Polycyclic Hydrocarbons | **Very Important Paper**

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Super-heptazethrene

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Abstract: *The challenging synthesis of a laterally extended heptazethrene molecule, the super-heptazethrene derivative* ***SHZ-CF3****, is reported. This molecule was prepared using a strategy involving a multiple selective intramolecular Friedel–Crafts alkylation followed by oxidative dehydrogenation. Compound* ***SHZ-CF3*** *exhibits an open-shell singlet diradical ground state with a much larger diradical character compared with the heptazethrene derivatives. An intermediate dibenzoterrylene* ***SHZ-2H*** *was also obtained during the synthesis. This study provides a new synthetic method to access large-size quinoidal polycyclic hydrocarbons with unique physical properties.*

Conjugated polycyclic hydrocarbons (PHs) with an open-shell singlet diradical ground state have attracted tremendous interest in structural chemistry, physical organic chemistry, and materials science as a result of their unique physical properties and potential applications in areas such as organic electronics, photonics, spintronics, and energy storage.[1] It was found that aromatic graphene-like molecules with zig-zag edges could display a singlet diradical ground state,[2] which is closely related to the edge states and magnetic properties of graphene nanoribbons (GNRs).[3] On the other hand, pro-aromatic quinoidal PHs tend to be diradical in nature due to the recovery of the aromaticity of the quinoidal benzenoid rings, and various relatively stable quinoidal open-shell PHs, such as bisphenalenyls,[4] zethrenes,[5] indenofluorenes,[6] and extended p-quinodimethanes,[7] have been successfully synthesized.

Our group has been working intensively on zethrene chemistry.[5] Zethrene is a Z-shaped quinoidal PH containing a fixed 1,3-butadiene moiety in the π-conjugated framework (Figure 1 a). The longer analogues of zethrene with extension along the y axis are called heptazethrene, octazethrene, nonazethrene, and so on. Interestingly, from heptazethrene on, these quinoidal PHs display significant diradical character (y_0; calculated at the UCAM-B3LYP/6-31G** level) which increases with the increase of the molecular length due to the recovery of aromatic benzene, naphthalene, and anthracene rings in heptazethrene ($y_0 = 17.0\,\%$), octazethrene ($y_0 = 36.6\,\%$), and nonazethrene ($y_0 = 50.4\,\%$), respectively.[8]

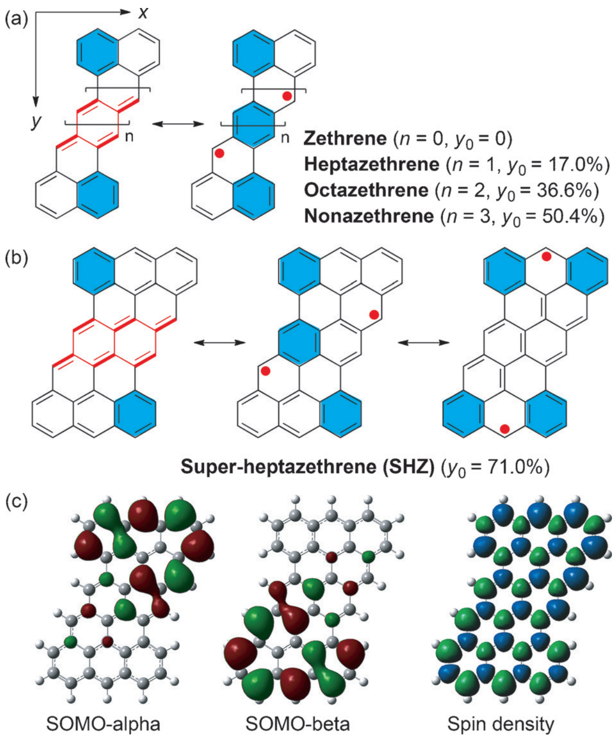

Figure 1. Resonance structures of zethrenes (a) and super-heptazethrene (b). c) The calculated (UCAM-B3LYP/6-31G**) molecular orbital profiles of α and β spins and the spin density distribution of the singlet diradical of **SHZ**.

