[^{3}H]galactose from the donor UDP-Gal (50 μM) to the acceptor molecule LacNAc(CH$_2$)$_8$CO$_2$CH$_3$ (0.36 mM) by the pα(1-3)GalT (10 μM) in an assay buffer system consisting of sodium cacodylate (100 mM; pH 6.5), 15 mM MnCl$_2$, and BSA (bovine serum albumin; 50 μg mL^{-1}) at 37 °C for 30 min. The radiolabeled product, [^{3}H]Galα(1-3)LacNAc(CH$_2$)$_8$CO$_2$CH$_3$, was separated from unincorporated label by adsorption onto a SepPac C$_{18}$ column[20]. The ratio of incorporated to total radioactivity is proportional to the activity of pα(1-3)GalT. We took precautions to ensure that the enzyme was the limiting reagent and that all other cofactors were close to the saturation point. Strictly speaking, the reported inhibition is an IC$_{50}$ value because we have not carried out the assays with different concentrations of cofactors.

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Polyphenylene Dendrimers as Sensitive and Selective Sensor Layers[**]

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Polyphenylene dendrimers (PDs) are monodisperse macromolecules, which—because of their rigid framework—contain internal voids. This property differentiates them from other dendrimers, which consist of flexible, aliphatic groups, and makes them attractive as selective layers for gravimetric sensors. Such sensors based upon the quartz microbalance (QMB)[1] are widely used to monitor the concentration of various volatile organic compounds (VOCs) in different environments. These types of sensors are of increasing significance in many aspects of daily life, be it monitoring the manufacture or storage of foodstuff,[2] controlling chem-

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ical reactions such as polymerization,[3] or safety standards in the chemical industry, such as monitoring the maximum allowed concentration of VOCs in the work environment.[4] QMBs are mass-sensitive devices, which are easy to apply, yet of low cost, and they provide both high selectivity and excellent sensitivity down to concentrations of VOCs of only 5 ppm.[5] Both properties of these gravimetric sensors crucially depend on the type of sensor-active layer coated on top of the QMBs. For this purpose, certain types of polymers[6] or organic compounds—such as lactam macrocycles or rotaxanes[7]—have been used successfully to date; even biomaterials have found application.[8] However, polymers such as polyvinylchloride (PVC) lack selectivity, and organic hosts as sensor-active layers yield insufficiently reproducible results, probably because of rearrangements or aging. Biological sensor layers are frequently rather unstable both chemically as well as thermally. For many analytes and applications specific sensor layers have to be specially prepared. Therefore, because of the variety of applications and the multitude of simultaneous requirements, high-quality sensor-active materials have to satisfy there is a high demand for durable sensor-active layers with high selectivity for many types of target guest molecules.

Herein the suitability of polyphenylene dendrimers (PDs) as sensor layers for monitoring VOCs in the gas phase will be demonstrated. PDs are ideally suited as host molecules, since PET (Positron Emission Tomography) studies have shown that they contain stable cavities in their interior.[9] Investigations of the crystal structure of different PDs of the first generation (G1) have revealed that solvent molecules are readily trapped within these cavities.[10] Accordingly, the most important prerequisites are met for PDs to qualify as hosts, namely sufficient free internal space, and the tendency to fill these voids with small guest molecules.

The synthesis of PDs starts from core units of different structure and proceeds by a cascade of Diels–Alder-type cycloadditions[11] leading to structurally quite different three-dimensional (3D) dendrimer architectures (Figure 1).[12]

The influx of functional groups in the periphery of the PDs on the sensor activity has also been investigated. For this purpose, dendrimers of the second generation (G2) have been synthesized carrying electron withdrawing (CN and COOH) or electron donating ($N{=}CPh_2$) substituents by using the correspondingly functionalized cyclopentadienone units **7**–**9** (Figure 2). This approach yields functionalized, monodisperse dendrimers in excellent yields.[13]

