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Facile Aromatization Reactions of Overcrowded Polycyclic Aromatic Enes Leading to Fullerene Fragments

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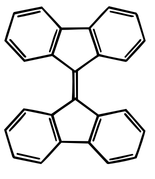
Overcrowded polycyclic aromatic enes (PAEs),[1,2] e.g., bi-9*H*-fluoren-9-ylidene (**1**),[3,4] are potential starting materials for the preparation of bowl-shaped fragments of fullerenes (buckybowls).[5−7] Recently, the thermal and catalyzed dehydrocyclization of **1** to diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**2**) via the intermediates benz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (**3**) and benz[*g*]indeno[1,2,3,4-*mnop*]chrysene (**4**) by flash vacuum pyrolysis (FVP) at temperatures above 700 °C in the gas phase have been reported by Zimmermann *et al.*[8,9] Buckybowl **2** could also be synthesized by a two-fold thermal (>1000 °C) elimination of CO from 7,14-dioxo-7,14-dihydrophenanthro[1,10,9,8-*opqra*]perylene[9] and by FVP of (*E*)-1,1′-dibromobi-9*H*-fluoren-9-ylidene at 1050 °C.[6] Previous claims of the formation of **3** by the debromocyclization of 9,9′-dibromo-1,1′-bifluorenyl[10] and from a fluorene pyrolyzate[11] have been questioned.[7] The oxidative photocyclization of **1** to give **3** has also been claimed.[12] However, the ^{1}H NMR data of the product was not consistent with those of **3** (*vide infra).*[13] The synthesis of bridged derivatives of **3** by oxidative photocyclization reactions of (*Z*)-2,2′-tethered bifluorenylidenes have been reported by Luh *et al.*[13] The success of the last method was attributed to the bridged (*Z*)-stereochemistry and to the tether functionality in the starting materials.[7,13] We report here a facile synthesis of **3**, and its 1-chloro-derivative **5**, by a reductive cyclodechlorination and a cyclodehydrochlorination of (*E*)- and (*Z*)-1,1′-dichlorobi-9*H*-fluoren-9-ylidene (**6**), using palladium acetate as a homogenous catalyst.[14,15] We note that **3** and **5** are fullerene fragments which are not buckybowls.[5]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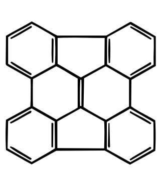
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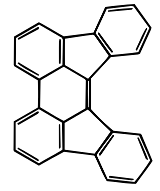
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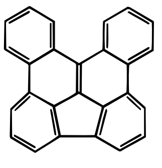
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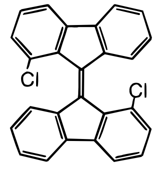
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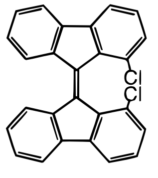
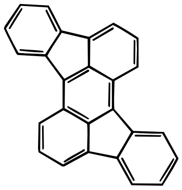

(*Z*)-6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The introduction of two chlorine atoms in the fjord regions (positions 1 and 1′) of **1** was aimed to serve several purposes. Firstly, an intramolecular reductive dechlorination (Ullman reaction)[16,17] of (*Z*)-**6** to **3** in solution under homogeneous catalysis conditions[14,15] at reasonable temperatures may be feasible. Secondly, the overcrowding in the fjord regions of (*E*)-**6** and (*Z*)-**6** was predicted to be more pronounced, as compared with **1**,[18] resulting in a further destabilization of the reactants. This spatial alignment could allow the cyclization of **6** to **3** to be carried out at lower temperatures (as compared e.g., with the FVP method[6]). Thirdly, the enhanced overcrowding of **6** *versus* **1** results in relatively fast *E*,*Z*-isomerizations.[18] Thus, both (*E*)-**6** and (*Z*)-**6** could be used as starting materials for affecting the aromatization of **6** to **3**.