On the other hand, lateral extension of zethrenes along the x axis will give rise to a new type of quinoidal PHs containing extended zig-zag edges and a quinodimethane moiety, which raises the question of their magnetic activity. For example, the laterally extended heptazethrene molecule, called "super-heptazethrene" (**SHZ**) herein, should exhibit very different properties to those of the heptazethrene derivatives. By applying Clar's sextet rule[2a,b,5f] to the **SHZ**, the molecule in the diradical form can gain a maximum of two additional aromatic sextets (Figure 1 b; shaded in blue), which is one more compared with that in heptazethrene, and thus is

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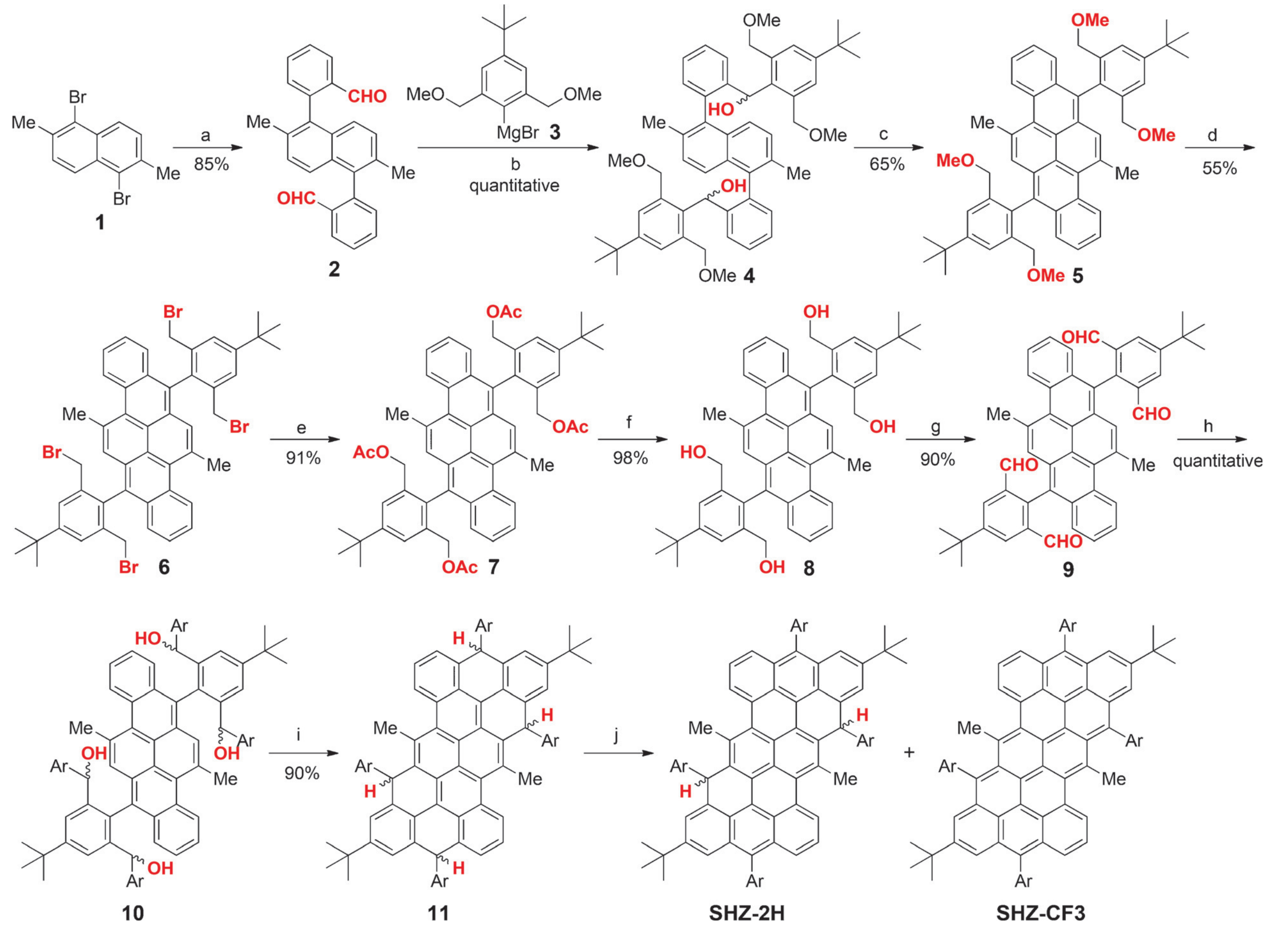
believed to have larger diradical character. Indeed, calculations predict that the singlet diradical form is lower in energy than the closed-shell and triplet biradical form, thus defining a singlet diradical ground state (see Table S2 in the Supporting Information). The singly occupied molecular orbitals (SOMOs) of the α and β spins are largely disjointed from each other (Figure 1c), and as a result, a large diradical character $y_0 = 71\,\%$ is calculated. The spins are delocalized throughout the whole π-conjugated framework, with the highest spin density localized at the zig-zag edges. However, the synthesis of this kind of molecule could be very challenging because of their expected high reactivity and the lack of suitable synthetic methods to construct such large PH frameworks. In response to these challenges, herein we report a strategy involving a multiple selective intramolecular Friedel–Crafts alkylation followed by oxidative dehydrogenation for the synthesis of a relatively stable SHZ derivative **SHZ-CF3**.