The coating of the QMBs with the PDs is by using a procedure from mass spectrometry known as electrospray.[7, 14] The PDs are dissolved in THF and accelerated by a high DC voltage through a thin capillary and sprayed onto the top electrode of the QMB. This leads to the formation of homogeneous, rigid layers, the thickness of which is controlled in situ by simultaneously monitoring the frequency of the QMBs to be coated. The resulting thickness is standardized corresponding to a frequency reduction of 10 kHz, at which point the coating is stopped. According to Sauerbrey this offset is equal to a mass of 44 $\mu g\,cm^{-2}$ of the coating on a 10 MHz QMB.[15] A standardized thickness (or mass) of the host compound on the QMB is a prerequisite for comparing the sensitivity and selectivity of the coatings and to assure reproducible results. QMBs coated accordingly have been sequentially exposed to different VOCs in a gas mixing chamber at 50 °C and at a universal concentration of 1000 ppm. The associated lowering of the resonance frequencies of the QMBs because of the reversible incorporation of the VOCs into the host compound is termed "sensor response" $\Delta\nu$. That the inclusion of the VOCs into the coatings occurs into the volume and is not merely a surface adsorption phenomenon follows from the observation that doubling the thickness of a coating yields twice the sensor response.

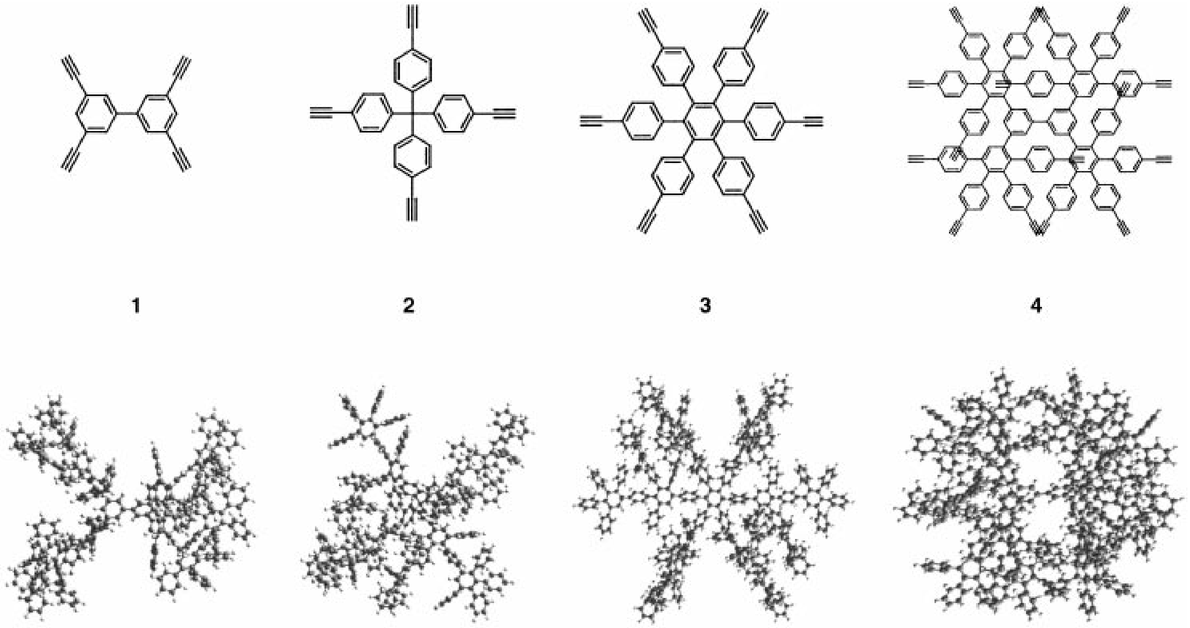

Figure 1. Various core units and resulting dendrimers. Tetraethynyl biphenyl (**1**; Biph), tetraethynyl tetraphenylmethane (**2**; Td), hexaethinyl hexaphenylbenzene (**3**; HPB) and the G1 dendrimer **4** with 16 ethynyl functions based upon the biphenyl core **1**.

