

Supporting Information of the manuscript:

## Quantum interference distinguishes between constitutional isomers

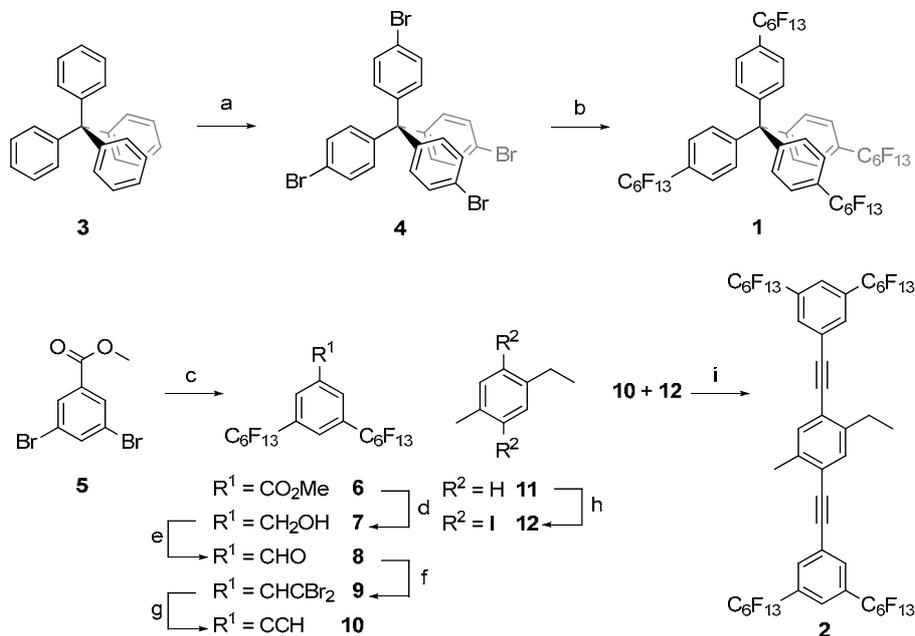
by Jens Tüxen, Stefan Gerlich, Sandra Eibenberger, Markus Arndt and Marcel Mayor

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### Synthetic protocols and analytical data of the precursors:

In the following, the synthetic procedures for the preparation of the target structures **1** and **2** as well as for their precursors **6-10** and **12** are described (see scheme 1). Tetrakis(4-bromophenyl)methane (**4**) was prepared according to a reported procedure.<sup>1</sup>



**Scheme 1:** Synthesis of the structural isomers **1** and **2**. *Reagents and conditions:* (a) Br<sub>2</sub>, rt, 25 min, 83% (b) IC<sub>6</sub>F<sub>13</sub>, Cu, DMF, 120 °C, 12 h, 27% (c) IC<sub>6</sub>F<sub>13</sub>, Cu, DMF, 120 °C, 12 h, 86% (d) LiAlH<sub>4</sub>, Et<sub>2</sub>O, rt, 16 h, 64% (e) PDC, CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h, 88% (f) CBr<sub>4</sub>, PPh<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 1 h, 85% (g) 1. *n*-BuLi, THF, -78 °C 2. H<sub>2</sub>O, 93% (h) I<sub>2</sub>, HIO<sub>3</sub>, glacial AcOH, H<sub>2</sub>SO<sub>4</sub>, CHCl<sub>3</sub>, H<sub>2</sub>O, 85 °C, 4 h, 53% (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, (*i*-Pr)<sub>2</sub>NH, THF, rt, 12 h, 22%.

<sup>1</sup> R. Rathore, C. L. Burns, I. A. Guzei, *J. Org. Chem.* **2004**, *69*, 1524.

