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Bent Ladder-Type Hexaphenylene with Carbazole Core and Spiro Linkage as Stable and Efficient Blue Emitter

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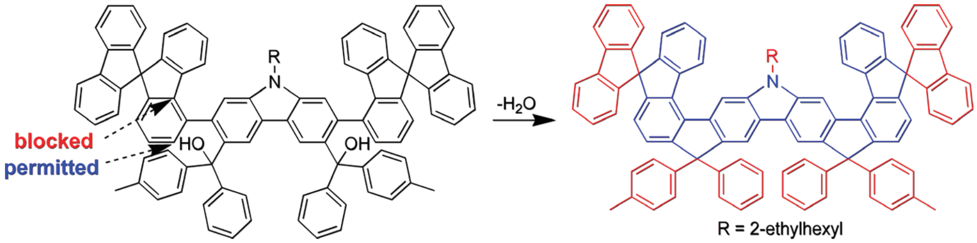
ABSTRACT



A bent ladder-type hexaphenylene with a carbazole core and spiro-linkage is designed and synthesized by using the *ortho*-linked spirobifluorene. The design eliminates the possibility of forming a positional isomer. As a blue-emitter, the BLHPC shows good thermal and color stability. A simple light-emitting device fabricated from BLHPC exhibits a maximum current efficiency of 1.46 cd/A and a maximum luminance of 505 cd/m^2.

In recent years, ladder-type oligomers and polymers have attracted considerable attention in the area of organic optoelectronic materials because their rigid coplanar conformations enhance π-conjugation degree, and endow them with high luminescence efficiency, good carrier mobility, and thermal stability.[1] Müllen and Scherf et al. have designed many ladder-type materials for various optoelectronic applications during the past two decades.[2] However, ladder-type materials incorporating spiro linkage have still been very limited.[3] Bo et al. reported spiro-bridged ladder-type oligo-

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(1) (a) Scherf, U.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 489. (b) Schlüter, A. D.; Löffler, M.; Enkelmann, V. *Nature* **1994**, *368*, 831. (c) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 6922. (d) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662. (e) Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656. (f) Qiu, S.; Lu, P.; Liu, X.; Shen, F.; Liu, L.; Ma, Y.; Shen, J. *Macromolecules* **2003**, *36*, 9823. (g) Xu, C.; Wakamiya, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638. (h) Wong, K.-T.; Chi, L.-C.; Huang, S.-C.; Liao, Y.-L.; Liu, Y.-H.; Wang, Y. *Org. Lett.* **2006**, *8*, 5029. (i) Li, L.; Xiang, J.; Xu, C. *Org. Lett.* **2007**, *9*, 4877. (j) Mouri, K.; Wakamiya, A.; Yamada, H.; Kajiwara, T.; Yamaguchi, S. *Org. Lett.* **2007**, *9*, 93. (k) Liu, L.; Qiu, S.; Wang, B.; Wang, H.; Xie, Z.; Ma, Y. *J. Phys. Chem. C* **2009**, *113*, 5799. (l) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586.

(2) (a) Scherf, U.; Müllen, K. *Macromolecules* **1992**, *25*, 3546. (b) Scherf, U.; Müllen, K. *Adv. Polym. Sci.* **1995**, *123*, 1. (c) Grimsdale, A. C.; Müllen, K. *Adv. Polym. Sci.* **2006**, *199*, 1. (d) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853. (e) Grimme, J.; Scherf, U. *Macromol. Chem. Phys.* **1996**, *197*, 2297. (f) Schindler, F.; Jacob, J.; Grimsdale, A. C.; Scherf, U.; Müllen, K.; Lupton, J. M.; Feldmann, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 1520l. (g) Jacob, J.; Sax, S.; Gaal, M.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *Macromolecules* **2005**, *38*, 9933. (h) Mishra, A. K.; Graf, M.; Grasse, F.; Jacob, J.; List, E. J. W.; Müllen, K. *Chem. Mater.* **2006**, *18*, 2879. (i) Laquai, F.; Mishra, A. K.; Ribas, M. R.; Petrozza, A.; Jacob, J.; Akcelrud, L.; Müllen, K.; Friend, R. H.; Wegner, G. *Adv. Funct. Mater.* **2007**, *17*, 3231. (j) Zhou, G.; Baumgarten, M.; Müllen, K. *J. Am. Chem. Soc.* **2007**, *129*, 12211. (k) Gao, P.; Feng, X.; Yang, X.; Enkelmann, V.; Baumgarten, M.; Müllen, K. *J. Org. Chem.* **2008**, *73*, 9207. (l) Laquai, F.; Mishra, A. K.; Müllen, K.; Friend, R. H. *Adv. Funct. Mater.* **2008**, *18*, 3265. (m) Zhou, G.; Baumgarten, M.; Müllen, K. *J. Am. Chem. Soc.* **2008**, *130*, 12477. (n) Patil, S. A.; Scherf, U.; Kadashchuk, A. *Adv. Funct. Mater.* **2003**, *13*, 609.

