{12}C_{109}H_{76}O_{16}Si_4^+$; calc. 1764.4), 1599 (7, $[M-C_5(SiMe_3)_2+K]^+$), 1583 (11, $[M-C_5(SiMe_3)_2+Na]^+$), 1560 (29, $[M-C_5(SiMe_3)_2]^+$), 1353 (100, $[M-2\,(C_5(SiMe_3)_2)]^+$), 1195 (9,$[M-2\,(C_5(SiMe_3)_2)-C(CO_2Et)_2]^+$).

*Octaethyl 3‴,3‴,3⁗,3⁗⁗-Tetraethynyl-3′*H,*3″*H,*3‴*H,*3⁗*H,*3⁗⁗*H,*3′⁗⁗*H-*hexacyclopropa[1,9:16,17:21,40:30,31:44,45:52,60](C$_{60}$-I$_h$)[5,6]fullerene-3′,3′,3″,3″,3′⁗⁗,3⁗⁗,3′⁗⁗,3′⁗⁗⁗-octacarboxylate* (**12**). Anhydr. Bu_4NF on SiO_2 (10 mg, 12.45 μmol) was added to a soln. of **11** (4.0 mg, 2.26 μmol) in dry THF (0.5 ml). After 1.5 h, sat. aq. NH_4Cl soln. was added and the mixture poured into PhMe. The org. phase was washed with sat. aq. NH_4Cl soln., H_2O, and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. FC (SiO_2; hexane, then hexane/CH_2Cl_2 gradient 1:1 → 1:4) afforded **12** (2.8 mg, 84%). Bright-yellow solid. M.p. >250°. UV/VIS (CH_2Cl_2): 271 (59200), 319 (sh, 39200), 336 (34700), 388 (sh, 5000), 436 (sh, 950), 449 (sh, 520). IR (KBr): 3289*m*, 2978*w*, 2922*w*, 2856*w*, 2122*w*, 1744*s*, 1628*w*, 1467*w*, 1444*w*, 1389*w*, 1367*w*, 1294*m*, 1261*s*, 1233*s*, 1172*w*, 1094*w*, 1078*m*, 1033*w*, 856*w*, 806*w*, 761*w*, 717*m*, 661*w*, 622*w*, 533*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.329 (*t*, *J* = 7.1, 12 H); 1.335 (*t*, *J* = 7.1, 12 H); 2.58 (*s*, 4 H); 4.33 (*q*, *J* = 7.1, 8 H); 4.35 (*q*, *J* = 7.1, 8 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 14.06; 14.08; 45.35; 45.62; 62.92; 63.02; 69.16; 69.43; 72.02; 72.55; 141.10; 141.30; 141.66; 145.81; 145.92; 146.05; 163.68; 163.83. MALDI-TOF-MS (THA/AHC): 1500 (35, $[M+Na]^+$), 1477 (100, M^+, $^{13}C^{12}C_{97}H_{44}O_{16}^+$; calc. 1477.4), 1432 (51, $[M-C(C{\equiv}CH)_2+NH_4]^+$), 1415 (50, $[M-C(C{\equiv}CH)_2]^+$), 1370 (28, $[M-2\,(C(C{\equiv}CH)_2)+NH_4]^+$), 1353 (27, $[M-2\,(C(C{\equiv}CH)_2)]^+$.

Hydrogen 2-[2-(2-Methoxyethoxy)ethoxy]ethyl Malonate (**21**). A mixture of triethyleneglycol monomethyl ether (4.8 ml, 31 mmol) and 2,2-dimethyl-1,3-dioxane-4,6-dione (*Meldrum*'s acid, 4.4 g, 31 mmol) was heated to 110° for 4 h. The by-product, acetone, was evaporated *in vacuo* to afford pure **21** (6.13 g, 80%). Colorless oil. IR ($CHCl_3$): 3467*m*, 3036*s*, 3005*s*, 2892*s*, 1728*s*, 1451*s*, 1410*s*, 1354*s*, 1246*s*, 1097*s*, 1041*s*, 949*m*, 851*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.37 (*s*, 3 H); 3.39 (*s*, 2 H); 3.54–3.71 (*m*, 10 H); 4.26–4.31 (*m*, 2 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 38.63; 56.28; 62.02; 66.25; 67.74; 67.90; 68.02; 69.36; 164.62; 166.49. HR-MALDI-MS (DHB): 273.0394 (100, $[M+Na]^+$, $C_{10}H_{18}O_7Na^+$; calc. 273.0950); 251.1126 (26, MH^+, $C_{10}H_{19}O_7^+$; calc. 251.1131). Anal. calc. for $C_{10}H_{18}O_7$ (250.25): C 48.00, H 7.25; found: C 47.99, H 7.27.

