TOC
Assessing the sensing limits of fluorescent dendrimer thin films for the detection of explosive vapors

Safa Shoaee, Simon S. Y. Chen, Hamish Cavaye†, Arthur R. G. Smith, Paul L. Burn*, Ian R. Gentle, Paul Meredith, Paul E. Shaw*

Centre for Organic Photonics & Electronics, The University of Queensland, Brisbane, Queensland, 4072, Australia.

Corresponding Author

p.burn2@uq.edu.au, p.shaw3@uq.edu.au

Present Addresses

† Centre for Defence Chemistry, Cranfield University, Defence Academy of United Kingdom, Shrivenham, Swindon, SN6 8LA, UK
Abstract

Photoluminescence quenching of organic thin films is a promising technique for the detection of vapors from explosives. The photoluminescence quenching response depends on the energetics of electron transfer from the photo-excited sensing material to the analytes, the vapor pressure of the analyte, and the diffusion process of the analytes in the sensing films. It is critical that the performance of a potential sensing material be evaluated in the solid-state with a range of analytes and across a range of vapor concentrations to ensure high sensitivities through non-contact sampling is achievable. We have investigated the photoluminescence quenching of three generations of carbazole-based dendrimers across a range of nitro-containing analyte vapor concentrations, including the TNT by-product 2,4-dinitrotoluene (DNT), and the tagging agent 2,3-dimethyl-2,3-dinitrobutane (DMNB). We show that the performance of all three dendrimer generations in the solid-state is near identical. Furthermore, we show that these dendrimers have a high affinity towards nitroaromatic compounds with parts per billion sensitivity, which makes them ideal for trace-level detection.

KEYWORDS Photoluminescence quenching, Dendrimers, Analyte detection, Explosives
Highlights

- Photoluminescence quenching based detection of vapors from explosives.
- Sensing materials evaluated in the solid-state.
- High sensitivity to a range of analytes and vapor concentrations via non-contact sampling.
- Three generations of carbazole-based dendrimers have similar solid-state detection.
- Dendrimers have a high affinity towards nitroaromatic compounds with ppb sensitivity.
Introduction

The capability to detect explosives at very low concentration is essential for the provision of security but also for the remediation of minefields left from past conflicts. While there are a number of technological solutions available, many of which are based on standard analytical chemistry techniques such as mass spectrometry and gas chromatography, they tend to employ bulky complex devices that are unsuitable for field use. Cheaper and more portable solutions are often based on colorimetric detector kits, but these require the user to collect a sample from the suspicious object in order to generate a reliable response, therefore placing the user in danger. One promising technology for the standoff detection of explosive vapors is by photoluminescence (PL) quenching, where the relative simplicity of the technology needed to generate and measure the luminescent signal means that detectors can be very compact, battery powered and rugged.

At a fundamental level the sensing material needs to be luminescent in the solid-state[1-5] with the energy of the excited electron in the S\textsubscript{1} state sufficiently higher than the electron affinity of the analyte to overcome the exciton binding energy and enable electron transfer between the fluorophore and the analyte. This process is often described in terms of the relative energies of the lowest unoccupied molecular orbital (LUMO) of the sensing material and analyte.[6, 7] The sensing of analytes using PL quenching is a straightforward process. In the absence of an analyte, photo-excitation of the fluorescent sensor leads to an exciton that can decay radiatively. However, in the presence of an analyte molecule the photo-excited electron of the exciton can transfer to the analyte and form a “charge transfer” state. This state relaxes non-radiatively to the ground state by back-electron transfer and, hence, the PL of the sensing material is quenched.
There is an extensive body of published literature on PL quenching studies of potential sensing materials by nitrated analytes, but most of these were performed in solution.[8-10] However, the relevance of solution-based characterization towards solid-state detection is questionable,[10] given that the manner in which the analytes and chromophores interact with each other is different in the two phases. Given that any real-world application of this technology will likely be based upon solid-state sensing media, it is therefore essential that the performance of any potential sensing material be evaluated in the solid-state with appropriate analytes and at vapor concentrations that are below the level of a saturated atmosphere to reflect the fact that in the real world explosives are likely to be concealed or encased, which will inhibit accumulation of vapors.