(3) Cocherel, N.; Poriel, C.; Rault-Berthelot, J.; Barriere, F.; Audebrand, N.; Slawin, A. M. A.; Vignau, L. *Chem.—Eur. J.* **2008**, *14*, 11328.

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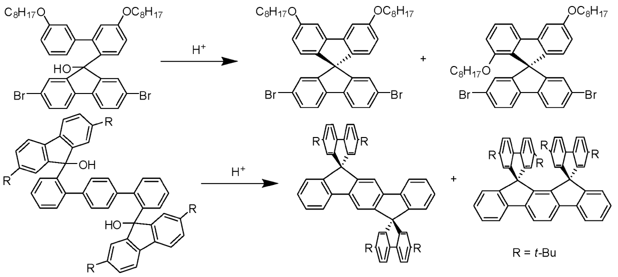
and poly(*p*-phenylene)s and demonstrated that the spiro-linkage could suppress the photo/thermal oxidation of the 9-position of the fluorene unit to the undesired ketonic defect.[4] On the other hand, carbazole derivatives have been widely applied in optoelectronic devices due to their good hole-transporting properties and high triplet energy.[5] In this context, we were intrigued to design a carbazole-cored and spiro-bridged ladder-type molecule. We anticipate that the carbazole implantation could improve the hole injection and transportation of ladder-type materials, and the spiro-configuration could effectively impede the intermolecular $\pi-\pi$ interactions and consequently lead to amorphous morphology of a ladder-type molecule. The above-mentioned two factors are crucial for OLEDs.[6]

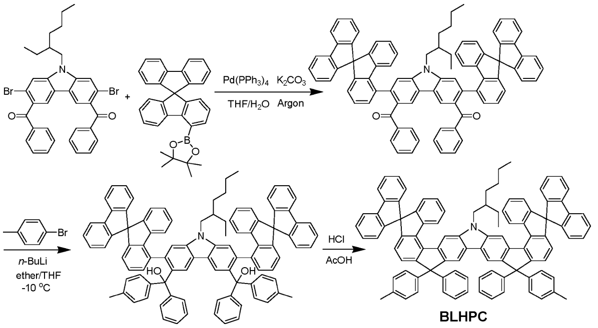
Up to now, all ladder-type structures have shown a linear backbone, and the established classic synthetic strategies involve acid-catalyzed intramolecular ring closure between a tertiary alcohol and adjacent aryl ring in the final step. From a statistical view, such cyclization may occur on either side of the terphenyl backbone and should lead to positional isomers. The separation of the isomers remains very difficult, which should hamper material applications because a mixture of isomers may cause the uncertainty and inconsistencies in the devices.[7]

For example, Lee et al. reported 2,7-dibromo-3′,6′-bis(octyloxy)-9,9′-spirobisfluorene and its geometrical isomer, 2,7-dibromo-1′,6′-bis(octyloxy)-9,9′-spirobisfluorene, formed in the last cyclization (Scheme 1).[8] Most recently, Poriel et al. also reported two dispiro positional isomers though the bulkiness of the *tert*-butyl substituents favor the less sterically hindered positional isomer (Scheme 1).[9] To avoid the problem, we report a strategy to eliminate the possibility of forming positional isomers by remaining only one reactive site in the final cyclization. In our design, the molecule is featured with the 4-position of spirobifluorene substituents at the C2 and C7 positions of the carbazole units. The molecular plane is subsequently flattened at the 3-position of spirobifluorene. The synthetic route is presented in Scheme 2.

Scheme 1. Positional Isomers Generated in Ring-Closure Reaction



Scheme 2. Synthesis of BLHPC



The two reactants,[10] 4-(9,9′-spirobifluorenyl)pinacol boronate for constructing bent configuration and 2,7-dibromo-*N*-(2-ethylhexyl)-3,6-bis(benzoyl)carbazole in which the alkyl chain ensures the solubility of the rigid molecule and the benzoyl group acts as precursor to bridge-link the carbazole and spirobifluorene, were coupled by Suzuki reaction to give the diketone in 69% yield. The addition of a slight excess of 4-methylphenyllithium, generated in situ by treatment 4-bromotoluene with *n*-butyllithium at −10 °C, to the carbonyl group of the diketone produced the corresponding tertiary alcohol as intermediate. Without further purification, the alcohol was subsequently subjected to intramolecular annulation under acidic conditions to afford a bent ladder-type hexaphenylene (BLHPC) in a good isolated yield (82%). As expected, the last cyclization occurs only on the C3 position of spirobifluorene, since the C1 position is blocked. The target compound is easily purified due to the elimination of the positional isomer. The compound was fully characterized by ^1H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis (see the Supporting Information).

