

## Electronic Supplementary Information

### **Self-assembly of partially fluorinated hexabenzocoronene derivatives in the solid state**

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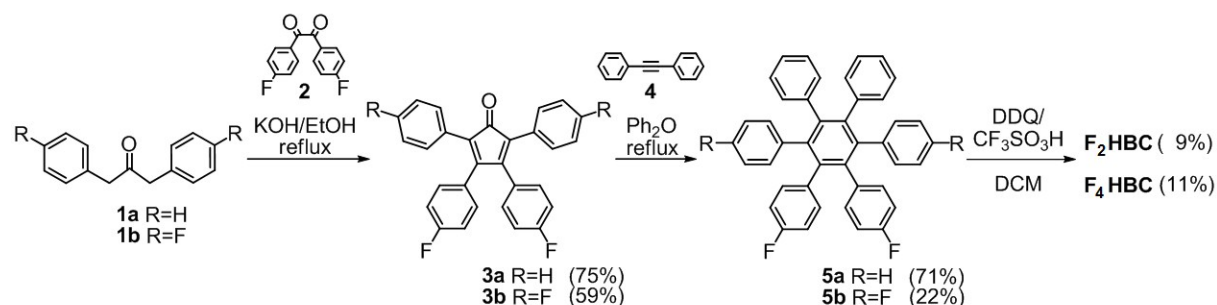
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## Synthesis and Characterization of F<sub>2</sub>HBC and F<sub>4</sub>HBC

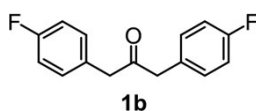
**General synthetic and analytical methods.** Commercially available starting material (compound **1a**, **2**, and **4**) were handled as received. Solvent distillation was carried out prior to the application. In need of inert conditions the solvents were subjected to additional drying and degassing and the reactions were performed under a blanket of argon. For thin-layer chromatography silica gel 60 F<sub>254</sub>-plates purchased from Merck were used. Silica gel (35-70 μm, 60 Å) by Acros was utilized for column chromatography. Analysis by means of NMR-spectroscopy were performed using a 300 MHz for <sup>1</sup>H-NMR (75 MHz for <sup>13</sup>C-NMR) Bruker AVANCE II 300 spectrometer at 25 °C. The received spectra were adjusted to the signals of the solvent (<sup>1</sup>H: δ (CDCl<sub>3</sub>) = 7.26 ppm and <sup>13</sup>C: δ (CDCl<sub>3</sub>) = 77.16 ppm). The UPLC-MS-measurements were performed on an Acquity UPLC (Waters) equipped with a ESI-MS-Detector LCT Premier XE for HR-MS (Waters) and a Photo diode arraydetector 2996. MALDI-MS spectra were measured on a Bruker Autoflex III MALDI-mass spectrometer using a smartbeam laser with a wavelength of 355 nm, 200 Hz, and 20 kV acceleration voltage, calibrated with PEG 1000. Elemental analysis was performed using a EuroVector EuroEA 3000 CHNS elemental analyser.

The synthetic route to **F<sub>2</sub>HBC** and **F<sub>4</sub>HBC** is shown below (Scheme S1).



**Scheme S1:** Synthesis of partially fluorinated **F<sub>2</sub>HBC** and **F<sub>4</sub>HBC**.

### 1,3-Bis(4-fluorophenyl)propan-2-one **1b**



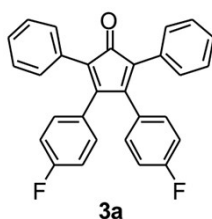
The synthesis was adapted from a literature procedure.<sup>[1]</sup> 4-Fluorophenylacetic acid (0.62 g, 4.0 mmol) and 4-dimethylaminopyridine (0.61 g, 5.0 mmol) were dissolved in 10 mL of dichloromethane (DCM). Afterwards *N,N'*-dicyclohexylcarbodiimide (DCC, 0.83 g, 4.0 mmol) was added to the solution and stirred at room temperature for 40 h. DCM and water were added to the reaction mixture and the organic layer was washed with aqueous HCl and subsequently with saturated aqueous NaHCO<sub>3</sub> and afterwards was dried over MgSO<sub>4</sub>.