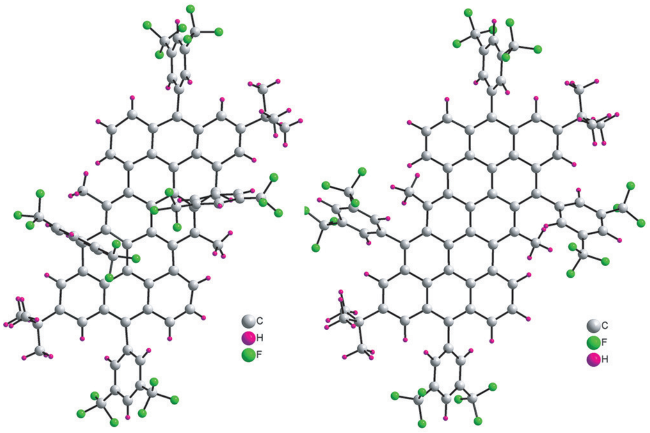
The key intermediate compound in the synthetic procedure is tetra-aldehyde **9**, which allowed us to construct the SHZ core through a fourfold Friedel–Crafts alkylation followed by dehydrogenation (Scheme 1). The direct synthesis of **9** and its precursor **5** by means of a Suzuki coupling reaction was not successful as a result of large steric hindrance and unfavorable electronic effects of the formyl and methoxymethyl substituents. Thus, the synthesis commenced with a Suzuki coupling reaction between 1,5-dibromo-2,6-dimethyl naphthalene (**1**) and 2-formylphenylboronic acid to give the dialdehyde **2**. Nucleophilic addition of **2** with the (4-*tert*-butyl-2,6-bis(methoxymethyl)phenyl)magnesium bromide (**3**) generated the diol **4**. Compound **4** underwent $BF_3{\cdot}Et_2O$-mediated Friedel–Crafts alkylation to afford the corresponding cyclized product and subsequent oxidative dehydrogenation by DDQ provided the dibenzopyrene derivative **5**. The existence of two methyl groups is necessary to avoid undesirable five-membered ring formation during the cyclization. It is also important that at this step, the methoxymethyl groups did not participate in the cyclization reaction as the cationic intermediates preferred to form at the diphenylmethylene sites. The methoxymethyl groups in **5** were then converted firstly into bromomethyl groups in **6** by treatment with concentrated hydrogen bromide, then into acetyl groups in **7** by reaction with potassium acetate, then into alcohol groups in **8** by hydrolysis, and finally into formyl groups in **9** by Swern