*1,1′-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethyl] 3,3′-[(6,7,9,10,17,18,20,21-Octahydrodibenzo[*b,k*][1,4,7,10,13,16]-hexaoxacyclooctadecin-2,13-diyl)dimethylene] Bis[malonate]* (**23**). $NaBH_4$ (45 mg, 1.2 mmol) was added to a suspension of **19** (230 mg, 0.55 mmol) in MeOH (40 ml) at 0°. After stirring for 1 h at 20°, the mixture was neutralized with 10% aq. CF_3COOH soln., and the solvent was evaporated *in vacuo*. The residue was dissolved in acetone and the solvent evaporated *in vacuo*. This sequence was repeated 3 times before solid crude **20** was dried, then used immediately in the subsequent esterification without further purification. DCC (357 mg, 1.73 mmol) was added to a soln. of crude **20**, DMAP (19 mg, 0.16 mmol), and malonate **21** in dry DMF (4.6 ml) at 0°, and the mixture was stirred for 14 h at 20°. The dicyclohexylurea formed was removed by filtration, and the mother liquor was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2/AcOEt 1:1, and the soln. was extracted with 0.1% aq. CF_3COOH soln. and H_2O. The org. layer was dried ($MgSO_4$) and evaporated *in vacuo*. To remove dicyclohexylurea completely, the residue was dissolved in CH_2Cl_2/AcOEt, and the soln. was cooled to −25° for 12 h. After filtration, the soln. was evaporated *in vacuo*, and precipitation (CH_2Cl_2/hexane) provided **23** (335 mg, 68% from **19**). Waxy white solid. IR ($CHCl_3$): 3005*m*, 2933*m*, 2882*m*, 1754*s*, 1733*s*, 1595*w*, 1518*s*, 1451*m*, 1431*m*, 1328*m*, 1267*s*, 1133*s*, 1036*m*, 851*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.38 (*s*, 6 H); 3.44 (*s*, 4 H); 3.54–3.72 (*m*, 20 H); 4.03–4.04 (*m*, 8 H); 4.17–4.19 (*m*, 8 H); 4.27–4.32 (*m*, 4 H); 5.09 (*s*, 4 H); 6.82–6.93 (*m*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 41.51; 59.12; 64.71; 67.38; 68.96; 69.11; 70.01; 70.23; 72.07; 113.52; 114.30; 122.00; 128.47; 149.07; 149.33; 166.67; 166.80 (4 signals missing due to overlap). HR-MALDI-MS (DHB): 907.3577 (54, $[M+Na]^+$, $C_{42}H_{60}NaO_{20}^+$; calc. 907.3575); 675.2607 (100, $[MH+Na-C_{10}H_{17}O_6]^+$, $C_{32}H_{44}NaO_{14}^+$; calc. 675.2629). Anal. calc. for $C_{42}H_{60}O_{20}$ (884.93): C 57.01, H 6.83; found: C 56.93, H 7.07.

*(±)-*out,out*-3′,3″-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethyl] 3′,3″-[(6,7,9,10,17,18,20,21-Octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecin-2,13-diyl)dimethylene] 3′*H,*3″*H-*Dicyclopropa[1,9:52,60]-(C$_{60}$-I$_h$)[5,6]fullerene-3′,3′,3″,3″-tetracarboxylate* ((±)-**17**). KPF_6 (63 mg, 0.34 mmol) in MeCN (80 ml) was added at 20° to a soln. of C_{60} (159 mg, 0.221 mmol), I_2 (125 mg, 0.490 mmol), and **23** (195 mg, 0.221 mmol) in PhMe (400 ml). DBU (200 μl, 1.34 mmol) in CH_2Cl_2 (1 ml) was injected dropwise *via* syringe, and the mixture was stirred for 48 h at 20°. The soln. was washed (H_2O), dried ($MgSO_4$), and filtered through a short plug (SiO_2-*H*), eluting first with PhMe to remove unreacted C_{60}, then with CH_2Cl_2/AcOEt 1:1, and finally with CH_2Cl_2/AcOEt/MeOH 1:1:0.01. Evaporation *in vacuo*, extraction of the residue with CH_2Cl_2/H_2O, drying of the org.

phase ($MgSO_4$), and FC (SiO_2-*H*; CH_2Cl_2/AcOEt 1:1) provided (±)-**17** (75 mg, 21%). Dark yellow-brown solid. UV/VIS (CH_2Cl_2): 263 (47200), 281 (sh, 28200), 324 (18600), 405 (sh, 2900), 441 (1500), 472 (2000). IR ($CHCl_3$): 3395*w*, 2944*m*, 1744*m*, 1646*m*, 1513*w*, 1456*w*, 1318*w*, 1251*m*, 1118*m*, 1072*m*, 851*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.38 (*s*, 6 H); 3.57–4.08 (*m*, 36 H); 4.72–4.75 (*m*, 4 H); 5.40 (*d*, *J* = 10.8, 2 H); 5.77 (*d*, *J* = 10.8, 2 H); 6.64 (*d*, *J* = 8.3, 2 H); 6.93 (*d*, *J* = 1.6, 2 H); 7.08 (*dd*, *J* = 8.3, 1.6, 2 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 45.19; 59.05; 66.42; 67.89; 68.71; 68.82; 69.40; 69.60; 69.74; 69.85; 70.02; 70.65; 70.74; 70.85; 71.97; 112.11; 114.16; 124.35; 127.82; 136.97; 137.76; 140.47; 140.61; 140.92; 141.01 (2×); 142.04; 142.33; 142.58; 143.11; 143.16; 143.21; 143.26; 143.60 (2×); 143.73; 144.29; 144.38; 144.60; 144.71; 144.96; 145.23 (2×); 148.06; 149.29; 164.13; 164.52 (4 signals missing due to overlap). HR-MALDI-MS (DHB): 1624.3278 (100, $[MH + Na]^+$, $C_{102}H_{57}NaO_{20}^+$; calc. 1624.3341); 1623.3240 (86, $[M + Na]^+$, $C_{102}H_{56}NaO_{20}^+$; calc. 1623.3262).