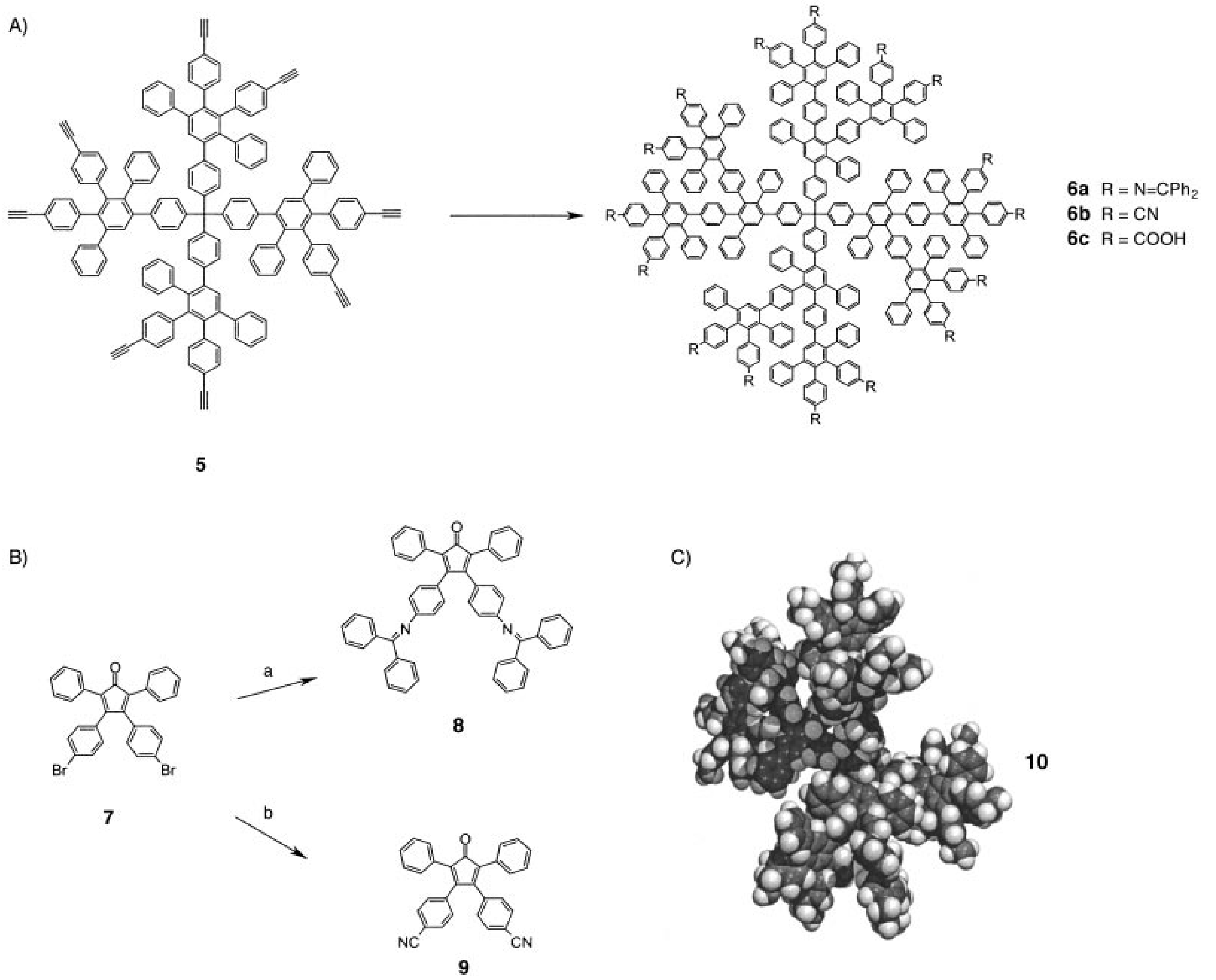

Figure 2. A) Functionalization of G2 PDs **6a**–**c** (Td-G2-(imine)$_{16}$, Td-G2-(CN)$_{16}$, and Td-G2-(COOH)$_{16}$), by Diels–Alder reaction of a G1 dendrimer **5**, which has eight ethynyl substituents, with functionalized cyclopentadienones. B) Syntheses of functionalized cyclopentadienones: **8** and **9** a) NH=CPh$_2$ (10 equiv), BINAP (12 %), CsCO$_3$ (15 equiv), [Pd(dba)$_2$] (5 mol %), toluene, 3 days, 80 °C, 86 %); b) CuCN (2.5 equiv), DMF, 90 %); BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, dba = dibenzylideneacetone C) 3D structure of a G2 PD (Td-G2-(NH$_2$)$_{16}$) **10** based upon the tetrahedral core **2** and with surface amine functions.