The starting material for the reductive dechlorination reaction was pure (*Z*)-**6**, obtained by recrystallization of a mixture of (*E*)-**6** and (*Z*)-**6**[19] from CH_2Cl_2. A solution of (*Z*)-**6** (under argon) in dry DMF was treated with K_2CO_3, *n*-Bu_4NHSO_4 and $Pd(OAc)_2$ and heated with magnetic stirring at 119−122 °C for 51 h. The crude products were purified by column chromatography and by fractional recrystallization. The following compounds were isolated: **6**, **3,** 1-chlorobenz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (**5**), 1-chloro-9*H*-fluoren-9-one, and 9*H*-fluoren-9-one. The structures of the products were established by mass and by 1D and 2D ^{1}H NMR and ^{13}C NMR spectroscopies. PAH **3** was isolated in 5.6% yield (49.7% based on consumed **6**) as yellow crystals. In C_{2v} **3**, as expected, no NOE cross peak between the protons at the overcrowded region (H_1, H_{14} and H_7, H_8) was observed. By contrast, in the isomeric C_{2h} rubicene (**7**),[20,21] an NOE cross peak between the overcrowded

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[1] Shoham, G.; Cohen, S.; Suissa, R. M.; Agranat, I. In *Molecular Structure: Chemical Reactivity and Biological Activity*; Stezowski, J. J.; Huang J.-L.; Shao, M.-C., Eds.; IUC Crystallographic Symposia 2, Oxford University Press: Oxford, 1988; pp 290−312.

[2] Biedermann, P. U.; Levy, A.; Stezowski, J. J.; Agranat, I. *Chirality* **1995**, *7*, 199.

[3] de la Harpe, C.; van Dorp, W. A. *Ber. Dtsch. Chem. Ges.* **1875**, *8*, 1048.

[4] Biedermann, P. U.; Levy, A.; Suissa, M. R.; Stezowski, J. J.; Agranat, I. *Enantiomer* **1996**, *1*, 75.

[5] Rabideau P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235.

[6] Scott, L. T. *Pure Appl. Chem.* **1996,** *68*, 291.

[7] Biedermann, P. U.; Luh, T.-Y.; Weng, D. T.-C.; Kuo, C.-H.; Stezowski, J. J.; Agranat, I. *Polycycl. Aromat. Compd.* **1996**, *8*, 167.

[8] Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Tetrahedron Lett.* **1994**, *35*, 7013.

[9] Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycyclic Aromat. Compd.* **1995**, *4*, 209.

[10] Yukhno, G. F.; Bikkulov, A. Z. *Dokl. Neftekhim. Sekts. Bashk. Resp. Vses. Khim. O-va.* **1971**, *7*, 5; *Chem. Abstr.* **1975**, *83*, 9606y.

[11] Lang, K. F.; Buffleb, H.; Kalowy, J. *Chem. Ber.* **1961**, *94*, 523.

[12] De Gunst, G. P. *Recl. Trav. Chim. Pay-Bas* **1969**, *88*, 801.

[13] Kuo, C.-H.; Tsau, M.-H.; Weng, D. T.-C; Lee, G. H.; Peng, S.-M.; Luh, T.-Y.; Biedermann, P. U.; Agranat, I. *J. Org. Chem.* **1995**, *60*, 7380.

[14] Dyker, G. *J. Org. Chem.* **1993**, *58*, 234.

[15] Grigg, R.; Teasdale A.; Sridharan, V. *Tetrahedron Lett.* **1991**, *32*, 3859.

[16] Bacon, R. G. R.; Hill, H. A. O. *Quart. Rev.* **1965**, *19*, 95.

[17] Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327.

[18] Agranat, I.; Rabinovitz, M.; Weitzen-Dagan, A.; Gosnay, I. *J. Chem. Soc., Chem. Commun.* **1972**, 732.

[19] Gosnay, I.; Bergmann, E. D.; Rabinovitz, M.; Agranat, I. *Isr. J. Chem.* **1972**, *10*, 423.

[20] Sachweh, V.; Langhals, H. *Chem. Ber.* **1990**, *123*, 1981.

[21] Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964; Vol. 2, p 345.