Scheme 1. The synthesis of **SHZ-CF3**. Reagents and conditions: a) 2-formylphenylboronic acid, $[Pd_2(dba)_3]$, Sphos, toluene, EtOH, Na_2CO_3 (aq, 2 M), 24 h; b) anhydrous THF, RT, 12 h; c) $BF_3{\cdot}OEt_2$, DDQ; d) HBr in AcOH, DCM, RT, 24 h; e) KOAc, CH_3CN, THF, reflux, 2 d; f) LiOH, H_2O, dioxane, reflux, 2 d; g) oxalyl chloride, DMSO, DCM, Et_3N; h) (3,5-bis(trifluoromethyl)phenyl)magnesium bromide, THF, RT, 24 h; i) excess $BF_3{\cdot}OEt_2$:TFA = 1:1, DCM, 30 min; j) *p*-chloranil, DCM. dba = dibenzylideneacetone; SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; DCM = CH_2Cl_2; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; TFA = trifluoroacetic acid; Ar = 3,5-di(trifluoromethyl)phenyl.

oxidation. Although a multiple-step synthesis was required, the overall yield from **5** to **9** was good (44%). X-ray crystallographic structures of **5**, **7**, and **9** were obtained and confirmed the success of all regioselective reactions (see data in the Supporting Information). It is necessary to stabilize the final SHZ compound and thus four electron-deficient 3,5-bis(trifluoromethyl)phenyl group were introduced at the most reactive sites (the meso positions of the four zigzag edges).[9] Treatment of **9** with (3,5-bis(trifluoromethyl)phenyl)magnesium bromide generated the tetraol **10** and subsequent Friedel–Crafts alkylation mediated by $BF_3{\cdot}Et_2O$:TFA (1:1) gave the tetrahydro compound **11**. Oxidative dehydrogenation of **11** with 1 equiv of *p*-chloranil generated primarily the partially dehydrogenated dibenzo-terrylene compound **SHZ-2H** (70% yield), but using 5 equiv of *p*-chloranil gave primarily the target super-heptazethrene derivative **SHZ-CF3** (50% yield); both can be separated by chromatography on triethylamine-deactivated silica gel. **SHZ-2H** is a very stable compound but the solution of **SHZ-CF3** is sensitive to ambient air and light conditions and has a half-life of 4.34 h (Figure S3).

A single crystal of **SHZ-2H** was obtained by slow diffusion of acetonitrile into a solution of the compound in CH_2Cl_2. The structure clearly showed a dibenzo-terrylene framework (Figure 2),[10] indicating that the dehydrogenation occurred preferentially at the top and bottom zig-zag edges rather than the zig-zag edges in the bay region. The two 3,5-bis(trifluoromethyl)phenyl groups linking with the sp^3 carbon atoms point to the same side, implying that only one isomer was crystallized. Attempts to crystallize **SHZ-CF3** under strictly inert conditions failed as a result of decomposition of the molecule. DFT calculations (UCAM-B3LYP/6-31G(d,p)) predicted that **SHZ-CF3** has a nonplanar SHZ core mainly because of the steric congestion caused by the methyl groups (Figure 2). Calculations also predicted that **SHZ-CF3** has a singlet diradical ground state with a large diradical character ($y_0 = 64.2\%$; see the Supporting Information for details). On the other hand, **SHZ-2H** was calculated to have a closed-shell ground state.



SHZ-2H SHZ-CF3

Figure 2. X-ray crystallographic structure of **SHZ-2H** (left) and the optimized structure (UCAM-B3LYP/6-31G(d,p)) of the singlet diradical of **SHZ-CF3** (right). Atom colors: C = gray; H = pink; F = green.