The first series of measurements was conducted using unsubstituted PDs of G2 derived from the four core units as outlined in Figure 1. All the investigated dendrimers show a similar behavior: all compounds react very selectively to polar aromatic VOCs, such as acetophenone, anilin, benzaldehyde, benzonitrile, fluorobenzene, nitrobenzene, and 2-methyl-benzonitrile. It is remarkable that neither chlorinated nor unsubstituted aliphatic hydrocarbons, alcohols, amines, aldehydes, or carbonyl compounds become included into these hosts; therefore, members of this list of VOCs cannot be monitored with dendrimer coatings of the type studied here. However, this observation shows that PDs are very selective host molecules (Figure 3). The sensor responses are totally reversible and reproducible: after 4 min (adsorption plus desorption time) these sensors are ready for the next measurement. The response times are very short; t_{90}-times (= the time until 90 % of the response is reached) below 2 min have been measured. A comparison of the data obtained using three different QMBs coated with the same dendrimer yielded practically identical results (deviations below 5 %).

The observed selectivity of PDs is attributed to their exclusively aromatic skeleton, which may form $\pi\pi$-electron-donor-acceptor complexes.[16] Therefore, this type of dendrimer shows a relatively weak affinity for benzene and toluene (cf. Figure 3), since the π-electron densities of these guests are virtually identical to that of the host molecule.

The host–guest interaction between the dendrimers **1**–**4** and the guest molecule acetophenone was investigated. The concentration of the analyte acetophenone was altered between 5, 10, 25, 50, 75, 100, 200, 300, and 400 ppm, at each of five different temperatures (50, 55, 60, 65, 70 °C). The plot of the resulting frequency shifts of the correspondingly coated QMBs for any of these temperatures against the concentration of the acetophenone yields isotherms (Figure 4), termed "sensor characteristics". At low concentrations they resemble the analogous Langmuir isotherms, whereas at higher concentrations they reach a linear domain. From the curvature

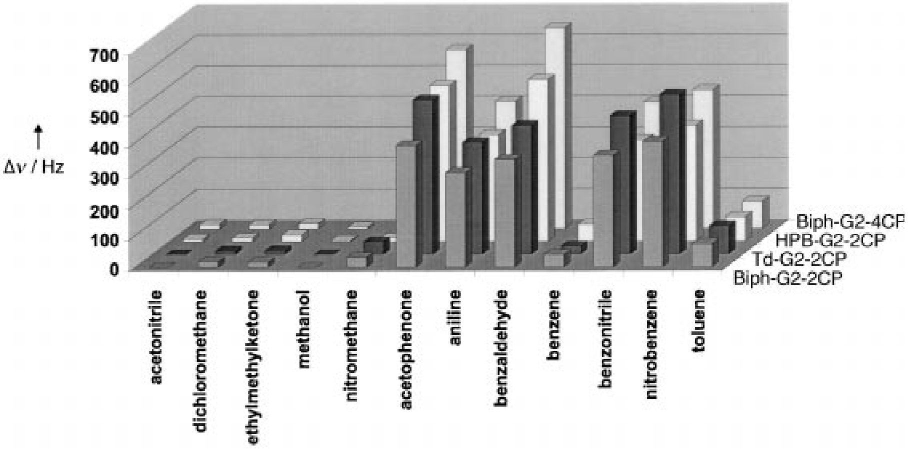

Figure 3. A selection of sensor responses of the unsubstituted G2 PDs to various volatile organic compounds (VOCs); measurement temperature = 50 °C, concentration = 1000 ppm (0.1 %). The nomenclature of the dendrimers follows from: 1) the core (Biph, Td, HPB, see Figure 1); 2) the generation; 3) the end group. 2Cp corresponds to the cyclopentadienone building-unit 3,4-bis-[4-(tri-*iso*-propylsilylethinyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (AB_2-building unit) and 4Cp corresponds to 2,3,4,5-tetrakis-[4-(tri-*iso*-propylsilylethinyl)phenyl]-2,5-diphenylcyclopenta-2,4-dienone (AB_4-building unit) leading to a higher number of phenyl rings. Both building-units are already known.[12]