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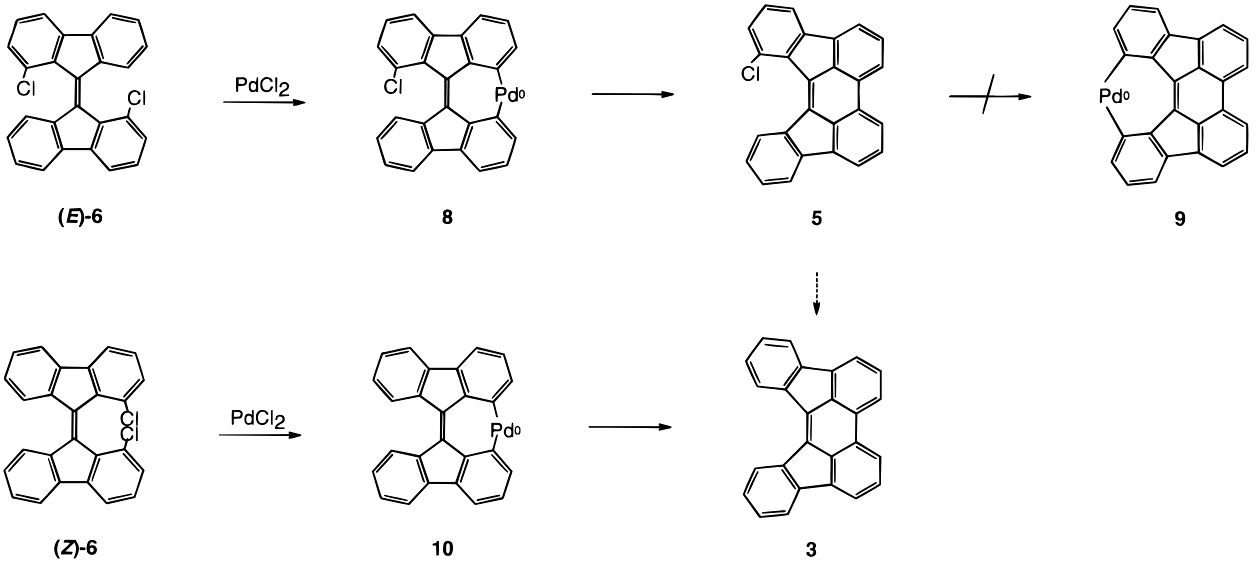
Scheme 1. Reaction Pathways for the Formation of 3 and Its Chloro Derivative 5 by a Palladium-Catalyzed Cyclization Reaction of 6



protons H_1 and H_{14} (and between H_7 and H_8) was observed. Compound **5** was obtained as a 4:1 mixture with **3** (free of **6**).

Semiempirical MNDO-PM3 calculations of $C_{26}H_n$ (n = 12,14,16) species[7] have recently shown that the aromatization of **1** to **3** by dehydrogenation is highly exothermic, while the dehydrogenation of **3** to the buckybowl **2** and of **1** to **2** are highly endothermic.[7] Furthermore, the planar **3** is more stable than its isomers, the twisted **4**, and the planar rubicene (**7**).[7] The overcrowded PAE **1** adopts a twisted conformation with experimental and calculated twist angles of 32.5° and 30.2°, respectively.[7] MNDO-PM3 calculations of (*E*)-**6** and (*Z*)-**6** show that their global minima are twisted-folded C_2 conformations, as compared with the twisted D_2 conformation of **1**. The pronounced overcrowding of (*E*)-**6** and (*Z*)-**6** vis-á-vis **1** is reflected, *inter alia*, in the higher twist around C9=C9′ (37.2° and 37.0° *versus* 30.2°) and in the pyramidalization of C9 and C9′. (*Z*)-**6** proved to be less stable than (*E*)-**6** by 2.5 kJ/mol, indicating an equilibrium mixture of ca. 27:73 (at 25 °C). In $CDCl_3$ solution, the corresponding equilibrium ratio is 30:70 (2.1 kJ/mol). Previous MINDO/3 calculations claimed that (*E*)-**6** (53° twist) is more stable than (*Z*)-**6** (58° twist) by 7 kJ/mol.[22] The MNDO-PM3 calculated barriers for (*E*)-**6** $\rightleftharpoons$ (*Z*)-**6** isomerization (assuming an orthogonal diradical transition state) are 80.8 and 78.2 kJ/mol. These values are in agreement with the results of a DNMR study of the conformational behavior of **6**.[18] The barriers are considerably higher than the reported MINDO/3 calculated values, 43 and 36 kJ/mol, respectively.[22] Although PAH **3** is planar, it is still overcrowded, as reflected in its very short H···H distance in the fjord region, 166 pm.[7] On the other hand, the nonbonded C···C distance in the fjord region of **3** is not particularly short, 353 pm.[7] The calculated global minimum C_1 conformation of **5** is helical, due to the overcrowding introduced by the chlorine. The nonbonded C···C, Cl···H, and Cl···C distances in the fjord region of **5** are 379, 241, and 304 pm, respectively. The dihedral angles in the fjord region are −20.2° ($C_1C_{14d}C_{14c}C_{14b}$), −6.8° ($C_{14d}C_{14c}C_{14b}C_{14a}$), and −12.0° ($C_{14c}C_{14b}C_{14a}C_{14}$).