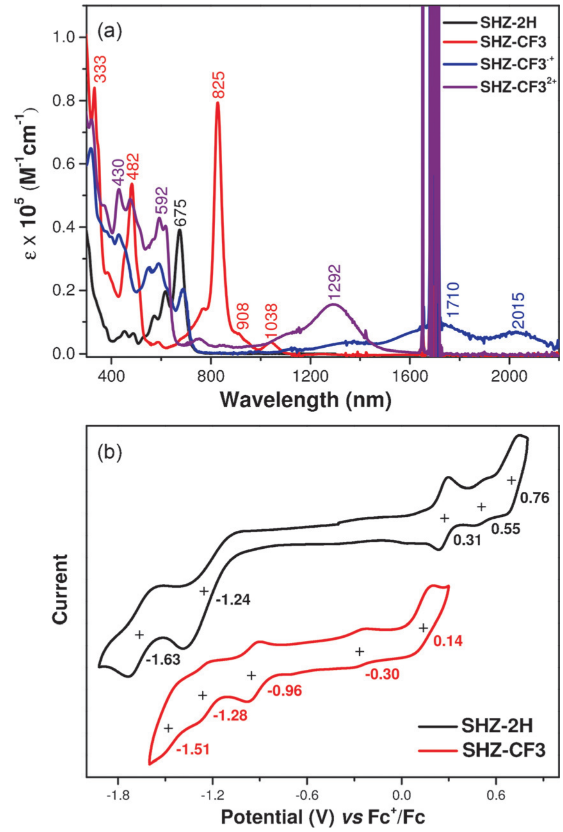


Figure 3. a) UV/Vis/NIR absorption spectra of **SHZ-2H**, **SHZ-CF3**, **SHZ-CF3**$^{\cdot+}$, and **SHZ-CF3**$^{2+}$ in CH_2Cl_2 ($c = 1.0\times10^{-5}$ M) at room temperature. ε is the molar extinction coefficient ($M^{-1}cm^{-1}$). b) Cyclic voltammograms of **SHZ-2H** (in CH_2Cl_2) and **SHZ-CF3** (in THF; $c = 1$ mM) with 0.1 M Bu_4NPF_6 as supporting electrolyte, Ag/AgCl as the reference electrode, Pt wire as the counter electrode, and a scan rate at 50 mV s^{-1}.

In accordance with the X-ray crystallographic structure, **SHZ-2H** exhibited a *p*-band in the absorption spectrum typical of rylene molecules,[11] with a maximum absorption band at $\lambda = 675$ nm (Figure 3a). However, **SHZ-CF3** displayed a very different absorption spectrum, with maximum at $\lambda = 825$ nm, together with two weak shoulder bands appearing at $\lambda = 908$ nm and 1038 nm. This type of band structure is similar to other singlet diradicaloids, such as octazethrene derivatives,[5b] and the long-wavelength shoulder bands originate from a low-lying singlet excited state dominated by a doubly excited electronic configuration (H,H→L,L).[12] Compared with heptazethrene derivative **HZ-TIPS** which behaves more like a closed-shell compound and has a similar absorption band to the closed-shell **SHZ-2H** with an absorption maximum at $\lambda = 634$ nm,[5e] **SHZ-CF3** shows a large red-shift of the absorption and a dramatic change of the band structure, indicative of a larger diradical character. Cooling the solution in 2-MeTHF to 193 K resulted in 5 nm redshift of the absorption maximum, implying a slight shift of the equilibrium to the singlet state (see Figure S4).[2b] **SHZ-2H** showed three oxidation waves in the cyclic voltammetry measurements at $E_{1/2}^{ox} = 0.31$, 0.55, 0.76 V, and two reduction waves at $E_{1/2}^{\text{red}} = -1.24$, -1.63 V (versus Fc^+/Fc), with an electrochemical energy gap (E_g^{EC}) of 1.55 eV. **SHZ-CF3** can be oxidized to form a radical cation and dication at $E_{1/2}^{\text{ox}} = -0.30$ and 0.14 V, respectively, and reduced to anionic species at $E_{1/2}^{\text{red}} = -0.96$, -1.28, -1.51 V, with a much smaller E_g^{EC} of 0.66 eV (Figure 3b; see also Figure S5 and Table S3). **SHZ-CF3** has high-lying HOMO energy level of -4.41 eV which explains its high reactivity. **SHZ-CF3** can be easily oxidized by $NOSbF_6$ in CH_2Cl_2 into its respective radical cation (**SHZ-CF3**$^{\cdot+}$) and dication (**SHZ-CF3**$^{2+}$; see Figure S6). These species show longest-wavelength absorption band maxima at $\lambda = 2015$ and 1292 nm, respectively (Figure 3a). An intense ESR signal was observed for the radical cation species (see Figure S7) but the dication is ESR silent.