## General Remarks

All commercially available starting materials were of reagent grade and used as received. Dry tetrahydrofuran (THF), dry *N,N'*-dimethylformamide (DMF) and dry dichloromethane were purchased from *Fluka*, stored over 4 Å molecular sieves, and handled under Argon. The solvents for chromatography, crystallization and extraction were of technical grade and distilled prior to use. Column chromatography purifications were carried out on *silica gel 60* (particle size 0.040-0.063 mm) from *Fluka*. Deuterated solvents were purchased from *Cambridge Isotope Laboratories*. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a *Bruker DMX 400* instrument (<sup>1</sup>H resonance 400 MHz) or a *Bruker DRX 500* instrument (<sup>1</sup>H resonance 500 MHz) at 298 K. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-ToF) mass spectra were performed on an *Applied Bio Systems Voyager-De™ Pro* mass spectrometer. Electron Impact (EI) mass spectra were recorded on a *Finnigan MAT 95Q* by H. Nadig. Elemental analyses were performed by W. Kirsch on a *Perkin-Elmer Analyticator 240*.

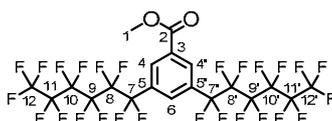
## Methyl-3,5-bis(perfluorohexyl)benzoate (6)

A few crystals of iodine were added under stirring to a suspension of copper (1.98 g, 31.1 mmol, 6.0 eq.) in acetone (5 mL). After 15 minutes the liquid phase was eliminated and the copper washed with hydrochloric acid in acetone, followed by acetone alone. The activated copper was added to 10 mL dry DMF under an argon atmosphere. The suspension was heated under stirring to 70 °C and *n*-perfluorohexyliodide (2.81 mL, 5.78 g, 3.89 mmol, 2.5 eq.) was then added dropwise to the suspension over five minutes. The mixture was heated to 120 °C and a solution of 3,5-dibromo-4-methylbenzoate (1.52 g, 5.18 mmol, 1.0 eq.) was added. After stirring overnight at 120 °C, the mixture was cooled to room temperature, diluted with water and Et<sub>2</sub>O and filtered through a Celite plug. The solid residue was washed with Et<sub>2</sub>O. The aqueous phase was extracted with Et<sub>2</sub>O. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporating the solvent the pale yellow crude was purified by column chromatography using silica gel (ethyl acetate/hexane 1:5) to give methyl-3,5-bis(perfluorohexyl)benzoate (**6**) (3.35 g, C<sub>20</sub>H<sub>6</sub>F<sub>26</sub>O<sub>2</sub>, 772.22 g/mol) as a white solid in 86% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ/ppm): 8.49 (2H, s, 4, 4'), 7.98 (1H, s, 6), 4.02 (3H, s, 1).

<sup>19</sup>F-NMR (377 MHz, CDCl<sub>3</sub>, δ/ppm): -82.0 (6F, t, *J* = 10 Hz, 12, 12'), -112.2 (4F, br, m), -122.5 (4F, br, m), -122.9 (4F, br, m), -124.0 (4F, br, m), -127.3 (4F, br, m).

- $^{13}\text{C-NMR}$**  (101 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 164.4 (1C, Cq, s, 2), 132.2 (1C, Cq, s, 3), 131.6 (2C, Ct, m, 4, 4'), 130.8 (2C, Cq, t,  $^2J_{\text{C-F}} = 25$  Hz, 5, 5'), 129.4 (1C, Ct, s, 6), 53.1 (1C, Cp, m, 1).
- MS** (EI, m/z): 772 (2%,  $\text{M}^+$ ); 741 (56%); 503 (100%).
- $T_M$**  58 °C – 60 °C.
- EA** calculated: C = 31.11, H = 0.78,  
found: C = 31.01, H = 0.93.