Hydrogen (Pyridin-4-yl)methyl Malonate (**22**). A mixture of *Meldrum*'s acid (10 g, 69 mmol) and 4-(hydroxymethyl)pyridine (7.6 g, 70 mmol) was stirred for 4 h at 110°. After cooling to 20°, CH_2Cl_2 was added. Upon cooling for 3 h to 0°, a white precipitate formed, which was isolated by filtration and washed with cold CH_2Cl_2 to give **22** (3.9 g, 29%). White powder. M.p. 172–174° (CH_2Cl_2). IR (KBr): 3456*w*, 3033*w*, 2945*w*, 1972*m*, 1728*s*, 1617*s*, 1511*m*, 1417*s*, 1339*s*, 1295*s*, 1217*s*, 1145*s*, 1072*s*, 1028*s*, 911*s*, 872*s*, 822*s*, 622*m*, 483*m*. ^{1}H-NMR (200 MHz, $(CD_3)_2SO$): 3.55 (*s*, 2 H); 5.23 (*s*, 2 H); 7.39 (*d*, *J* = 5.8, 2 H); 8.59 (*d*, *J* = 5.8, 2 H). ^{13}C-NMR (50.3 MHz, $(CD_3)_2SO$): 39.64; 62.47; 120.02; 143.35; 148.01; 165.09; 166.36. ESI-MS (MeOH): 413.2 (30, $[2\ M + Na]^+$), 391.2 (8, 2 MH^+), 196.2 (100, MH^+). Anal. calc. for $C_9H_9NO_4$ (195.17): C 55.39, H 4.65, N 7.18; found: C 55.58, H 4.83, N 7.23.

*1,1′-Bis[(pyridin-4-yl)methyl] 3,3′-[(6,7,9,10,17,18,20,21-Octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecin-2,13-diyl)dimethylene] Bis[malonate]* (**24**). $NaBH_4$ (80 mg, 2.1 mmol) was added to a suspension of **19** (404 mg, 0.971 mmol) in MeOH (70 ml) at 0°. After stirring for 1 h at 20°, the mixture was neutralized with a 10% aq. CF_3COOH soln., and the solvent was evaporated *in vacuo*. The residue was dissolved in acetone and the solvent evaporated *in vacuo*. This sequence was repeated 3 times before solid crude **20** was dried, and then used immediately in the subsequent esterification without additional purification. DCC (617 mg, 2.95 mmol) was added at 0° to a soln. of crude **20**, DMAP (25 mg, 0.2 mmol) and malonate **22** (575 mg, 2.95 mmol) in dry DMF (8.1 ml), and the mixture was stirred for 14 h at 20°. Precipitated dicyclohexylurea was removed by filtration and the solvent evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2/AcOEt 1:1, and the mixture was extracted with 0.1% aq. CF_3COOH soln. and H_2O. The org. phase was dried ($MgSO_4$) and evaporated *in vacuo* to give **24** (600 mg, 80% from **19**). White solid. M.p. 105–109° (CH_2Cl_2/AcOEt). IR ($CHCl_3$): 3005*w*, 2933*w*, 1733*s*, 1610*w*, 1518*m*, 1451*w*, 1431*w*, 1380*w*, 1333*m*, 1267*s*, 1174*m*, 1144*s*, 1067*w*, 990*w*, 959*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.51 (*s*, 4 H); 4.01–4.03 (*m*, 8 H); 4.14–4.18 (*m*, 8 H); 5.11 (*s*, 4 H); 5.18 (*s*, 4 H); 6.77–6.90 (*m*, 6 H); 7.23 (*d*, *J* = 5.9, 4 H); 8.59 (*d*, *J* = 5.9, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 41.52; 65.16; 67.57; 68.95; 69.03; 70.03; 113.39; 114.35; 122.13; 128.26; 144.94; 149.02; 149.38; 149.93; 166.27; 166.35 (2 signals missing due to overlap). HR-MALDI-MS (DHB): 797.2532 (11, $[M + Na]^+$, $C_{40}H_{42}N_2NaO_{14}^+$; calc. 797.2534), 775.2742 (7, MH^+, $C_{40}H_{43}N_2O_{14}^+$; calc. 775.2714), 580.2197 (100, $[M - C_9H_8NO_4]^+$, $C_{31}H_{34}NO_{10}^+$; calc. 580.2183). Anal. calc. for $C_{40}H_{42}N_2O_{14}$ (774.78): C 62.01, H 5.46, N 3.62; found: C 62.12, H 5.56, N 3.59.