Broadened signals in the NMR spectrum were detected for **SHZ-CF3** in [D$_8$]THF at room temperature and the resonance signals became sharper when the temperature was lowered to 193 K (see Figures S19, S20). These results indicated that **SHZ-CF3** has a singlet diradical ground state and that the NMR broadening is due to thermal population of singlet species to paramagnetic triplet species at higher temperatures. A broad single-line ESR signal with $g_e = 2.0020$ was detected in both solution and in the solid sample (Figure 4a). The superconducting quantum interference device (SQUID) measurements further confirmed the singlet ground states as the magnetic susceptibility increases with increasing temperature. The singlet-triplet energy gap $\Delta E_{\text{S-T}}$ was roughly estimated to be -473.4 K (-0.94 kcal mol^{-1}) by fitting the data using the Bleaney–Bowers equation.[13] Such as a small energy gap is in accordance with the large diradical character of **SHZ-CF3**.

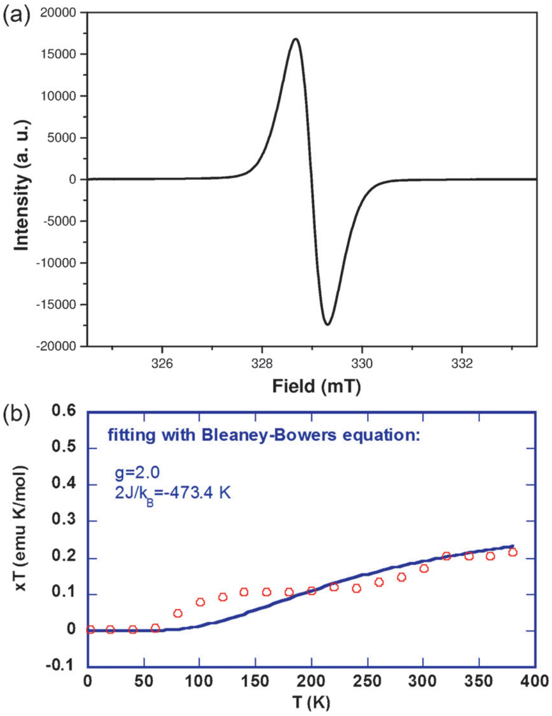


Figure 4. a) ESR spectrum of **SHZ-CF3** recorded at room temperature in the powder form. b) χT–T curves from the SQUID measurements for the powder of **SHZ-CF3** (χ = magnetic susceptibility). The solid lines are the fitting curves according to the Bleaney–Bowers equation; g-factor was taken to be 2.0.

In summary, a new synthetic strategy involving a multiple selective Friedel–Crafts alkylation followed by oxidative dehydrogenation was developed for the synthesis of the synthetically challenging molecule super-heptazethrene. This method provides a facile way to expand the π-conjugated framework using simple reactions and leads to the formation of large-size PHs with unusual properties. The obtained compound **SHZ-CF3** is reasonably stable as a result of thermodynamic and kinetic stabilization by the four 3,5-bis(trifluoromethyl)phenyl groups, enabling us to conduct full characterization of the system. In contrast to its heptazethrene analogues, **SHZ-CF3** has a large diradical character, displays a remarkably different electronic absorption spectrum, and has a much smaller energy gap. The molecule also shows unique magnetic activity. We believe that this synthetic method can be further applied to the synthesis of various large-size quinoidal PHs with significant diradical character.

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[1] For recent reviews, see: a) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* **2012**, *41*, 7857; b) A. Shimizu, Y. Hirao, T. Kubo, M. Nakano, E. Botek, B. Champagne, *AIP Conf. Proc.* **2012**, *1504*, 399; c) M. Abe, *Chem. Rev.* **2013**, *113*, 7011; d) Z. Sun, Z. Zeng, J. Wu, *Acc. Chem. Res.* **2014**, *47*, 2582; e) T. Kubo, *Chem. Rec.* **2015**, *15*, 218; f) Z. Zeng, X. Shi, C. Chi, J. T. López Navarrete, J. Casado, J. Wu, *Chem. Soc. Rev.* **2015**, *44*, 6578; g) T. Kubo, *Chem. Lett.* **2015**, *44*, 111; h) H. Miyoshi, S. Nobusue, A. Shimizu, Y. Tobe, *Chem. Soc. Rev.* **2015**, *44*, 6560.