After removal of the solvent column chromatography (silica gel using petroleum ether/DCM = 2:1 as the eluent) gave **1b** as a solid in 35% yield (0.34 g, 1.38 mmol).

**<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.07-7.14 (m, 4H), 6.97-7.05 (m, 4H), 3.70 (s, 4H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 205.3, 162.1 (d), 131.1 (d), 129.6 (d), 115.7 (d), 48.3.

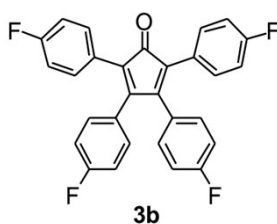
*3,4-Bis(p-fluorophenyl)-2,5-diphenylcyclopentadienone 3a*



The synthesis was adapted from a literature procedure.<sup>[1]</sup> A solution of 4,4'-difluorobenzil **2** (2.34 g, 9.5 mmol) and 1,3-diphenylacetone **1a** (2.00 g, 9.5 mmol) in 18 mL of ethanol was heated to reflux. A solution of KOH (0.3 g, 7.03 mmol) in 4 mL of ethanol was added. After 20 min the refluxing mixture was cooled to room temperature. The formed precipitate was washed with methanol affording cyclopentadienone **3a** as a dark purple solid in 75% yield (2.98 g, 6.87 mmol).

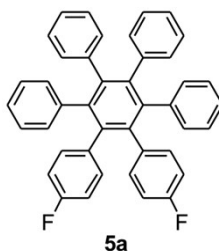
**<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 6.73-6.92 (m, 10H), 6.9 (d, 8H). **<sup>13</sup>C{<sup>1</sup>H}-NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 200.0, 162.9 (d), 131.5 (d), 153.1, 130.6, 130.2, 129.0 (d), 128.3, 127.8, 125.7, 115.6 (d). **MS (ES<sup>+</sup>):**  $m/z$  = 421.142 [M+H]<sup>+</sup>.

*2,3,4,5-Tetrakis(4-fluorophenyl)cyclopentadienone 3b*



Analogously to cyclopentadienone **3a**, the related tetrasubstituted derivate **3b** is obtained from 4,4'-difluorobenzil **2** (0.33 g, 1.35 mmol), 1,3-bis(4-fluorophenyl)propan-2-one **1b** (0.33 g, 1.35 mmol), and KOH (0.06 g, 1.00 mmol) in 3.2 mL of ethanol in 59% yield (0.34 g, 0.74 mmol).

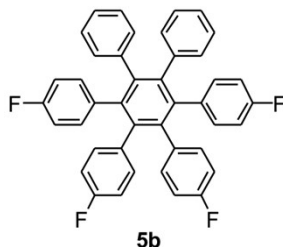
**<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.15-7.22 (m, 4H), 6.85-7.00 (m, 12H). **<sup>13</sup>C{<sup>1</sup>H}-NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 199.9, 162.1 (2xd), 153.1, 132.0, 131.4 (d), 128.7, 126.5 (d), 124.7, 115.7 (d), 115.5 (d).

*1,2-Bis(p-fluorophenyl)-3,4,5,6-tetraphenylbenzene 5a*

Adopting a literature procedure<sup>[1]</sup> a suspension of cyclopentadienone **3a** (0.84 g, 2 mmol) and diphenylacetylene **4** (0.36 g, 2 mmol) in 8 mL of diphenylether was refluxed at 260 °C overnight. During the reaction the purple suspension turned into an orange solution. Addition of methanol induced precipitation of the crude product, which was purified by column chromatography (silica gel using petroleum ether/DCM = 3:1 as the eluent) to yield the desired hexaphenylbenzene **5a** as a white solid in 71% yield (0.8 g, 1.42 mmol).