*(±)-*out-out*-3′,3″-Bis[(pyridin-4-yl)methyl] 3′,3″-[(6,7,9,10,17,18,20,21-Octahydrodibenzo[*b,k*][1,4,7,10,13,16]-hexaoxacyclooctadecin-2,13-diyl)dimethylene] 3′*H*,3″*H*-dicyclopropa[1,9:52,60](*C_{60}*-I_h)[5,6]fullerene-3′,3′,3″,3″-tetracarboxylate* ((±)-**18**). DBU (464 µl, 3.1 mmol) in CH_2Cl_2 (3 ml) was added dropwise *via* syringe to a soln. of **24** (400 mg, 0.52 mmol), C_{60} (376 mg, 0.522 mmol), and I_2 (307 mg, 1.20 mmol) in PhMe/MeCN 10:1 (880 ml). After stirring for 14 h at 20°, the mixture was filtered through a short plug (SiO_2-*H*), eluting first with PhMe to remove unreacted C_{60}, then with CH_2Cl_2/AcOEt 1:1 containing 10% Me_2CO and 0.1% Et_3N. Evaporation *in vacuo* and FC (SiO_2-*H*; CH_2Cl_2/AcOEt/Me_2CO/Et_3N 1:1:0.1:0.001) provided (±)-**18** (149 mg, 19%). Dark yellow-brown solid. M.p. >350° (CH_2Cl_2/AcOEt). UV/VIS (CH_2Cl_2): 263 (87700), 280 (sh, 55000), 323 (34500), 400 (sh, 6300), 435 (sh, 3200), 469 (3600). IR ($CHCl_3$): 3005*w*, 2933*w*, 1739*s*, 1605*m*, 1518*m*, 1451*w*, 1431*w*, 1359*w*, 1267*s*, 1246*s*, 1169*m*, 1144*m*, 1072*m*, 954*w*, 862*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.72–4.19 (*m*, 16 H); 5.43 (*d*, *J* = 10.8, 2 H); 5.61 (*d*, *J* = 13.6, 2 H); 5.66 (*d*, *J* = 13.6, 2 H); 5.81 (*d*, *J* = 10.8, 2 H); 6.65 (*d*, *J* = 8.3, 2 H); 6.94 (*d*, *J* = 1.8, 2 H); 7.09 (*dd*, *J* = 8.3, 1.8, 2 H); 7.5 (*d*, *J* = 6.1, 4 H); 8.74 (*d*, *J* = 6.1, 4 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 44.70; 66.62; 67.96; 68.44; 69.56; 69.71 (2×); 69.74; 70.00; 111.92; 114.11; 122.08; 124.34; 127.60; 137.17; 138.00; 140.40; 140.52; 140.55; 140.98; 141.10 (2×); 141.73; 141.99; 142.28; 143.19 (2×); 143.29 (2×); 143.44; 143.65; 143.74 (2×); 144.25; 144.32; 144.51; 144.68; 144.81; 145.05; 145.14; 145.23; 148.10; 149.35; 150.34; 164.01; 164.17 (2 signals missing due to overlap). HR-MALDI-MS (DHB): 1514.2221 (92, $[MH + Na]^+$, $C_{100}H_{39}N_2NaO_{14}^+$; calc. 1514.2299); 1492.2394 (18, $[M + 2\,H]^+$, $C_{100}H_{40}N_2O_{14}^+$; calc. 1492.2479); 1491.2373 (14, MH^+, $C_{100}H_{39}N_2O_{14}^+$; calc. 1491.2401).

*Tetrakis[(3-{[(*tert*-butyl)dimethylsilyloxy]methyl}phenyl)methyl] 3′*H,*3″*H-*Dicyclopropa[1,9:52,60](C*$_{60}$-I$_h$*)[5,6]fullerene-3′,3′,3″,3″-tetracarboxylate* (**27**). A soln. of (±)-**13** (137 mg, 96.4 μmol) and $TsOH \cdot H_2O$ (733 mg, 3.85 mmol) in PhMe (60 ml) was heated to reflux for 12 h. The brown precipitate of **25** was isolated by centrifugation, washed with PhMe, dried, then washed again with H_2O, and dried. To a suspension of crude **25** in dry CH_2Cl_2 (15 ml), $(COCl)_2$ (2.5 ml, 29.5 mmol) was added *via* syringe. The mixture was stirred at 40° under Ar for 48 h. Excess $(COCl)_2$ was removed by vacuum distillation, and the residual crude **26** was dried. This solid was suspended in dry CH_2Cl_2 (20 ml), and mono-(*t*-Bu)Me_2Si-protected benzene-1,3-dimethanol [30] (0.531 g, 2.10 mmol) and dry pyridine (64 μl, 790 μmol) were added at 0°. After stirring at 20° for 14 h, the mixture was washed with 1% aq. CF_3COOH soln. and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. FC (SiO_2; CH_2Cl_2/hexane 1:1, then 6:4) yielded **27** (37 mg, 21% from (±)-**13**). Dark-brown, crystalline solid. M.p. 151–152°. UV/VIS (CH_2Cl_2): 264 (99500), 325 (37700), 440 (2480), 469 (4040). IR (KBr): 3456*m*, 2944*m*, 2844*m*, 1739*s*, 1461*w*, 1361*w*, 1249*m*, 1205*m*, 1166*m*, 1105*m*, 1077*m*, 1005*m*, 938*w*, 833*s*, 777*m*, 694*w*, 666*w*, 527*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.11 (*s*, 24 H); 0.95 (*s*, 36 H); 4.75 (*s*, 8 H); 5.57 (*s*, 8 H); 7.35–7.36 (*m*, 12 H); 7.44 (br. *s*, 4 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): −5.24; 18.42; 25.96; 45.42; 64.66; 69.02; 70.03; 126.44; 126.48; 127.40; 128.68; 134.53; 139.13; 141.12; 142.01; 143.11; 143.46; 143.59; 144.71; 145.11; 145.26; 163.88. FAB-MS: 1861.3 (27, M^+), 719.8 (100, C_{60}^+). HR-MALDI-MS (DHB): 1883.555 ($[M+Na]^+$, $C_{122}H_{92}O_{12}Si_4Na^+$; calc. 1883.556).