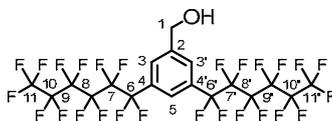


### 3,5-Bis(perfluorohexyl)benzylic alcohol (7)

A solution of ester **6** (17.2 g, 22.2 mmol, 1.0 eq.) in  $\text{Et}_2\text{O}$  (150 mL) was added dropwise to a suspension of  $\text{LiAlH}_4$  (1.27 g, 33.4 mmol, 1.5 eq.) in  $\text{Et}_2\text{O}$  (50 mL). This mixture was stirred at room temperature under an argon atmosphere for 16 hours, before  $\text{EtOAc}$  (4 mL) was added. After 15 minutes,  $\text{H}_2\text{SO}_4$  (10%, 5 mL) was slowly dropped into the reaction mixture, which was stirred for another 15 minutes. The organic phase was removed and the aqueous phase was extracted with  $\text{Et}_2\text{O}$ . The combined organic layers were washed with brine and dried over  $\text{MgSO}_4$ . Evaporation of the solvent afforded a pale yellow solid that was recrystallized from hexane to give pure 3,5-bis(perfluorohexyl)benzylic alcohol (10.7 g,  $\text{C}_{19}\text{H}_6\text{F}_{26}\text{O}$ , 744.21 g/mol) as a white solid in 64% yield.

- $^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 7.83 (2H, s, 3, 3'), 7.72 (1H, s, 5), 4.89 (2H, d,  $^3J_{\text{HH}} = 5.7$  Hz, 1), 2.02 (1H, t,  $^3J_{\text{HH}} = 5.7$  Hz, OH).
- $^{19}\text{F-NMR}$**  (377 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): -82.0 (6F, t,  $J = 10$  Hz, 11, 11'), -112.2 (4F, br, m), -122.6 (4F, br, m), -123.0 (4F, br, m), -124.0 (4F, br, m), -127.4 (4F, br, m).
- $^{13}\text{C-NMR}$**  (101 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 143.1 (1C, Cq, s, 2), 138.9 (1C, Cq, s, 5), 128.4 (2C, Ct, m, 3, 3'), 124.6 (1C, Ct, m, 5), 130.3 (2C, Cq, t,  $^2J_{\text{C-F}} = 25$  Hz, 4, 4'), 63.8 (1C, Cs, s, 1).
- MS** (EI, m/z): 744 (16%,  $\text{M}^+$ ); 475 (100%); 425 (36%).
- $T_M$**  58 °C – 59 °C.

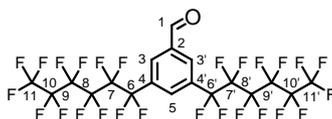
**EA**           calculated:           C = 30.66, H = 0.81,  
                  found:                C = 30.71, H = 0.90.



### 3,5-Bis(perfluorohexyl)benzaldehyde (8)

To a solution of alcohol **7** (7.05 g, 9.47 mmol, 1.0 eq.) in dichloromethane (300 mL) was added pyridinium dichromate (5.35 g, 14.2 mmol, 1.5 eq.). The reaction mixture was stirred at room temperature under an argon atmosphere for 24 h, before Et<sub>2</sub>O (30 mL) was added. Filtration of the reaction mixture and evaporation of the solvent afforded a pale yellow solid that was purified by column chromatography using silica gel (ethyl acetate/hexane 1:5) to give 3,5-bis(perfluorohexyl)benzaldehyde (6.21 g, C<sub>19</sub>H<sub>4</sub>F<sub>26</sub>O, 742.19 g/mol) as a white solid in 88% yield.

**<sup>1</sup>H-NMR**   (400 MHz, CDCl<sub>3</sub>, δ/ppm): 10.16 (1H, s, 1), 8.34 (2H, s, 3, 3'), 8.05 (1H, s, 5).  
**<sup>19</sup>F-NMR**   (377 MHz, CDCl<sub>3</sub>, δ/ppm): -81.9 (6F, t, *J* = 10 Hz, 11, 11'), -112.3 (4F, br, m),  
                  -122.5 (4F, br, m), -122.8 (4F, br, m), -123.9 (4F, br, m), -127.3 (4F, br, m).  
**<sup>13</sup>C-NMR**   (101 MHz, CDCl<sub>3</sub>, δ/ppm): 189.0 (1C, Ct, s, 1), 137.3 (1C, Cq, s, 2), 131.6  
                  (2C, Cq, t, <sup>2</sup>*J*<sub>C-F</sub> = 25 Hz, 4, 4'), 131.2 (2C, Ct, m, 3, 3'), 130.5 (1C, Cp, m, 5).  
**MS**         (EI, *m/z*): 742 (2%, M<sup>+</sup>); 723 (7%); 473 (100%).