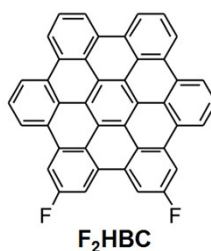
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ = 7.18-7.30 (m, 24H), 6.58 (tt, 8H). **<sup>13</sup>C{<sup>1</sup>H}-NMR** (75 MHz, CDCl<sub>3</sub>): δ = 160.8 (d), 140.8, 140.7, 140.5, 140.5, 139.5, 136.6 (d), 132.9 (d), 131.4, 131.4, 126.9, 126.8, 125.5, 125.4, 113.9 (d).

**MS** (MALDI+, matrix: tetracyanoquinodimethane): *m/z* = 569.8 ([C<sub>42</sub>H<sub>28</sub>F<sub>2</sub>]<sup>+</sup>).

*1,2,3,4-Tetrakis(p-fluorophenyl)-5,6-diphenylbenzene 5b*

Analogously to **4a**, the reaction of cyclopentadienone **3b** (0.33 g, 0.72 mmol) and diphenylacetylene **6** (0.13 g, 0.72 mmol) in 3 mL of diphenyl ether resulted in the desired hexaphenylbenzene **5b** after column chromatography (silica gel using petroleum ether/DCM = 3:1 as the eluent) in 22% yield (0.09 g, 0.16 mmol).

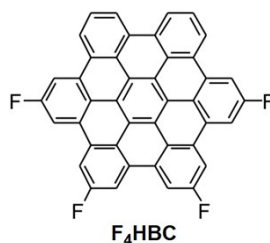
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ = 6.84-6.92 (m, 6H), 6.70-6.82 (m, 12H), 6.59 (m, 8H). **<sup>13</sup>C{<sup>1</sup>H}-NMR** (75 MHz, CDCl<sub>3</sub>): δ = 160.7 (2xd), 140.9, 140.1, 139.7, 139.6, 136.2 (d), 132.6 (d), 131.2, 126.8, 125.5, 114.0 (d), 113.8 (d). **MS** (MALDI+, matrix: tetracyanoquinodimethane): *m/z* = 605.957 ([C<sub>42</sub>H<sub>26</sub>F<sub>4</sub>]<sup>+</sup>).

*2,5-Difluoro-hexa-peri-hexabenzocoronene F<sub>2</sub>HBC*

Adopting a literature procedure<sup>[2]</sup> a dried Schlenk flask was charged with 100 mL of dry DCM. **5a** (0.71 g, 1.25 mmol) was added and the solution was degassed, put under Ar atmosphere, and cooled down to 0 °C. First 2,3-dichloro-5,6-dichlorobenzoquinone (DDQ, 1.92 g, 8.46 mmol) and afterwards trifluoromethanesulfonic acid (1.5 mL, 17.31 mmol) were added. The reaction mixture was stirred at ambient temperature for 3 h and then 100 mL of methanol were added. The precipitate was collected by filtration and washed with methanol and DCM. The crude product was purified via sublimation to afford the target **F<sub>2</sub>HBC** as a bright yellow solid in 9% yield (60 mg, 0.11 mmol).