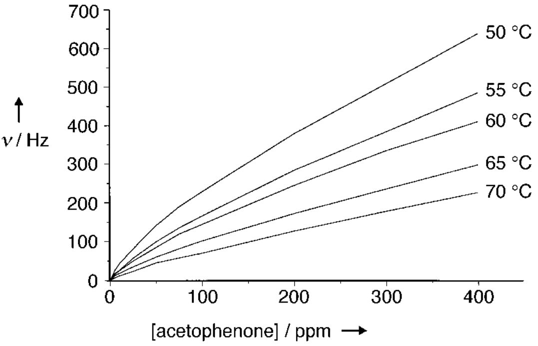

Figure 4. Plot of the sensor response Δν of Td-G2-2CP to different concentrations of acetophenone at various temperatures (sensor characteristics).

parameter of the Langmuir component the host–guest interaction can be determined using Equation (1) where b = Parameter of curvature of the Langmuir isotherm, k_A = rate constant of adsorption, k_D = rate constant desorption, E_B = binding energy, k_B = Boltzmann constant ($1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}$), T = temperature.[17]

$$b(T) = \frac{k_A}{k_D} \propto e^{\frac{E_B}{k_B T}} \qquad (1)$$

The interaction energy for the four unsubstituted PDs of the G2 **1**–**4** (Figure 1) and acetophenone as the analyte gas lies between 13.4 and 21.3 kJ mol^{-1}. From Table 1 it can be concluded qualitatively that the identity of the specific dendrimer used significantly influences the energy of the host–guest interaction with the analyte. Since the outer diameter of all four dendrimers is almost the same (about 4 nm), and since the different binding energies do not correlate with the number of the phenyl rings, the four dendrimers must contain voids of individual size or shape, into which the guests become incorporated by physisorption.

Table 1. Energy of interaction E between the PDs with acetophenone as the guest.

Host compound	E [kJ mol^{-1}]	Number of phenyl rings
Biph-G2-2CP[a]	19.1	62
Biph-G2-4CP[a]	21.3	102
Td-G2-2CP[a]	13.4	64
HPB-G2-2CP[a]	14.4	97

[a] unsubstituted.

Next, the selectivity of the sensors has been analyzed as a function of the generation of the dendrimers. For this purpose members of the G3, G3, and G4 dendrimers have been used. Thereby it has to be considered that at constant thickness of sensor layer with the increasing size (or generation) of the dendrimers the number of the host molecules is cut in half whenever the molecular weight of the dendrimer is doubled. However, whenever the size of the dendrimer is doubled, twice as many guest can be incorporated.[18] Table 2 outlines the obtained results for acetophenone as the guest molecule (1000 ppm).

Table 2. Influence of the generation n (and thus diameter d) of the PDs on the inclusion of gaseous acetophenone (1000 ppm) and thus on Δν.

n	M [g mol^{-1}]	d [nm]	Δν [Hz]	Number of guest molecules[18]
2	4868	3.8	498	1.31×10^{15}
3	9544	5.1	835	2.21×10^{15}
4	20072	6.4	2175	5.75×10^{15}

Accordingly, PDs are capable of incorporating polar aromatic guest molecules very selectively into their voids, whereby the number of the included guest molecules depends upon their size and shape. To determine the significance of various factors for the sensor characteristic of the dendrimers in more detail, the influence of terminal substituents on the inclusion properties was investigated. It was found that the PDs of G2 **6a**–**c** (cf. Figure 2), namely those based upon the tetrahedral core, each carrying 16 cyano-, carboxyl-, or imino-substituents, respectively, yield the sensor responses outlined in Figure 5. Depending on the substituent, either an enhancement or an attenuation of the binding affinity has been found using acetophenone, benzaldehyde, or 1-methyl-2-pyrrolidine (NMP) as guests. Thereby, both the electron densities of the host as well as of the guests change, as do the possibilities for adsorption. In this fashion, even nonpolar, aromatic solvents such as benzene or toluene can be detected. Remarkable is the behavior of the acid-determined dendrimer **6c**, which—for the first time—shows a striking affinity for inclusion of guest molecules carrying amine substituents (NMP, diethylamine). Therefore, dendrimer **6c** can be used to detect even