As shown in the optimized molecular structure of BLHPC calculated with PM3 (Figure 1), the molecule exhibits a crablike profile with a pair of spirobifluorenes as the pincers. The rigid molecular structure of BLHPC imparted by the spiro-fused orthogonal linkages is very beneficial to the

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[4] (a) Wu, Y.; Zhang, J.; Bo, Z. *Org. Lett.* **2007**, *9*, 4435. (b) Wu, Y.; Zhang, J.; Fei, Z.; Bo, Z. *J. Am. Chem. Soc.* **2008**, *130*, 7192.

[5] (a) Yoshiyuki Kuwabara, H. O.; Hiroshi, I.; Naoki, N.; Yasuhiko, S. *Adv. Mater.* **1994**, *6*, 677. (b) Bouchard, J.; Wakim, S.; Leclerc, M. *J. Org. Chem.* **2004**, *69*, 5705. (c) Wakim, S.; Bouchard, J.; Blouin, N.; Michaud, A.; Leclerc, M. *Org. Lett.* **2004**, *6*, 3413. (d) Brunner, K.; Van Dijken, A.; Boerner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. *J. Am. Chem. Soc.* **2004**, *126*, 6035. (e) Wong, K.-T.; Chen, Y.-M.; Lin, Y.-T.; Su, H.-C.; Wu, C.-c. *Org. Lett.* **2005**, *7*, 5361. (f) Qiu, S.; Liu, L.; Wang, B.; Shen, F.; Zhang, W.; Li, M.; Ma, Y. *Macromolecules* **2005**, *38*, 6782. (g) Li, J.; Liu, D.; Li, Y.; Lee, C.-S.; Kwong, H.-L.; Lee, S. *Chem. Mater.* **2005**, *17*, 1208.

[6] (a) Kimura, M.; Kuwano, S.; Sawaki, Y.; Fujikawa, H.; Noda, K.; Taga, Y.; Takagi, K. *J. Mater. Chem.* **2005**, *15*, 2393. (b) Vak, D.; Jo, J.; Ghim, J.; Chun, C.; Lim, B.; Heeger, A. J.; Kim, D.-Y. *Macromolecules* **2006**, *39*, 6433. (c) Tsai, M.-H.; Hong, Y.-H.; Chang, C.-H.; Su, H.-C.; Wu, C.-C.; Matoliukstyte, A.; Simokaitiene, J.; Grigalevicius, S.; Grazulevicius, J. V.; Hsu, C.-P. *Adv. Mater.* **2007**, *19*, 862. (d) Jiang, Z.; Chen, Y.; Yang, C.; Cao, Y.; Tao, Y.; Qin, J.; Ma, D. *Org. Lett.* **2009**, *11*, 1503.

[7] Chiang, C.-L.; Shu, C.-F.; Chen, C.-T. *Org. Lett.* **2005**, *7*, 3717.

[8] Lee, H.; Oh, J.; Chu, H. Y.; Lee, J.-I.; Kim, S. H.; Yang, Y. S.; Kim, G. H.; Do, L.-M.; Zyung, T.; Lee, J.; Park, Y. *Tetrahedron* **2003**, *59*, 2773.

[9] Poriel, C.; Rault-Berthelot, J.; Barriere, F.; Slawin, A. M. Z. *Org. Lett.* **2008**, *10*, 373.

[10] (a) Dierschke, F.; Grimsdale, A. C.; Müllen, K. *Synthesis* **2003**, 2470. (b) Jiang, Z.; Yao, H.; Zhang, Z.; Yang, C.; Liu, Z.; Tao, Y.; Qin, J.; Ma, D. *Org. Lett.* **2009**, *11*, 2607.