We have previously reported a series of three generations of carbazole dendrimers (which we will refer to henceforth as G1, G2 and G3) that display large PL quenching responses to nitroaromatic analogues of the high explosive 2,4,6-trinitrotoluene (TNT) in solution.[11] For each dendrimer generation, four carbazole dendrons were attached to the spirobifluorene core, which leads to macromolecules with a more three-dimensional shape. It was observed that the Stern-Volmer constants with 2,4-dinitrotoluene (DNT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) approximately doubled in magnitude between G1 and G2 and then remained the same for G3.[11] These differences were caused by a change in the location of the chromophore between G1 and the higher generations. In this work we investigate the PL quenching of these dendrimers in the solid-state and the impact of dendrimer generation on the PL quenching efficiency and recovery with respect to the vapors of DNT, 4-nitrotoluene (pNT) and DMNB over a range of vapor concentrations and exposure times. Furthermore, to understand how the vapors of DNT interact with and are distributed within the dendrimer films we performed a
combination of neutron reflectometry with *in situ* PL measurements. We show that despite the significant differences in solution all three dendrimer generations perform similarly in the solid-state although the responses between the analytes themselves are different. We find that ~40 nm thick films exhibit saturated responses to DNT within 10 seconds even at concentrations as low as 4 ppb with the vapors able to diffuse throughout the film.

**Experimental**

**Sample preparation**

The synthesis of the dendrimers has been previously reported.[11] Thin films of G1, G2 and G3 on fused silica substrates were formed by spin-coating from toluene solutions at a concentration of 10 mg.mL$^{-1}$ at a speed of 2000 rpm. The substrates were rinsed with acetone and 2-propanol prior to spin-coating. The toluene was distilled by rotary evaporation, prior to use. Film thicknesses were in the range of 35-40 nm based on linear extraction of absorption measurements and thickness measurements using a Dektak 150 (Vecco).

**Steady state spectroscopy**

UV-Visible absorption spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. PL spectra were recorded on a Horiba Jobin-Yvon Fluorolog 3 fluorimeter with an excitation wavelength of 320 nm. Quenching response measurements were carried out on fused silica substrates. The samples were clamped in a custom-built sample holder (Scheme 1) in the fluorimeter. The analyte vapor was introduced into the chamber in a controlled manner by running nitrogen through a coiled section of quarter inch diameter stainless steel tubing coated on the inside with analyte. The vapor concentration delivered by the coil was calibrated by bubbling known volumes of the nitrogen stream at different flow rates through acetonitrile and determining the concentration of the dissolved analyte. To ensure all the analyte vapor was
captured by the acetonitrile, three bubblers were used in series. The flow rate and hence concentration of analyte was controlled using a mass flow controller (MFC1). The output from MFC 1 was mixed with that of a second mass flow controller (MFC2) with the resulting flow directed face-on towards the film of the sensing material. Disabling the output of MFC1 resulted in a flow of nitrogen over the sensing material film for the “recovery” experiments. Measurements were repeated 5 times and the absorbance and PL from before and after the (analyte exposed) quenching experiments was also collected to assess the level of photodegradation.

Thin film photoluminescence quantum yield (PLQY) measurements were performed using the procedure described by Greenham et al.[12] Thin film samples were photoexcited using the 325 nm output of a HeCd laser in a nitrogen-purged integrating sphere. Unless otherwise stated, the excitation wavelength used for the PL measurements was 320 nm.

**Neutron reflectometry**

Neutron reflectometry was performed using the Platypus time-of-flight neutron reflectometer and a cold neutron spectrum (2.8 Å < λ < 18.0 Å) at the OPAL 20 MW research reactor [Australian Nuclear Science and Technology Organisation (ANSTO), Sydney, Australia].[13] Neutron pulses of 23 Hz were generated using a disk chopper system (EADS Astrium GmbH) in the medium resolution mode (Δλ/λ = 4%) and recorded on a 2-dimensional helium-3 neutron detector (Denex GmbH). Reflected beam spectra were collected at 0.5° for 1 h (0.4 mm slits) and 2.0° for 4 h (1.6 mm slits). Direct beam measurements were collected under the same collimation conditions for 1 and 3 h (with attenuator) for each respective slit size. *In situ* PL spectra of the films were simultaneously measured with an Ocean Optics USB2000 spectrometer exciting with a 365 nm Nichia UV-LED. For the neutron reflectometry measurements, films of G1, G2 and G3
were spin-coated onto 2 in. silicon wafers (Si-Mat, Germany) from solutions with concentrations of 25 mg mL\(^{-1}\) in toluene at 2000 rpm to give films of thickness in the range of 85-90 nm. Glass jars containing approximately 50 mg of per-deuterated DNT (prepared by dinitration of d8-toluene) covered with cotton wool were left to equilibrate overnight. For saturated film measurements the films of the dendrimers were placed in the jars for approximately 5 h at room temperature, which ensured equilibrium between analyte vapors and analyte in the films was reached. A small amount of solid analyte was also placed in the neutron sample chamber in order to maintain equilibrium throughout the neutron reflectivity measurement. To remove the d-DNT vapors from the film and recover the PL the films were placed in a stream of clean, dry air for 5 minutes. Analysis of the reflectivity profiles was performed using the Motofit reflectometry analysis program.[14] All models include a 0.8-1.5 nm silicon oxide layer on the surface of the substrate and consist of a single organic layer of uniform scattering length density (SLD). Interfacial roughness values for the organic layers were all between 0.5 and 1.2 nm and showed little change upon exposure to and removal of the d-DNT vapors. The quoted uncertainties are calculated from the statistical uncertainties based upon the quality of the fit to the measured data.