*Tetrakis{[3-(hydroxymethyl)phenyl]methyl} 3′*H,*3″*H-*Dicyclopropa[1,9:52,60](C*$_{60}$-I$_h$*)[5,6]fullerene-3′,3′,3″,3″-tetracarboxylate* (**28**). Compound **27** (15 mg, 5.4 μmol) was added to a 15-ml polyethylene centrifuge tube, followed by dry CH_2Cl_2 (5 ml). The uniform brown soln. was cooled to 0°, and several drops of $HF \cdot$ pyridine were added *via* syringe. The mixture was stirred for 1 h at 0°, during which time it turned colorless while a dark-brown precipitate formed. The vessel was warmed to 20°, centrifuged, and the soln. was removed *via* pipette. The remaining dark-brown solid was washed with CH_2Cl_2, then dried to yield **28** (7 mg, 93%). Dark-brown solid. M.p. >250°. UV/VIS (THF): 259 (75900), 287 (sh, 33900), 324 (29700), 407 (sh, 2800), 439 (1700), 470 (2800), 519 (sh, 440), 553 (sh, 420), 589 (sh, 330), 651 (sh, 140). IR (KBr): 3322*m*, 2956*w*, 2922*w*, 2856*w*, 1740*s*, 1650*w*, 1444*w*, 1422*w*, 1372*w*, 1317*w*, 1250*s*, 1206*m*, 1167*m*, 1078*m*, 1022*w*, 994*w*, 939*w*, 889*w*, 779*m*, 739*m*, 700*w*, 672*w*, 522*w*, 483*w*. ^{1}H-NMR (500 MHz, $(CD_3)_2SO$): 4.49 (*d*, $J=3.9$, 8 H); 5.24 (*t*, $J=3.9$, 4 H); 5.62 (*s*, 8 H); 7.32–7.37 (*m*, 12 H); 7.49 (*s*, 4 H). ^{13}C-NMR (125.8 MHz, $(CD_3)_2SO$): 45.64; 62.64; 68.93; 69.64; 126.69; 127.08; 128.33; 134.64; 138.53; 140.62; 142.83; 142.89; 142.92; 143.05; 144.13; 144.57; 144.79; 162.95. FAB-MS: 1405.3 (35, M^+). HR-MALDI-MS (DHB): 1427.210 ($[M+Na]^+$, $C_{98}H_{36}O_{12}Na^+$; calc. 1427.210).

*Tetrakis[(3-{[(ethoxycarbonyl)acetoxy]methyl}phenyl)methyl] 3′*H,*3″*H-*Dicyclopropa[1,9:52,60](C*$_{60}$-I$_h$*)[5,6]fullerene-3′,3′,3″,3″-tetracarboxylate* (**29**). A suspension of **28** (5.0 mg, 3.6 μmol) and dry CH_2Cl_2 (25 ml) in a dry 50-ml round-bottomed flask under Ar was cooled to 0°, then *N*,*N*-dimethylaniline (22 μl, 74 μmol) and ethyl malonyl chloride (18 μl, 141 μmol) were added. The soln. was stirred at 0° for 20 min, then for 14 h at 20°. The pale-yellow soln. was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo* to yield a dark solid. FC (SiO_2; CH_2Cl_2/MeOH 100:1) provided **29** (5.2 mg, 80%). Dark-brown solid. M.p. 98–99°. UV/VIS (CH_2Cl_2): 263 (91400), 288 (sh, 39400), 324 (37600), 407 (sh, 3700), 438 (2200), 468 (3300), 512 (sh, 600), 547 (sh, 600), 591 (sh, 400), 645 (sh, 200). IR (KBr): 3444*w*, 2944*w*, 1733*s*, 1450*w*, 1372*m*, 1317*m*, 1244*s*, 1200*m*, 1167*m*, 1139*m*, 1072*m*, 1028*m*, 939*w*, 883*w*, 194*w*, 700*w*, 578*w*, 550*w*, 522*w*, 472*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.26 (*t*, $J=7.2$, 12 H); 3.42 (*s*, 8 H); 4.20 (*q*, $J=7.2$, 8 H); 5.19 (*s*, 8 H); 5.58 (*s*, 8 H); 7.39–7.51 (*m*, 16 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 14.06; 41.51; 45.29; 61.62; 66.74; 68.64; 70.00; 128.59; 128.70; 128.82; 129.07; 135.08; 135.92; 139.10; 141.16; 143.04; 143.44; 143.62; 144.75; 145.07; 145.24; 163.76; 166.31; 166.36. FAB-MS: 1862 (56, M^+). HR-MALDI-MS (DHB): 1883.335 ($[M+Na]^+$, $C_{118}H_{60}O_{24}Na^+$; calc. 1883.337).