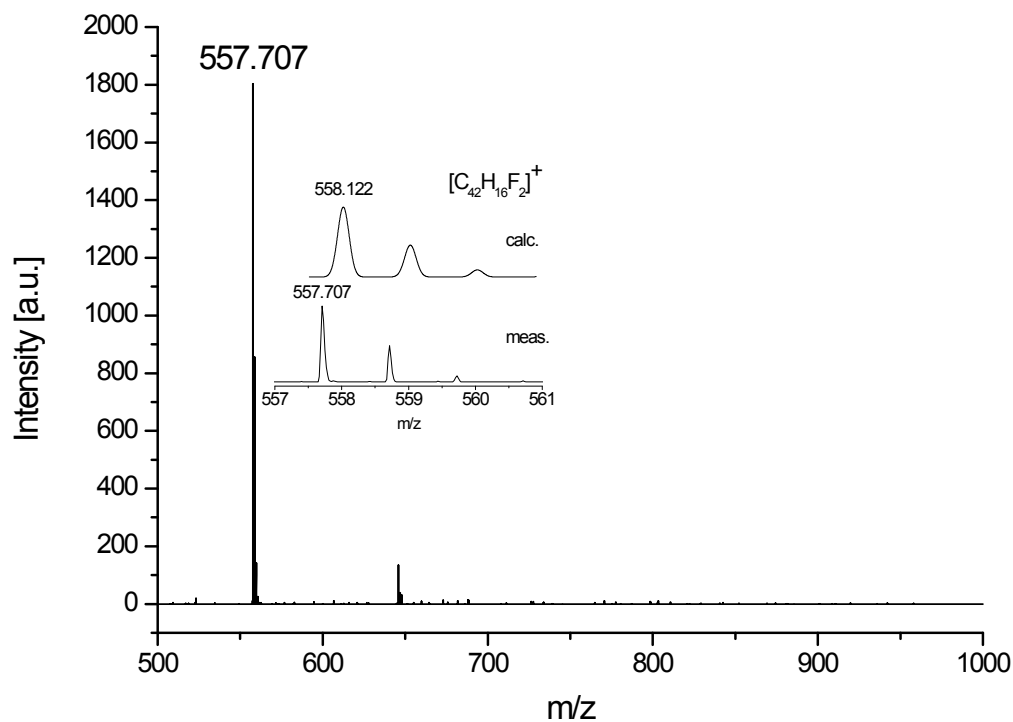
**MS** (MALDI+, matrix: tetracyanoquinodimethane, Fig. S1):  $m/z = 557.707$  ( $[C_{42}H_{16}F_2]^+$ ).

**Elemental analysis:** found C: 88.80%, H: 2.82% (calc. C: 90.31%, H: 2.89%).

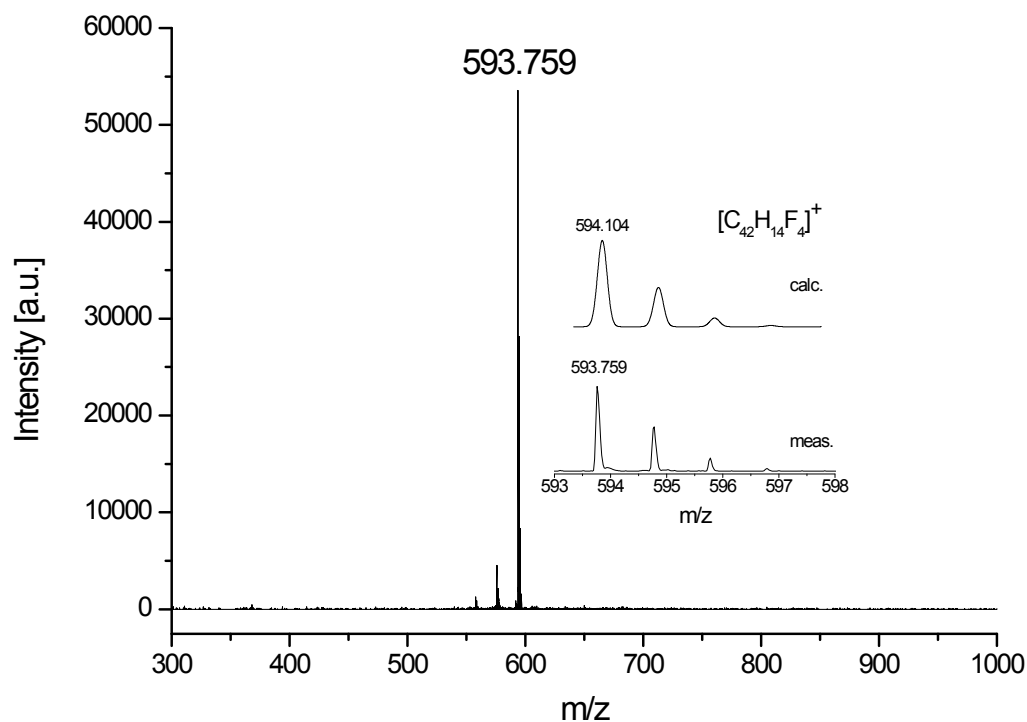
*2,5,8,11-Tetrafluoro-hexa-peri-hexabenzocoronene F<sub>4</sub>HBC*

Analogously to the doubly fluorinated **F<sub>2</sub>HBC**, the related **F<sub>4</sub>HBC** was obtained from **5b** (80 mg, 0.14 mmol), DDQ (0.21 g, 0.91 mmol), and trifluoromethanesulfonic acid (0.1 mL, 1.87 mmol) in 10 mL of DCM. The crude product was purified via sublimation to afford the target **F<sub>4</sub>HBC** as a yellow solid in 11% yield (9 mg, 0.015 mmol).