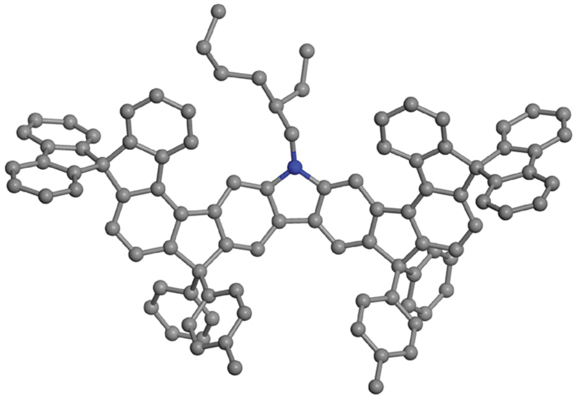

Figure 1. Optimized molecular structure of BLHPC calculated with PM3.

thermal stability,[11] as manifested by the high thermal decomposition temperatures (T_d, corresponding to 5% weight loss in the thermogravimetric analysis) of 510 °C and a very high glass-transition temperature (T_g) of 319 °C determined through differential scanning calorimetry (DSC).The incorporation of both carbazole cores with a long alkyl chain and spiro-configuration leads to good amorphous morphology, which is highly important to improve the lifetime of OLEDs.

The electrochemical property of BLHPC is studied by cyclic voltammetry, and the compound shows two reversible oxidation processes in CH_2Cl_2 solution. The first oxidation occurs at 1.10 V and the second occurs at 1.51 V, which can be attributed to carbazole and spirobifluorene moieties, respectively. The electrochemical behavior of BLHPC is similar to those reported polymers containing fluorene and carbazole.[12] The HOMO energy level determined from the onset of the oxidation is 5.30 eV (relative to vacuum energy level), which is higher than that of other ladder-type *p*-phenylenes due to the introduction of the carbazole moiety and means a lower barrier for hole injection.[13] This is also consistent with the DFT-calculated results. As shown in the inset of Figure 2, the HOMO orbital mainly locates at the hole-transporting carbazole moiety. The LUMO energy level deduced from the difference between the HOMO level and the optical band gap is 2.41 eV.

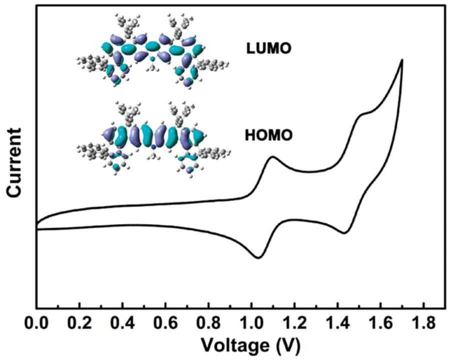

Figure 2. Cyclic voltammogram of BLHPC (inset: distribution of the HOMO and LUMO levels from DFT calculation of BLHPC).

The UV−vis absorption and PL spectra of BLHPC in CH_2Cl_2 solution are shown in Figure 3. The symmetric mirror images of the absorption and emission spectra, as well as the small Stokes shift (462 cm^{-1}), coincide with the rigid molecular structure of BLHPC.[14] The almost 100% fluorescence quantum yield of BLHPC in CH_2Cl_2 solution measured by an integrating sphere indicates that nonradiative decay pathways are completely suppressed by restricting bond rotation in such confined and rigid backbones.[4] Noticeably, BLHPC reveals a very stable emission upon heat treatment. As shown in Figure 4, almost no PL spectral change was observed after heating for 12 and 36 h at 150 °C in air. The result clearly indicates the enhancement of stability of the compound with respect to aggregate formation and/or thermo-oxidation, which should be attributed to the rigid and

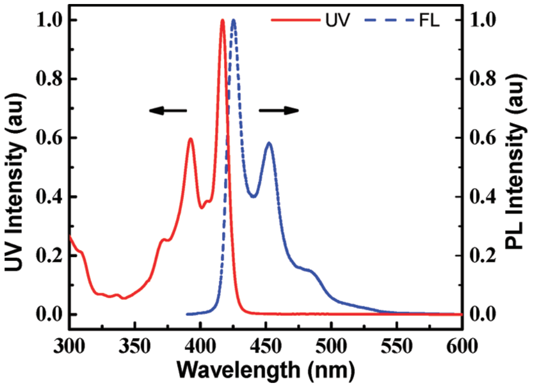

Figure 3. Normalized electronic absorption and photoluminescent spectra of BLHPC in CH_2Cl_2 solution.