*(±)-*out,out:out,out:out,out:out,out:out,out-*3′,3‴,3⁗,3′′′′′-Tetraethyl 3′,3″:3″,3‴:3‴,3⁗:3⁗,3′′′′′:3′′′′′,3′′′′′′-Tetrakis[(benzene-1,3-diyl)dimethyl] 3′*H,*3″*H,*3‴*H,*3⁗*H,*3′′′′′*H,*3′′′′′′*H-*Hexacyclopropa[1,9:3,15:22,23:34,35:43,57:49,59](C*$_{60}$-I$_h$*)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3⁗,3⁗,3′′′′′,3′′′′′,3′′′′′′,3′′′′′′-dodecacarboxylate* ((±)-**1**). DBU (87 μl, 0.58 mmol) in CH_2Cl_2 (5 ml) was added dropwise *via* syringe at 20° to a soln. of **29** (90 mg, 0.048 mmol) and I_2 (49 mg, 0.19 mmol) in PhMe (900 ml), and the mixture was stirred for 10 min before $(CD_3)_2SO$ (55 ml) was added dropwise. The soln. was stirred for 12 h before being extracted with H_2O (3×), dried ($MgSO_4$), and concentrated *in vacuo*. FC (SiO_2-*H*; CH_2Cl_2/AcOEt 98:2) provided three main fractions. The first and the last contained a mixture of partially reacted compounds. Further chromatography of the middle fraction (SiO_2-*H*; CH_2Cl_2/AcOEt 99.5:0.5) afforded (±)-**1** (9 mg, 10%). Dark-red solid. UV/VIS (CH_2Cl_2): 264 (sh, 78400), 315 (41800), 496 (3000), 514 (3100), 531 (3200), 576 (4100). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.36 (*t*, $J=7.0$, 12 H); 4.22–4.46 (*m*, 8 H); 5.10 (*d*, $J=13.2$, 4 H); 5.14 (*d*, $J=12.8$, 4 H); 5.60 (*d*, $J=13.2$, 4 H); 5.88 (*d*, $J=12.8$, 4 H); 7.18–7.38 (*m*, 16 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 14.08; 43.28; 62.95; 65.31; 65.43; 67.08; 67.21; 73.03; 123.82; 126.52; 128.50; 129.55; 136.51; 136.61; 136.69; 137.31; 139.40; 140.32; 140.93; 142.91; 143.14; 145.08; 145.13; 146.09; 146.29; 162.84; 163.11; 163.45 (one $^{13}C(sp^3)$ and one $^{13}C(sp^2)$ resonance missing). FAB-MS: 1853 (100,

M^+). HR-MALDI-MS (DHB): 1875.275 ($[M+Na]^+$, $C_{118}H_{52}O_{24}Na^+$; calc. 1875.275). X-Ray Analysis: see [11].

(±)-out,out:out,out:out,out:out,out:out,out-*3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴,3⁗⁗,3⁗⁗′-Hexaethyl 3′,3″:3′,3‴:3′,3⁗:3′,3⁗′:3′,3⁗″:3′,3⁗‴:3′,3⁗⁗:3′,3⁗⁗′-Tetrakis-[(benzene-1,3-diyl)dimethyl] 3′*H,*3″*H,*3‴*H,*3⁗*H,*3⁗′*H,*3⁗″*H,*3⁗‴*H-Heptacyclopropa[1,9:3,15:21,40:24,25:36,37:46,58:52,60](*C_{60}-I_h*)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3⁗,3⁗,3⁗′,3⁗′,3⁗″,3⁗″,3⁗‴,3⁗‴,3⁗⁗,3⁗⁗-tetradecacarboxylate* ((±)-**30**) *and (±)*-out,out:out,out:out,out:out,out:out,out-*3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴,3⁗⁗,3⁗⁗′-Octaethyl 3′,3″:3′,3‴:3′,3⁗:3′,3⁗′:3′,3⁗″:3′,3⁗‴:3′,3⁗⁗:3′,3⁗⁗′-Tetrakis[(benzene-1,3-diyl)dimethyl] 3′*H,*3″*H,*3‴*H,*3⁗*H,*3⁗′*H,*3⁗″*H,*3⁗‴*H,*3⁗⁗*H-Octacyclopropa[1,9:3,15:21,40:24,25:30,31:36,37:46,58:52,60](*C_{60}-I_h*)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3⁗,3⁗,3⁗′,3⁗′,3⁗″,3⁗″,3⁗‴,3⁗‴,3⁗⁗,3⁗⁗-hexadecacarboxylate* ((±)-**31**). To (±)-**1** (1.7 mg, 0.91 μmol) and diethyl 2-bromomalonate (0.32 μl, 1.9 μmol) in PhMe/Me_2SO 1:1 (4 ml), DBU (0.90 μl, 6.4 μmol) was added *via* syringe. After stirring for 12 h, the soln. was washed with H_2O (3×), dried ($MgSO_4$), and chromatographed (SiO_2-*H*; CH_2Cl_2/AcOEt 99:1). The first fraction contained unreacted (±)-**1**, which was recovered, and the second fraction afforded (±)-**30** (*ca.* 0.7 mg, 40%) as the only product isolated. The recovered starting material (±)-**1** was treated under the same exper. conditions with an excess of diethyl 2-bromomalonate (3.2 μl, 1.9×10^{-2} mmol) and DBU (9 μl, 6.4×10^{-2} mmol). After stirring for 12 h, the soln. was washed with H_2O (3×), dried ($MgSO_4$), and chromatographed (FC, SiO_2-*H*; CH_2Cl_2/AcOEt 98:2) to give (±)-**31** (*ca.* 0.7 mg, 80%) as the main fraction together with traces of (±)-**30**.

Data of (±)-**30**: UV/VIS (CH_2Cl_2): 316, 364 (sh), 511, 543, 556 (sh). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.20–1.33 (*m*, 18 H); 4.11–4.42 (*m*, 12 H); 4.98 (*d*, *J* = 12.9, 2 H); 5.10 (*d*, *J* = 12.6, 6 H); 5.51 (*d*, *J* = 12.6, 2 H); 5.62 (*d*, *J* = 12.6, 2 H); 5.86 (*d*, *J* = 12.6, 2 H); 5.89 (*d*, *J* = 12.6, 2 H); 7.1–7.35 (*m*, 16 H). HR-MALDI-MS (DHB): 2033.331 ($[M+Na]^+$, $C_{125}O_{28}H_{62}Na^+$; calc. 2033.332).