[2] a) A. Konishi, Y. Hirao, M. Nakano, A. Shimizu, E. Botek, B. Champagne, D. Shiomi, K. Sato, T. Takui, K. Matsumoto, H. Kurata, T. Kubo, *J. Am. Chem. Soc.* **2010**, *132*, 11021; b) A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata, R. Kishi, Y. Shigeta, M. Nakano, K. Tokunaga, K. Kamada, T. Kubo, *J. Am. Chem. Soc.* **2013**, *135*, 1430; c) J. Liu, P. Ravat, M. Wagner, M. Baumgarten, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.* **2015**, *54*, 12442; *Angew. Chem.* **2015**, *127*, 12619.

[3] a) M. Fujita, K. Wakabayashi, K. Nakada, K. Kusakabe, *J. Phys. Soc. Jpn.* **1996**, *65*, 1920; b) K. Nakada, M. Fujita, G. Dresselhaus, M. S. Dresselhaus, *Phys. Rev. B* **1996**, *54*, 17954; c) Y. Miyamoto, K. Nakada, M. Fujita, *Phys. Rev. B* **1999**, *59*, 9858; d) P. Ruffieux, S. Wang, B. Yang, C. Sánchez, J. Liu, T. Dienel, L. Taliraz, P. Shinde, C. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Müllen, R. Fasel, *Nature* **2016**, *531*, 489.

[4] a) K. Ohashi, T. Kubo, T. Masui, K. Yamamoto, K. Nakasuji, T. Takui, Y. Kai, I. Murata, *J. Am. Chem. Soc.* **1998**, *120*, 2018; b) T. Kubo, M. Sakamoto, M. Akabane, Y. Fujiwara, K. Yamamoto,

M. Akita, K. Inoue, T. Takui, K. Nakasuji, *Angew. Chem. Int. Ed.* **2004**, *43*, 6474; *Angew. Chem.* **2004**, *116*, 6636; c) T. Kubo, A. Shimizu, M. Sakamoto, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasuji, *Angew. Chem. Int. Ed.* **2005**, *44*, 6564; *Angew. Chem.* **2005**, *117*, 6722; d) A. Shimizu, M. Uruichi, K. Yakushi, H. Matsuzaki, H. Okamoto, M. Nakano, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, *Angew. Chem. Int. Ed.* **2009**, *48*, 5482; *Angew. Chem.* **2009**, *121*, 5590; e) A. Shimizu, T. Kubo, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Hirao, K. Matsumoto, H. Kurata, Y. Morita, K. Nakasuji, *J. Am. Chem. Soc.* **2010**, *132*, 14421; f) A. Shimizu, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, M. Uruichi, K. Yakushi, *Chem. Commun.* **2012**, *48*, 5629.

[5] a) R. Umeda, D. Hibi, K. Miki, Y. Tobe, *Org. Lett.* **2009**, *11*, 4104; b) T. C. Wu, C. H. Chen, D. Hibi, A. Shimizu, Y. Tobe, Y. T. Wu, *Angew. Chem. Int. Ed.* **2010**, *49*, 7059; *Angew. Chem.* **2010**, *122*, 7213; c) Z. Sun, K.-W. Huang, J. Wu, *Org. Lett.* **2010**, *12*, 4690; d) Z. Sun, K.-W. Huang, J. Wu, *J. Am. Chem. Soc.* **2011**, *133*, 11896; e) Y. Li, K.-W. Heng, B. S. Lee, N. Aratani, J. L. Zafra, N. Bao, R. Lee, Y. M. Sung, Z. Sun, K.-W. Huang, R. D. Webster, J. T. López Navarrete, D. Kim, A. Osuka, J. Casado, J. Ding, J. Wu, *J. Am. Chem. Soc.* **2012**, *134*, 14913; f) Z. Sun, S. Lee, K. Park, X. Zhu, W. Zhang, B. Zheng, P. Hu, Z. Zeng, S. Das, Y. Li, C. Chi, R. Li, K. Huang, J. Ding, D. Kim, J. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 18229; g) L. Shan, Z.-X. Liang, X.-M. Xu, Q. Tang, Q. Miao, *Chem. Sci.* **2013**, *4*, 3294; h) Y.-C. Hsieh, H.-Y. Fang, Y.-T. Chen, R. Yang, C.-I. Yang, P.-T. Chou, M.-Y. Kuo, Y.-T. Wu, *Angew. Chem. Int. Ed.* **2015**, *54*, 3069; *Angew. Chem.* **2015**, *127*, 3112; i) P. Hu, S. Lee, T. S. Herng, N. Aratani, T. P. Gonçalves, Q. Qi, X. Shi, H. Yamada, K.-W. Huang, J. Ding, D. Kim, J. Wu, *J. Am. Chem. Soc.* **2016**, *138*, 1065.