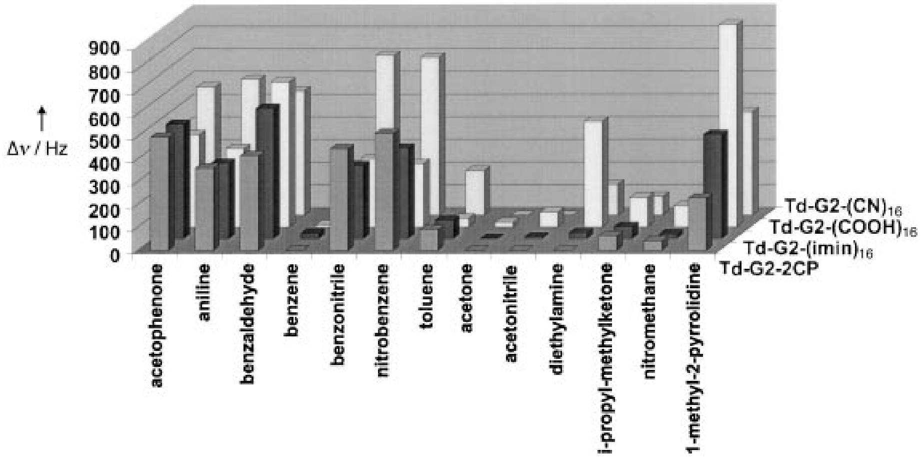

Figure 5. Change of the sensor characteristic upon terminal functionalization of the PDs; concentration of the gaseous guest compounds = 1000 ppm, measurement temperature = 50 °C.

the non-aromatic solvents acetone, acetonitrile, isopropyl methyl ketone, and nitromethane with very good sensitivity.

To demonstrate the uniqueness of these—admittedly difficult to synthesize—monodisperse macromolecules as highly selective sensor layers, series of measurements have also been performed using the hyperbranched polyphenylenes for comparison.[19, 20] The results show that these compounds yield sensor characteristics similar to those of the PDs, that is, a high selectivity for substituted aromatic solvents. However, by contrast to the dendritic analogues, the sensor responses using the hyperbranched relatives of the PDs are not reproducible, as different measurements using one and the same host yield considerable deviations of up to 80%.[20] Apparently, this is the consequence of the lack of a defined structure of the hyperbranched polyphenylenes; therefore, any individual coating of the QMBs results in different three-dimensional orientations of the macromolecules on the surface of the QMB electrodes, which gives rise to intrinsically different voids. Similar shortcomings have been observed when using commercially available, aliphatic Starburst-(PAMAM)-dendrimers.[20] The poor reproducibility of coatings consisting of the latter is probably because of their lack of structural stability. If namely the end groups of the dendrimers dive back into the interior, this causes a change in the density distribution, upon which the structures collapse.[21] By contrast, the very rigid molecular framework of the PDs assures a rather narrow variation of the voids in their interior, which in turn guarantees a high degree of reproducibility and hence assures accurate recognition and quantification of the guest molecules.

Accordingly, PDs allow the selective detection with high sensitivity and accuracy of polar aromatic target molecules (= "analytes"). The number of included guest molecules depends both on the structure and the size of the dendrimer and may be predicted, that is, a structure-property relationship applies. Incorporating functional groups enables fine tuning of the sensor properties, which makes it possible to detect even aliphatic solvents. The sensitivity of dendrimer-coated QMB sensors is remarkably high: for aniline and acetophenone it is around 5 ppm. In addition, the PDs are very stable both chemically and temperature-wise, which ensures a long-term stability of 12 to 24 months, and it guarantees reproducible results.

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