Data of (±)-**31**: UV/VIS (CH_2Cl_2): 276 (sh), 320, 335 (sh), 478 (sh), 504 (sh), 551. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.24–1.32 (*m*, 24 H); 4.09–4.36 (*m*, 16 H); 4.98 (*d*, *J* = 13.4, 4 H); 5.07 (*d*, *J* = 12.8, 4 H); 5.53 (*d*, *J* = 12.8, 4 H); 5.87 (*d*, *J* = 13.4, 4 H); 7.12–7.35 (*m*, 16 H). HR-MALDI-MS (DHB): 2191.388 ($[M+Na]^+$, $C_{132}O_{32}H_{72}Na^+$; calc. 2191.390).

REFERENCES

[1] I. S. Neretin, K. A. Lyssenko, M. Y. Antipin, Y. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Y. Lukonin, L. N. Sidorov, R. Taylor, *Angew. Chem.* **2000**, *112*, 3411; *Angew. Chem., Int. Ed.* **2000**, *39*, 3273.

[2] G. Schick, M. Levitus, L. Kvetko, B. A. Johnson, I. Lamparth, R. Lunkwitz, B. Ma, S. I. Khan, M. Garcia-Garibay, Y. Rubin, *J. Am. Chem. Soc.* **1999**, *121*, 3246; K. Hutchison, J. Gao, G. Schick, Y. Rubin, F. Wudl, *J. Am. Chem. Soc.* **1999**, *121*, 5611.

[3] M. Hetzer, H. Clausen-Schaumann, S. Bayerl, T. M. Bayerl, X. Camps, O. Vostrowsky, A. Hirsch, *Angew. Chem.* **1999**, *111*, 2103; *Angew. Chem., Int. Ed.* **1999**, *38*, 1962; M. Brettreich, S. Burghardt, C. Böttcher, T. Bayerl, S. Bayerl, A. Hirsch, *Angew. Chem.* **2000**, *112*, 1915; *Angew. Chem., Int. Ed.* **2000**, *39*, 1845.

[4] P. J. Fagan, J. C. Calabrese, B. Malone, *J. Am. Chem. Soc.* **1991**, *113*, 9408.

[5] a) A. Hirsch, I. Lamparth, T. Grösser, *J. Am. Chem. Soc.* **1994**, *116*, 9385; b) I. Lamparth, C. Maichle-Mössmer, A. Hirsch, *Angew. Chem.* **1995**, *107*, 1755; *Angew. Chem., Int. Ed.* **1995**, *34*, 1607; c) I. Lamparth, A. Herzog, A. Hirsch, *Tetrahedron* **1996**, *52*, 5065; d) X. Camps, A. Hirsch, *J. Chem. Soc., Perkin Trans. 1* **1997**, 1595.

[6] a) B. Kräutler, J. Maynollo, *Angew. Chem.* **1995**, *107*, 69; *Angew. Chem., Int. Ed.* **1995**, *34*, 87; b) B. Kräutler, J. Maynollo, *Tetrahedron* **1996**, *52*, 5033; c) R. Schwenninger, T. Müller, B. Kräutler, *J. Am. Chem. Soc.* **1997**, *119*, 9317.

[7] a) L. Isaacs, R. F. Haldimann, F. Diederich, *Angew. Chem.* **1994**, *106*, 2434; *Angew. Chem., Int. Ed.* **1994**, *33*, 2339; b) L. Isaacs, P. Seiler, F. Diederich, *Angew. Chem.* **1995**, *107*, 1636; *Angew. Chem., Int. Ed.* **1995**, *34*, 1466; c) P. Timmerman, L. E. Witschel, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1996**, *79*, 6; d) P. Seiler, L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1996**, *79*, 1047; e) L. Isaacs, F. Diederich, R. F. Haldimann, *Helv. Chim. Acta* **1997**, *80*, 317.

[8] W. Qian, Y. Rubin, *Angew. Chem.* **1999**, *111*, 2504; *Angew. Chem., Int. Ed.* **1999**, *38*, 2356; W. Qian, Y. Rubin, *Angew. Chem.* **2000**, *112*, 3263; *Angew. Chem., Int. Ed.* **2000**, *39*, 3133; W. Qian, Y. Rubin, *J. Am. Chem. Soc.* **2000**, *122*, 9564.

[9] F. Diederich, R. Kessinger, *Acc. Chem. Res.* **1999**, *32*, 537; F. Diederich, R. Kessinger, in 'Templated Organic Synthesis', Eds. F. Diederich, P. J. Stang, Wiley-VCH, Weinheim, 1999, pp. 189–218.