Both diastereomers of **6** may play a role in the aromatization reactions. The formation of **5** may be rationalized by a cyclopalladation reaction[23] of (*E*)-**6** (bearing a reactive chlorine and a hydrogen at a suitable distance) leading to the intermediate palladacycle **8**,[23] followed by a reductive elimination of Pd to give **5**. A second sequence of cyclopalladation−reductive elimination coupling reaction[23] via the intermediate palladacycle **9** does not occur, presumably because of the long distance between the designated carbon atoms in **9**. PAH **3** is probably formed by a palladium-catalyzed intramolecular coupling reaction of (*Z*)-**6**, via the palladacycle intermediate **10**. PAH **3** could also be formed from **5** by dechlorination (Scheme 1).

In conclusion, the palladium-catalyzed aromatizations of the overcrowded (*E*)-**6** and (*Z*)-**6** facilitate the first step in the sequence: twisted bifluorenylidene → planar **3** → buckybowl **2**.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded at 400.1 MHz using $CDCl_3$ or CD_2Cl_2 as solvent and as internal standard ($\delta(CHCl_3) = 7.26$ ppm; $\delta(CHDCl_2) = 5.36$ ppm). ^{13}C NMR spectra were recorded at 100.6 MHz using $CDCl_3$ as solvent and as internal standard ($\delta(CHCl_3) = 77.01$ ppm).

(*E*)- and (*Z*)-1,1′-Dichlorobi-9*H*-fluoren-9-ylidene (6). A mixture of (*E*)-**6** and (*Z*)-**6**, mp 259−260 °C, was obtained according to the literature.[19] Pure (*Z*)-**6**[24] was obtained from the mixture of the diastereomers by recrystallization from CH_2Cl_2 as dark red crystals, mp 262−264 °C.

(*Z*)-**6**: ^1H NMR (CD_2Cl_2, 182 K): δ = 8.34 (d, J = 7.8 Hz, H_8, $H_{8'}$), 7.77 (d, J = 7.7 Hz, H_5, $H_{5'}$), 7.73 (d, J = 7.1 Hz, H_4, $H_{4'}$), 7.42 (t, J = 7.8 Hz, H_3, $H_{3'}$), 7.36 (t, J = 7.3 Hz, H_6, $H_{6'}$), 7.28 (d, J = 7.0 Hz, H_2, $H_{2'}$), 7.23 (t, J = 7.4 Hz, H_7, $H_{7'}$).

(*E*)- and (*Z*)-**6**: ^1H NMR ($CDCl_3$, 298 K): (*E*):(*Z*) = 2.2:1; δ = 8.39 (d, J = 7.9 Hz, *Z*-H_8), 7.71 (d, J = 7.6 Hz, *Z*-H_5), 7.70 (d, J = 7.3 Hz, *E*-H_4), 7.69 (d, J = 7.5 Hz, *E*-H_5), 7.66 (d, J = 7.3 Hz, *Z*-H_4), 7.38 (dd, J = 8.0 Hz, J = 7.2 Hz, *E*-H_3), 7.36 (d, J = 7.8 Hz, *E*-H_8), 7.34 (dd, J = 8.0 Hz, J = 7.3 Hz, *Z*-H_3), 7.33 (d, J = 8.0 Hz, *E*-H_2), 7.31 (t, J = 7.5 Hz, *Z*-H_6), 7.28 (t, J = 7.4 Hz,

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(22) Kikuchi, O.; Matsushita, K.-I.; Morihashi, K.; Nakayama, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3043.

(23) Dyker, G.; Körning, J.; Nerenz, F.; Siemsen, P.; Sostmann, S.; Wiegand, A.; Jones, P. G.; Bubenitschek, P. *Pure Appl. Chem.* **1996**, *68*, 323.

(24) The molecular and crystal structure of (*Z*)-**6** will be published elsewhere.