**MS** (MALDI+, matrix: no matrix, Fig. S2):  $m/z = 593.759$  ( $[C_{42}H_{14}F_4]^+$ ); **Elemental analysis:** found C: 83.69%, H: 2.87% (calc. C: 84.84%, H: 2.37%).

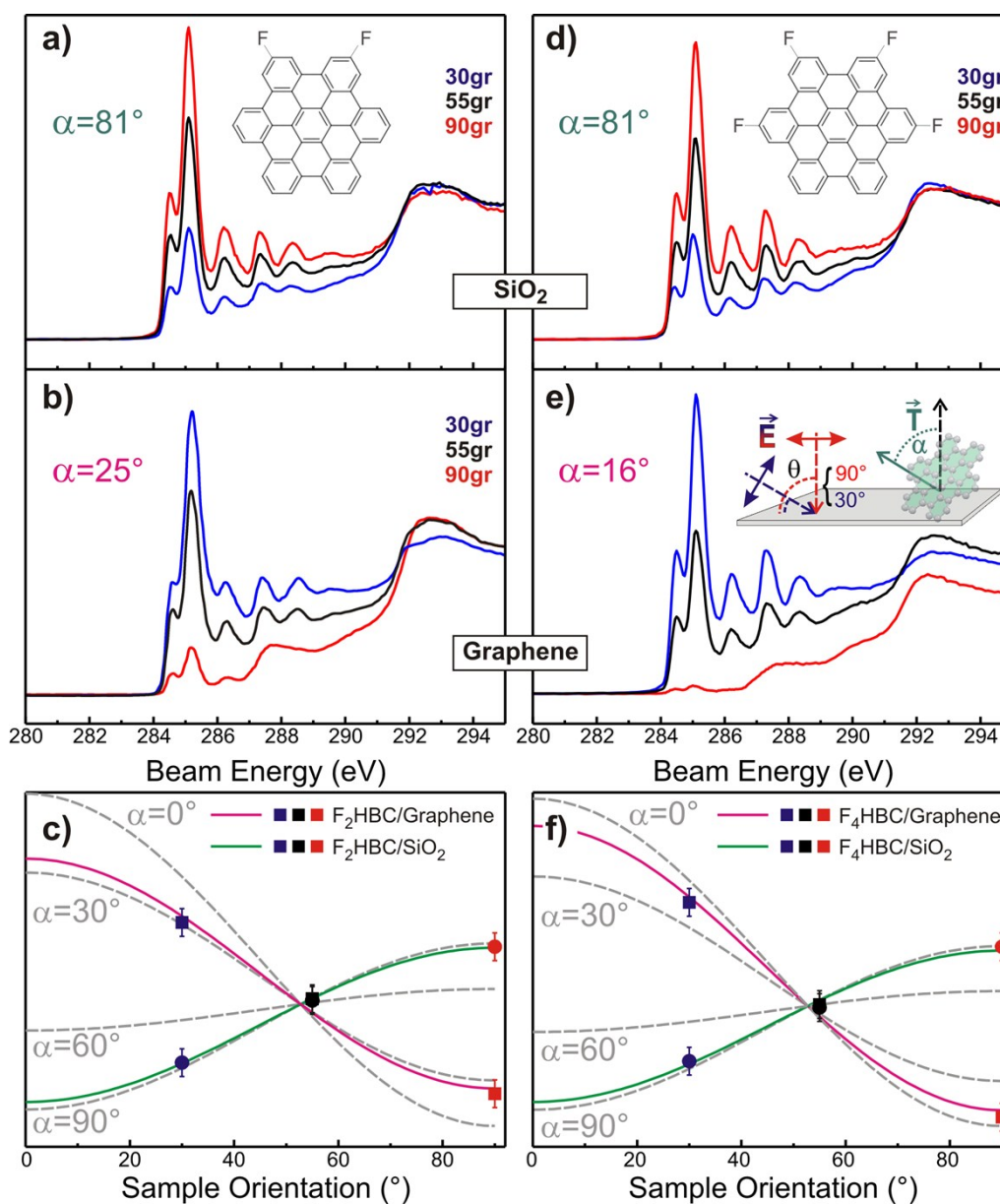


**Fig. S1:** MALDI-TOF mass spectrum of compound **F<sub>2</sub>HBC**. The inset shows the comparison between simulated (top) and experimentally determined (bottom) isotopic distributions.



**Fig. S2:** MALDI-TOF mass spectrum of compound **F<sub>4</sub>HBC**. The inset shows the comparison between simulated (top) and experimentally determined (bottom) isotopic distributions.

## NEXAFS Dichroism Measurements



**Fig. S3:** C1s-NEXAFS dichroism measurements of a,b) F<sub>2</sub>HBC and d,e) F<sub>4</sub>HBC on SiO<sub>2</sub> (a,c) and graphene (b,d) substrates with sketch of experimental geometry in the inset of d). The inverse dichroisms correspond to upright molecular orientations on SiO<sub>2</sub> and recumbent configurations on graphite substrates as obtained from the quantitative evaluation shown in c) (F<sub>2</sub>HBC) and f) (F<sub>4</sub>HBC). In addition to the experimental points and fit results for graphene (squares, pink curve) and SiO<sub>2</sub> substrates (circles, green curve), dichroism curves corresponding to 0°, 30°, 60°, and 90° are presented.

The NEXAFS spectroscopy measurements also provide information on the molecular orientation of the molecules in processed thin films. This is because the absorption efficiency depends on the relative orientation between the X-ray beam polarization and the transition

dipole moment (TDM) orientation of the respective transitions. Therefore, measurements under different angles of incidence yield different absorption efficiencies which can be translated into the tilt of the molecular normal with respect to the sample normal (cf. inset in Fig. S3e).<sup>[3]</sup>