### 1-(2,2-Dibromovinyl)-3,5-bis(perfluorohexyl)benzene (9)

A solution of carbon tetrabromide (8.10 g, 24.4 mmol, 3.0 eq.) and triphenylphosphine (12.8 g, 48.8 mmol, 6.0 eq.) in degassed dichloromethane (250 mL) was cooled to 0 °C. To this yellow solution was added dropwise a solution of aldehyde **8** (6.04 g, 8.14 mmol, 1.0 eq.) in degassed dichloromethane (100 mL). The reaction mixture was stirred at 0 °C under an argon atmosphere for 1 h. Evaporation of the solvent and purification by column chromatography using silica gel (ethyl acetate/hexane 1:10) yielded the desired product **9** (6.22 g, C<sub>20</sub>H<sub>4</sub>Br<sub>2</sub>F<sub>26</sub>, 898.01 g/mol) as a colorless oil in 85% yield.

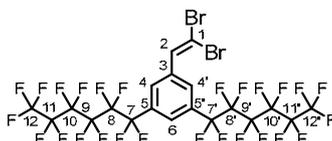
**<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>, δ/ppm): 7.97 (2H, s, 4, 4'), 7.76 (1H, s, 6), 7.58 (1H, s, 2).

**<sup>19</sup>F-NMR** (377 MHz, CDCl<sub>3</sub>, δ/ppm): -81.1 (6F, t, *J* = 10 Hz, 12, 12'), -111.4 (4F, br, m), -121.6 (4F, br, m), -122.1 (4F, br, m), -123.0 (4F, br, m), -126.4 (4F, br, m).

**<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>, δ/ppm): 137.2 (1C, Cq, s, 3), 133.9 (1C, Ct, s, 2), 130.4 (2C, Cq, t, <sup>2</sup>*J*<sub>C-F</sub> = 25 Hz, 5, 5'), 130.3 (2C, Ct, m, 4, 4'), 125.1 (1C, Ct, m, 6), 94.7 (1C, Cq, s, 1).

**MS** (EI, *m/z*): 898 (86%, M<sup>+</sup>); 629 (100%); 469 (66%).

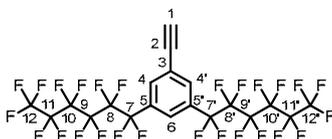
**EA** calculated: C = 26.75, H = 0.45,  
found: C = 26.92, H = 0.55.



### 5-Ethynyl-1,3-bis(perfluorohexyl)benzene (10)

*n*-Butyllithium (1.6 M in hexane, 2.69 mL, 6.0 eq.) was slowly added to a solution of **9** (1.36 g, 1.51 mmol, 1.0 eq.) in THF (40 mL) at -78 °C. After one hour stirring at this temperature, the mixture was left to warm up to room temperature, and the stirring was continued for another 2 h. The reaction was quenched by the addition of a saturated NH<sub>4</sub>Cl solution (20 mL), and the mixture was diluted with hexane (100 mL). The organic phase was washed with water and dried over magnesium sulfate. Purification by column chromatography with hexane as eluent gave compound **10** (1.04 g, C<sub>20</sub>H<sub>4</sub>F<sub>26</sub>, 738.20 g/mol) as a white solid in 93% yield.