E-H$_6$), 7.27 (d, *J* = 7.8 Hz, *Z*-H$_2$), 7.21 (dd, *J* = 7.8 Hz, *J* = 7.4 Hz , *E*-H$_7$), 7.20 (dd, *J* = 7.9 Hz, *J* = 7.3 Hz, *Z*-H$_7$). The assignments were based on a DQF-COSY 2D NMR experiment. ^{13}C NMR (CDCl$_3$, 298 K): (*E*)-**6**: δ = 144.42 (2C$_q$), 140.37 (2C$_q$), 138.67 (2C$_q$), 138.65 (2C$_q$), 135.41 (2C$_q$), 133.10 (2C$_q$), 130.34 (2C$_t$), 129.64 (2C$_t$), 128.23 (2C$_t$), 127.74 (2C$_t$), 127.55 (2C$_t$), 119.80 (2C$_t$), 118.48 (2C$_t$); (*Z*)-**6**: δ = 142.58 (2C$_q$), 140.15 (2C$_q$), 139.66 (2 × 2C$_q$), 137.52 (2C$_q$), 133.35 (2C$_q$), 130.07 (2C$_t$), 129.44 (2C$_t$), 128.98 (2C$_t$), 127.38 (2C$_t$), 126.81 (2C$_t$), 120.20 (2C$_t$), 118.02 (2C$_t$). MS, *m/z* (%): 398.04 (62) [$C_{26}H_{14}{}^{37}Cl^{35}Cl^+$], 396.05 (91) [$C_{26}H_{14}{}^{35}Cl_2{}^+$], 363.08 (2) [$C_{26}H_{14}{}^{37}Cl^{35}Cl^+ - {}^{35}Cl$], 362.07 (4) [$C_{26}H_{14}{}^{37}Cl^{35}Cl^+ - H^{35}Cl$], 361.08 (7) [$C_{26}H_{14}{}^{35}Cl_2{}^+ - {}^{35}Cl$], 360.07 (11) [$C_{26}H_{14}{}^{35}Cl_2{}^+ - H^{35}Cl$], 326.11 (100) [$M^+ - 2Cl$], 163.05 (24) [$M^{2+} - 2Cl$].

Synthesis of Benz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (3) and 1-Chlorobenz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (5) by Palladium-Catalyzed Reductive Cyclodechlorination Reaction of 6. The reaction was carried out under an argon atmosphere in a 25-mL round-bottomed flask equipped with a Y adaptor, a reflux condenser (protected from moisture), and a magnetic stirrer. A solution of (*Z*)-**6** (50.0 mg, 0.126 mmol) in 3.7 mL of dry DMF was treated with K$_2$CO$_3$ (134.0 mg, 0.970 mmol), *n*-Bu$_4$NHSO$_4$ (82.0 mg, 0.240 mmol), and Pd(OAc)$_2$ (5.4 mg, 0.025 mmol) and stirred at 119−122 °C for 51 h. The reaction mixture was diluted with water, the precipitate was filtered off, dissolved in CH$_2$Cl$_2$, and dried with Na$_2$SO$_4$, and the solvent was evaporated in vacuum to give the crude products as a red solid. The crude products were purified by column chromatography on silica gel 60, using a gradient of petroleum ether (bp 65−75 °C)−CH$_2$Cl$_2$ as eluent (starting with 3% CH$_2$Cl$_2$). The following fractions were collected:

(1) A mixture of **3**, **5**, and **6** (see below).

(2) 1-Chloro-9*H*-fluoren-9-one: 7.3 mg, 12.2% yield; dark greenish-yellow crystals; mp 138−141 °C (CH$_2$Cl$_2$; lit.[19] mp 132−134 °C).

(3) 9*H*-Fluorene-9-one: 1.0 mg, 1.6% yield; yellow crystals; mp 80−82 °C.

Repeated fractional crystallization of the mixture of **3**, **5**, and **6** from CH$_2$Cl$_2$ afforded pure (*Z*)-**6**, pure **3**, and a 4:1 mixture of **5** and **3** (free of **6**).