[10] M. J. van Eis, R. J. Alvarado, L. Echegoyen, P. Seiler, F. Diederich, *Chem. Commun*. **2000**, 1859; M. Diekers, A. Hirsch, C. Luo, D. M. Guldi, K. Bauer, U. Nickel, *Org. Lett*. **2000**, *2*, 2741; G. A. Burley, P. A. Keller, S. G. Pyne, G. E. Ball, *Chem. Commun*. **2000**, 1717.
[11] C. R. Woods, J.-P. Bourgeois, P. Seiler, F. Diederich, *Angew. Chem*. **2000**, *112*, 3971; *Angew. Chem., Int. Ed*. **2000**, *39*, 3813.
[12] a) R. F. Haldimann, C. Fokas, F. Diederich, *Helv. Chim. Acta* **2001**, *84*, in press; b) R. F. Haldimann, F.-G. Klärner, F. Diederich, *Chem. Commun*. **1997**, 237.
[13] T. Habicher, J.-F. Nierengarten, V. Gramlich, F. Diederich, *Angew. Chem*. **1998**, *110*, 2019; *Angew. Chem., Int. Ed*. **1998**, *37*, 1916.
[14] P. J. Stang, *Chem. Eur. J*. **1998**, *4*, 19; P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502.
[15] F. L. Minn, C. L. Trichilo, C. R. Hurt, N. Filipescu, *J. Am. Chem. Soc*. **1970**, *92*, 3600.
[16] C. Bingel, *Chem. Ber*. **1993**, *126*, 1957.
[17] A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem*. **1994**, *106*, 453; *Angew. Chem., Int. Ed*. **1994**, *33*, 437; F. Djojo, A. Hirsch, *Chem. Eur. J*. **1998**, *4*, 344.
[18] F. Diederich, L. Echegoyen, M. Gómez-López, R. Kessinger, J. F. Stoddart, *J. Chem. Soc., Perkin Trans. 2* **1999**, 1577; M. T. Rispens, L. Sánchez, J. Knol, J. C. Hummelen, *Chem. Commun*. **2001**, 161; J. J. González, S. González, E. M. Priego, C. Luo, D. M. Guldi, J. de Mendoza, N. Martín, *Chem. Commun*. **2001**, 163.
[19] a) F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343; b) C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 1334.
[20] F. Prat, R. Stackow, R. Bernstein, W. Qian, Y. Rubin, C. S. Foote, *J. Phys. Chem. A* **1999**, *103*, 7230.
[21] H. L. Anderson, R. Faust, Y. Rubin, F. Diederich, *Angew. Chem*. **1994**, *106*, 1427; *Angew. Chem., Int. Ed.* **1994**, *33*, 1366; P. Timmerman, H. L. Anderson, R. Faust, J.-F. Nierengarten, T. Habicher, P. Seiler, F. Diederich, *Tetrahedron* **1996**, *52*, 4925; H. L. Anderson, C. Boudon, F. Diederich, J.-P. Gisselbrecht, M. Gross, P. Seiler, *Angew. Chem.* **1994**, *106*, 1691; *Angew. Chem., Int. Ed*. **1994**, *33*, 1628.
[22] Y.-Z. An, Y. Rubin, C. Schaller, S. W. McElvany, *J. Org. Chem*. **1994**, *59*, 2927.
[23] Y. Rubin, F. Diederich, in 'Stimulating Concepts in Chemistry', Eds. F. Vögtle, J. F. Stoddart, M. Shibasaki, Wiley-VCH, Weinheim, 2000, 163 – 186.
[24] P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem*. **2000**, *112*, 2740; *Angew. Chem., Int. Ed*. **2000**, *39*, 2632.
[25] a) J.-P. Bourgeois, L. Echegoyen, M. Fibbioli, E. Pretsch, F. Diederich, *Angew. Chem.* **1998**, *110*, 2203; *Angew. Chem., Int. Ed*. **1998**, *37*, 2118; b) J.-P. Bourgeois, P. Seiler, M. Fibbioli, E. Pretsch, F. Diederich, L. Echegoyen, *Helv. Chim. Acta* **1999**, *82*, 1572.
[26] B. Kräutler, T. Müller, J. Maynollo, K. Gruber, C. Kratky, P. Ochsenbein, D. Schwarzenbach, H.-B. Bürgi, *Angew. Chem.* **1996**, *108*, 1294; *Angew. Chem., Int. Ed*. **1996**, *35*, 1204.
[27] J.-P. Bourgeois, F. Diederich, L. Echegoyen, J.-F. Nierengarten, *Helv. Chim. Acta* **1998**, *81*, 1835; N. Armaroli, G. Marconi, L. Echegoyen, J.-P. Bourgeois, F. Diederich, *Chem. Eur. J.* **2000**, *6*, 1629.
[28] B. C. Chen, *Heterocycles* **1991**, *32*, 529.
[29] J.-P. Bourgeois, ETH Dissertation No. 13956, Zürich, 2000.
[30] A. G. Myers, P. S. Dragovich, E. L. Kuo, *J. Am. Chem. Soc*. **1992**, *114*, 9369.
[31] a) J.-F. Nierengarten, V. Gramlich, F. Cardullo, F. Diederich, *Angew. Chem*. **1996**, *108*, 2242; *Angew. Chem., Int. Ed*. **1996**, *35*, 2101; b) J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 2238.
[32] J.-F. Nierengarten, D. Felder, J.-F. Nicoud, *Tetrahedron Lett*. **1999**, *40*, 273; J.-F. Nierengarten, C. Schall, J.-F. Nicoud, *Angew. Chem*. **1998**, *110*, 2037; *Angew. Chem., Int. Ed*. **1998**, *37*, 1934.
[33] M. Gross, J.-P. Gisselbrecht, C. Boudon, unpublished results.
[34] O. V. Boltalina, V. Y. Markov, P. A. Troshin, A. D. Darwish, J. M. Street, R. Taylor, *Angew. Chem*. **2001**, *113*, 809; *Angew. Chem., Int. Ed.* **2001**, *40*, 787.
[35] *Sybyl* force field from *Spartan V.5.0, Wavefunction*, Irvine, CA, 1997.
[36] a) C. Thilgen, I. Gosse, F. Diederich, *Top. Stereochem.*, in press; b) R. Kessinger, C. Thilgen, T. Mordasini, F. Diederich, *Helv. Chim. Acta* **2000**, *83*, 3069.

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