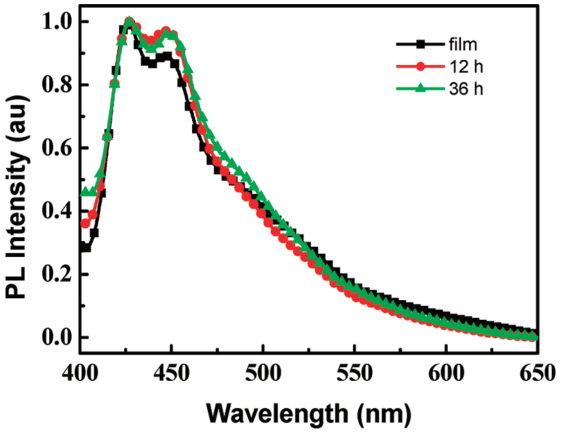

Figure 4. PL spectra of BLHPC in film before and after annealing at 150 °C in air.

bulky molecular configuration, as well as the inhibition of ketonic defects by fully aryl-substituted and spiro-carbons at the 9-position of fluorene units.[15,4a]

To evaluate the potential of BLHPC as a blue emitter in OLED applications, a double-layer EL device was fabricated with the simple configuration: ITO/BLHPC (40 nm)/1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene (TPBI, 30 nm)/LiF (1 nm)/Al (100 nm). TPBI is utilized as electron-transporting and hole-block material; LiF serves as the electron-injecting layer. Because of the low hole injection barrier of BLHPC, it can act as emission layer as well as hole-transport layer. The device exhibits blue emission with 1931 Commission International de L'Eclairage *x*, *y* coordinates of (0.21, 0.18). Current−voltage−luminance (J−V−L) characteristics and current efficiency versus current density of the device are shown in Figure 5. A maximum current efficiency of 1.46 cd/A and a maximum luminance of 505 cd/m^2 were achieved. The blue electroluminescence efficiency is one of the highest among those ladder-type materials.[1f,2h,4b,14] For example, a ladder-type polymer containing carbazole units reported by Müllen et al. exhibits a maximum current efficiency of 0.1 cd/A with CIE coordinates (0.19, 0.19) in a device of ITO/PEDOT/ladder-type polymer/Ca/Al;[2g] a ladder-type hexaphenylene containing a spirostructure recently reported by Poriel et al. shows a maximum current efficiency of 0.16 cd/A with CIE coordinates (0.30, 0.27) in a device of ITO/PEDOT/ladder-type hexaphenylene /BCP/Ca.[3]

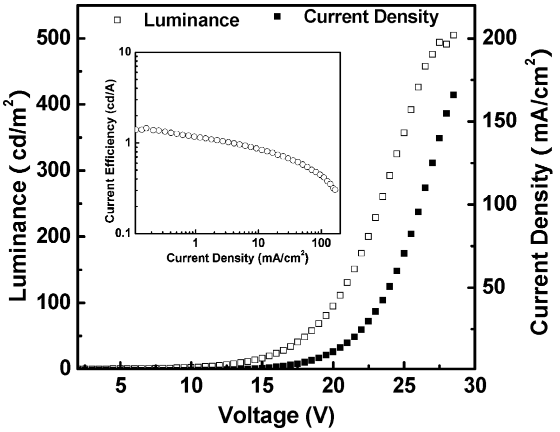

Figure 5. J−V−L curves of the device. (Inset: the current efficiency−current density curve of the device.)

In summary, we have synthesized a novel ladder-type molecule with carbazole core and spiro linkage. This is the first report of ladder-type hexaphenylene with bent conformation. The judicious design removes the possibility of forming geometrical isomers by using the *ortho*-linked spirobifluorene, which are usually encountered in the synthesis of conventional ladder-type molecules. As a blue-emitter, the BLHPC shows good thermal and color stabilities. The incorporation of the central carbazole core significantly reduces the ionization potential, and therefore the OLED device configurations could be simplified without using PEDOT:PSS as hole-injection layer. To our knowledge, the blue emitter represents one of the best blue fluorescent ladder-type materials to date.

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Supporting Information Available: General experimental information; synthesis and characterization of BLHPC. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576. (b) Wong, K.-T.; Liao, Y.-L.; Lin, Y.-T.; Su, H.-C.; Wu, C.-c. *Org. Lett.* **2005**, *7*, 5131.

(12) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem. Mater.* **2004**, *16*, 2165.

(13) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854.

(14) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Mullen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987.

(15) (a) Romaner, L.; Heimel, G.; Wiesenhofer, H.; Scandiucci de Freitas, P.; Scherf, U.; Bredas, J.-L.; Zojer, E.; List, E. J. W. *Chem. Mater.* **2004**, *16*, 4667. (b) Liu; Qiu, S.; Wang, B.; Zhang, W.; Lu, P.; Xie, Z.; Hanif, M.; Ma, Y.; Shen, J. *J. Phys. Chem. B* **2005**, *109*, 23366. (c) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910.