We have analyzed the molecular orientation by fitting the average TDM orientation  $\alpha$  to the intensity dependence for  $\pi^*$  transitions for adsorbates of at least threefold-symmetry (with molecular twist  $\gamma=0^\circ$ ):<sup>[3]</sup>

$$I_{\pi^*} \propto P \cos^2(\theta) \left( \frac{3 \cos^2(\alpha)}{2} - \frac{1}{2} \right) + \frac{\sin^2(\alpha)}{2}$$

where  $\theta$  is the relative orientation between the transition dipole moment (TDM) of the excitation and the polarization of the synchrotron light and P is the polarization factor of the beamline (0.91).

For both fluorinated derivatives, thin films prepared on SiO<sub>2</sub> substrates exhibit dichroisms which correspond to TDM orientations of  $\alpha=81^\circ$ . Since the respective TDMs are known to be oriented perpendicular to the molecular plane, such a dichroism corresponds to molecules in an upright configuration as similarly observed for thin films of non-fluorinated HBC on SiO<sub>2</sub>.<sup>[4]</sup> On graphene, however, an inverse dichroism is found, revealing that the molecules adopt a lying configuration on these substrates, again in perfect congruence with the situation found for the parent HBC. All dichroism measurements are in perfect agreement with the XRD analysis presented in the main paper, which has equivalently revealed upright molecular alignments on SiO<sub>2</sub> and lying molecular geometries on graphene. The observed deviations from an idealized TDM orientation of  $0^\circ$  for the latter case can be explained by defect-induced upright growth, which is also observed in the XRD experiments.

## References

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- [4] P. Beyer, T. Breuer, S. Ndiaye, A. Zykov, A. Viertel, M. Gensler, J. P. Rabe, S. Hecht, G. Witte and S. Kowarik, *ACS Appl. Mater. Interfaces*, 2014, **6**, 21484-21493.