[6] a) D. T. Chase, B. D. Rose, S. P. McClintock, L. N. Zakharov, M. M. Haley, *Angew. Chem. Int. Ed.* **2011**, *50*, 1127; *Angew. Chem.* **2011**, *123*, 1159; b) A. Shimizu, Y. Tobe, *Angew. Chem. Int. Ed.* **2011**, *50*, 6906; *Angew. Chem.* **2011**, *123*, 7038; c) A. Shimizu, R. Kishi, M. Nakano, D. Shiomi, K. Sato, T. Takui, I. Hisaki, M. Miyata, Y. Tobe, *Angew. Chem. Int. Ed.* **2013**, *52*, 6076; *Angew. Chem.* **2013**, *125*, 6192.

[7] a) Z. Zeng, M. Ishida, J. L. Zafra, X. Zhu, Y. M. Sung, N. Bao, R. D. Webster, B. S. Lee, R.-W. Li, W. Zeng, Y. Li, C. Chi, J. T. López Navarrete, J. Ding, J. Casado, D. Kim, J. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 6363; b) Z. Zeng, S. Lee, J. L. Zafra, M. Ishida, X. Zhu, Z. Sun, Y. Ni, R. D. Webster, R.-W. Li, J. T. López Navarrete, C. Chi, J. Ding, J. Casado, D. Kim, J. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 8561; *Angew. Chem.* **2013**, *125*, 8723; c) Z. Zeng, S. Lee, J. L. Zafra, M. Ishida, N. Bao, R. D. Webster, J. T. López Navarrete, J. Ding, J. Casado, D.-H. Kim, J. Wu, *Chem. Sci.* **2014**, *5*, 3072; d) Z. Zeng, S. Lee, M. Son, K. Fukuda, P. M. Burrezo, X. Zhu, Qi. Qi, R.-W. Li, J. T. López Navarrete, J. Ding, J. Casado, M. Nakano, D. Kim, J. Wu, *J. Am. Chem. Soc.* **2015**, *137*, 8572.

[8] The diradical character (y_0) is a theoretical index that depends on the calculation method. A list of y_0 values calculated at different level of theory is shown in Table S1.

[9] We also synthesized the mesityl-substituted analogue of **11**. However, dehydrogenation led to highly reactive SHZ compound. When the mesityl is replaced by the more electron-deficient pentafluorophenyl group, the final dehydrogenation by DDQ does not work.

[10] Crystallographic data for **SHZ-2H**: $C_{328}H_{192}F_{96}$. m_w: 5956.97; monoclinic; space group P 1 2(1)/*n* 1; $a = 38.865(3)$ Å, $b = 21.1861(12)$ Å, $c = 40.572(3)$ Å, $\alpha = 90.0000°$, $\beta = 115.733(11)°$, $\gamma = 90.0000°$; $V = 30094(5)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.315$ Mg m^{-3}; $R1 = 0.1916$, $wR2 = 0.4323$ ($I > 2\sigma(I)$); $R1 = 0.4535$, $wR2 = 0.5458$ (all data). CCDC 1444589 (**SHZ-2H**), 1441884 (**5**), 1441886 (**7**), and 1441885 (**9**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[11] T. Weil, T. Vosch, J. Hofkens, K. Peneva, K. Müllen, *Angew. Chem. Int. Ed.* **2010**, *49*, 9068; *Angew. Chem.* **2010**, *122*, 9252.

[12] S. Di Motta, F. Negri, D. Fazzi, C. Castiglioni, E. V. Canesi, *J. Phys. Chem. Lett.* **2010**, *1*, 3334.

[13] B. Bleaney, K. D. Bowers, *Proc. R. Soc. London Ser. A* **1952**, *214*, 451.

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