- <sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, δ/ppm): 7.91 (2H, s, 4, 4'), 7.76 (1H, s, 6), 3.29 (1H, s, 1).
- <sup>19</sup>F-NMR** (377 MHz, CDCl<sub>3</sub>, δ/ppm): -82.0 (6F, t, *J* = 10 Hz, 12, 12'), -112.5 (4F, br, m), -122.6 (4F, br, m), -123.0 (4F, br, m), -124.0 (4F, br, m), -127.3 (4F, br, m).
- <sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>, δ/ppm): 133.8 (2C, Ct, m, 4, 4'), 130.5 (2C, Cq, t, <sup>2</sup>*J*<sub>C-F</sub> = 25 Hz, 5, 5'), 125.4 (1C, Ct, m, 6), 124.5 (1C, Cq, s, 3), 81.0 (1C, Ct, s, 1), 80.5 (1C, Cq, s, 2).
- MS** (EI, *m/z*): 738 (18%, M<sup>+</sup>); 469 (100%).
- T<sub>M</sub>** 51 °C – 52 °C.
- EA** calculated: C = 32.54, H = 0.55,  
found: C = 32.35, H = 0.70.

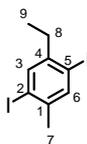


### 1-Ethyl-2,5-diiodo-4-methylbenzene (12)

4-Ethyltoluene (**7**, 1.39 mL, 1.20 g, 10.0 mmol, 1.0 eq.) iodine (2.03 g, 8.00 mmol, 0.8 eq.) and iodic acid (774 mg, 4.40 mmol, 0.44 eq.) were dissolved in glacial acetic acid (5 mL), concentrated sulfuric acid (0.5 mL), water (0.5 mL) and chloroform (0.5 mL), The reaction mixture was stirred at 85 °C for 4 hours and then poured into 20 ml 10 % aq. NaHSO<sub>3</sub>. After extracting with Et<sub>2</sub>O the solvent was evaporated. Purification by column chromatography using silica gel and hexane as eluent followed by recrystallization from methanol yielded 1-ethyl-2,5-diiodo-4-methylbenzene (1.97 g, C<sub>9</sub>H<sub>10</sub>I<sub>2</sub>, 371.98 g/mol) as white crystals in 53% yield.

- <sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>, δ/ppm): 7.65 (1H, s, 6), 7.61 (1H, s, 3), 2.64 (2H, q, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, 8), 2.34 (3H, s, 7), 1.17 (3H, t, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, 9).
- <sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>, δ/ppm): 145.8 (1C, Cq, s, 4), 140.7 (1C, Cq, s, 1), 139.7 (1C, Ct, s, 6), 138.2 (1C, Ct, s, 3), 101.0 (1C, Cq, s, 2), 99.9 (1C, Cq, s, 5), 33.1 (1C, Cp, s, 8), 26.9 (1C, Cs, s, 7) 14.5 (1C, Cp, s, 9).
- MS** (EI, *m/z*): 372 (100%, M<sup>+</sup>); 357 (39%).

**EA**           calculated:           C = 29.06, H = 2.71,  
                  found:                C = 29.12, H = 2.61.



### 2,5-Di((3',5'-diperfluorohexyl)ethynyl)-4-ethyltoluene (2)

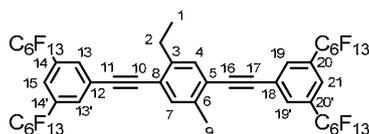
1-Ethynyl-3,5-bis(perfluorohexyl)benzene (1.50 g, 2.03 mmol, 2.0 eq.) and 1-ethyl-2,5-diiodo-4-methylbenzene (378 mg, 1.02 mmol, 1.0 eq.) was added to a solution of 10 ml dry THF and 2 ml (*i*-Pr)<sub>2</sub>NH. The solution was degassed before Pd(PPh<sub>3</sub>)<sub>4</sub> (117 mg, 102 μmol, 10 mol%) and CuI (19.3 mg, 102 μmol, 10 mol%) were added. The reaction mixture was stirred at room temperature overnight. The solvent was evaporated and the crude was purified by CC using silica gel and hexane/acetone (500:1) as eluent yielding the product **2** (357 mg, C<sub>49</sub>H<sub>16</sub>F<sub>52</sub>, 1592.57 g/mol, 22%) as a white solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub>, δ/ppm): 8.02 (4H, br, m, 13, 13', 19, 19'), 7.84 (2H, br, m, 15, 21), 7.41 - 7.39 (2H, m, 4, 7), 2.91 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2), 2.54 (3H, s, 9), 1.37 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 1).