(*Z*)-**6**: 41.7 mg, 69.9% recovery; dark red crystals; mp 262−264 °C (CH$_2$Cl$_2$; lit.[19] mp 252−254 °C);

3: 3.4 mg, 5.6% yield (49.7% based on consumed **6**); yellow needles; mp 270−276 °C (CH$_2$Cl$_2$; lit.[8] mp 277−278 °C); ^{1}H NMR (CDCl$_3$, 298 K): δ = 8.59 (d, *J* = 7.5 Hz, H$_1$, H$_{14}$), 8.46 (d, *J* = 8.1 Hz, H$_7$, H$_8$), 8.04 (d, *J* = 7.1 Hz, H$_5$, H$_{10}$), 8.03 (d, *J* = 7.8 Hz, H$_4$, H$_{11}$), 7.80 (dd, *J* = 8.0 Hz, *J* = 7.1 Hz, H$_6$, H$_9$), 7.56 (t, *J* = 7.4 Hz, H$_2$, H$_{13}$), 7.52 (t, *J* = 7.5 Hz, H$_3$, H$_{12}$); ^{13}C NMR (CDCl$_3$, 298 K) = 77.01 ppm): δ = 141.88 (2C$_q$), 137.81 (2C$_q$), 137.71 (2C$_q$), 134.68 (2C$_q$), 133.13 (2C$_q$), 128.69 (C$_3$, C$_{12}$), 128.39 (C$_6$, C$_9$), 127.80 (2C$_q$), 127.74 (C$_2$, C$_{13}$), 126.01 (C$_1$, C$_{14}$), 122.04 (C$_7$, C$_8$), 121.35 (C$_4$, C$_{11}$), 119.57 (C$_5$, C$_{10}$). The assignments were based on the following 2D NMR experiments: DQF-COSY and 1-bond HSQC correlation (see NMR of **7**[25] for comparision). MS, *m/z* (%): 326.11 (100) [M^+], 324.09 (26) [$M^+ - 2H$], 163.05 (22) [M^{2+}], 162.05 (25) [$M^{2+} - 2H$].

5: 1.9 mg, 3.2% yield (25.6% based on consumed **6**); ^{1}H NMR (CDCl$_3$, 298 K): δ = 8.47 (d, *J* = 8.1 Hz, H$_8$), 8.43 (d, *J* = 8.1 Hz, H$_7$), 8.19 - 8.14 (m, H$_{14}$), 8.05 (d, *J* = 7.1 Hz, H$_5$), 8.04 (d, *J* = 7.2 Hz, H$_{10}$), 7.99−7.94 (m, H$_4$, H$_{11}$), 7.81 (dd, *J* = 8.0 Hz, *J* = 7.2 Hz, H$_6$), 7.80 (dd, *J* = 8.0 Hz, *J* = 7.1 Hz, H$_9$), 7.52−7.46 (m, H$_2$, H$_3$, H$_{12}$, H$_{13}$). The assignments were based on a DQF-COSY 2D NMR experiment. MS, *m/z* (%): 362.07 (24) [$C_{26}H_{13}{}^{37}Cl^+$], 360.07 (71) [$C_{26}H_{13}{}^{35}Cl^+$], 325.10 (8) [$M^+ - Cl$], 324.09 (25) [$M^+ - HCl$], 181.03 (6) [$C_{26}H_{13}{}^{37}Cl^{2+}$], 180.03 (16) [$C_{26}H_{13}{}^{35}Cl^{2+}$], 162.55 (8) [$M^{2+} - Cl$], 162.05 (27) [$M^{2+} - HCl$].

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[25] **7**: ^{1}H NMR (CDCl$_3$, 298 K, δ(CHCl$_3$) = 7.26 ppm): δ = 8.64 (d, *J* = 8.4 Hz, H$_1$, H$_8$), 8.36 (d, *J* = 7.6 Hz, H$_7$, H$_{14}$), 8.05 (d, *J* = 6.7 Hz, H$_3$, H$_{10}$), 7.99 (d, *J* = 7.4 Hz, H$_4$, H$_{11}$), 7.81 (dd, *J* = 8.5 Hz, *J* = 6.7 Hz, H$_2$, H$_9$), 7.48 (t, *J* = 7.5 Hz, H$_6$, H$_{13}$), 7.41 (t, *J* = 7.4 Hz, H$_5$, H$_{12}$); an NOE cross peak between H$_1$ and H$_{14}$ (and between H$_7$ and H$_8$) was observed. ^{13}C NMR (CDCl$_3$, 298 K, δ(CHCl$_3$) = 77.01 ppm): δ = 139.91 (2C$_q$), 139.42 (2C$_q$), 138.23 (2C$_q$), 133.53 (2C$_q$), 133.08 (2C$_q$), 129.01 (2C$_t$), 128.12 (2C$_t$), 126.97 (2C$_t$), 125.53 (2C$_q$), 124.56 (2C$_t$), 123.72 (2C$_t$), 121.64 (2C$_t$), 120.31 (2C$_t$).