**<sup>19</sup>F-NMR** (377 MHz, CDCl<sub>3</sub>/Freon113, δ/ppm): -82.0 (6F, t, *J* = 10 Hz), -112.2 (4F, br, m), -122.1 (4F, br, m), -122.3 (4F, br, m), -123.5 (4F, br, m), -127.0 (4F, br, m).

**MS** (MALDI-ToF, *m/z*): 1592 (100%, M<sup>+</sup>).

**EA**           calculated:           C = 36.96, H = 1.01,  
                  found:                C = 38.20, H = 1.30.



### Tetrakis(4-(perfluorohexylphenyl)methane (1)

A few crystals of iodine were added under stirring to a suspension of copper (960 mg, 15.1 mmol, 12.0 eq.) in acetone. After 15 minutes the liquid phase was eliminated and the copper washed with hydrochloric acid in acetone, followed by acetone alone. The activated copper and tetrakis(4-bromophenyl)methane (800 mg, 1.26 mmol, 1.0 eq.) were added to dry DMF (10 mL) under an argon atmosphere at 70 °C. The suspension was stirred at 70 °C and *n*-perfluorohexyliodide (1.63 mL, 3.37 g, 7.55 mmol, 6.0 eq.) was added dropwise to the suspension over a period of five minutes. After stirring at 120 °C overnight, the mixture was cooled to room temperature, diluted with water and Et<sub>2</sub>O and filtered through a plug of Celite. The solid residue was washed with Et<sub>2</sub>O and the aqueous phase was extracted with Et<sub>2</sub>O. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After evaporating the solvent, the crude was purified by CC using silica gel and hexane as eluent to give tetrakis(4-perfluorohexylphenyl)methane (549 mg, C<sub>49</sub>H<sub>16</sub>F<sub>52</sub>, 1592.57 g/mol, 27%) as a white solid.

**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, δ/ppm): 7.56 (8H, m, 4, 4', 8, 8', 12, 12', 16, 16'), 7.33 (8H, m, 3, 3', 7, 7', 11, 11', 15, 15').

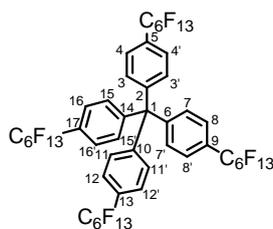
**<sup>19</sup>F-NMR** (377 MHz, CDCl<sub>3</sub>, δ/ppm): -82.0 (12F, m, CF<sub>3</sub>), -112.0 (8F, br, m), -122.7 (8F, br, m), -123.0 (8F, br, m), -124.0 (8F, br, m), -127.3 (8F, br, m).

**<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, δ/ppm): 148.6 (4C, Cq, s, 2, 6, 10, 14), 130.9 (8C, Ct, s, 3, 3', 7, 7', 11, 11', 15, 15'), 127.8 (4C, Cq, m, 5, 9, 13, 17), 126.9 (8C, Ct, m, 4, 4', 8, 8', 12, 12', 16, 16'), 65.0 (1C, Cq, s, 1).

**MS** (MALDI-ToF, m/z): 1592 (11%, M<sup>+</sup>); 1197 (100%).

**T<sub>M</sub>** 104 °C – 105 °C.

**EA** calculated: C = 36.96, H = 1.01,  
found: C = 37.09, H = 0.99.



### **Explanation of the weighted average of Figure 2**

The mean susceptibility values were computed from an average of the individual susceptibilities for each voltage point. The weight was taken to be inversely proportional to  $1/\sigma^2$ , with  $\sigma$  the size of the error bar. The only exception was the 10 kV point of compound **2**. Here the statistical error bar is extremely small, differing from the mean by 49 standard deviations. This is statistically extremely unlikely and rather points to an uncontrolled phase shift in this particular and singular event, which was therefore not included in the calculation of the mean value.

### **Complete reference [14] describing the Gaussian program used**

Gaussian 03W, Version 6.0, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03W, Version 6.0, Gaussian Inc., Pittsburgh, PA, 2003.