Results and Discussion

The chemical structures of the three generations of carbazole dendrimers are shown in Scheme 2. Thin films of G1, G2 and G3 were prepared by spin coating from 10 mg mL\(^{-1}\) toluene solutions. The resultant films were 35-40 nm thick and were optically non-scattering. The UV/visible absorption and PL spectra of the spin-coated films are shown in Figure 1. The emission of the G2 and G3 films show a slight red shift in the PL peak position compared to G1, which is consistent with our previous observations in solution of a shift in the location of the chromophore from the core of G1 to the dendrons in G2 and G3.[11]
The solid-state photoluminescence quantum yield (PLQY) was found to follow the order of G1 (29 ± 2)% > G2 (25 ± 2)% > G3 (13 ± 1)%. The solution PLQY of G1 has been previously measured to be 65%[11] with the decrease in the film value assigned to inter-dendrimer inter-chromophore interactions. In contrast to G1, the solution PLQY values for G2 and G3 were very similar (within experimental error) to their solid-state counterparts.[11] The invariant PLQY along with an increase of FWHM of the PL and the emission tail at longer wavelengths observed for G2 and G3 are consistent with the emission originating from excimer-like states, as we have previously observed and discussed in this and related systems.[11, 15]

To determine whether the differences in sensing performance previously observed in solution-based measurements translate to the solid-state, we measured the changes in film PL as they were exposed to analyte vapor across a range of concentrations and exposure times using a more controlled method to that previously reported.[16] It is worth noting that while Stern-Volmer measurements provide a means of quantitatively comparing the quenching efficiency of different sensing material and analyte combinations, an equivalent methodology does not exist for the solid-state. This is a natural consequence of the fact that PL quenching in the solid-state is not just the product of interactions between individual fluorophores and analyte molecules but the interaction of the analyte vapor with multiple fluorophores within the film. This becomes very clear when you consider that although a film is exposed to a known concentration of analyte vapor it is unknown how much of that vapor is absorbed by the film or where it is located. For this reason we chose a standard film preparation method for all three dendrimers that would give films approximately 35-40 nm thick, which is relatively thick when compared to some of the thin films (<10 nm) that have been reported in the literature.[6, 17-21] The analytes used in this study were DNT, pNT and DMNB; both DNT and pNT are chemically similar to TNT with DNT an
impurity found in TNT, while DMNB is a taggant added to plastic explosives to facilitate their detection by trained canines. Crucially they all have sufficiently high electron affinities to quench the PL although they differ significantly in terms of their vapor pressures.[9]

Figure 2a shows the PL of G1 films over time as a series of 20 second pulses of analyte vapor are delivered. The traces have been offset so that their form can be compared. It is worth noting that these traces were obtained for the lowest analyte concentrations tested and therefore demonstrate the unambiguousness of the quenching response. With each analyte there is a very rapid initial quenching of the PL followed by a recovery phase where the absorbed analyte vapor is released by the film. Although the initial PL response was very similar between the analytes, the recovery behavior was very different. The PL recovery was faster for the pNT and DMNB exposed films than the respective DNT films; a typical 3% PL quench by DNT only showed an 80% recovery following 10 s of nitrogen flow, whilst films exhibiting 88% quenching efficiency by pNT analyte had a >99% photoluminescence recovery in the same timeframe. The slower desorption of the DNT molecules may be due to their distribution in the film, slower analyte vapor diffusion, i.e., the analyte molecules take longer to reach the surface and be removed, and the strength of the binding interaction with the dendrimer. We note that the first response was not as pronounced as those that followed, a feature that was repeated throughout our data. We believe this is the result of the film being conditioned by the first exposure. Quartz crystal microbalance measurements on G1 have shown that pNT diffuses into the films by Super Case II diffusion, where swelling of the film drives an accelerating analyte front through the film.[22] Hence, the deformation of the film caused by that first front facilitates the transport of subsequent fronts, which may allow the front to travel further into the film. We also note that although the PL of films exposed to DNT vapor did not fully recover between pulses, the
quenching efficiency was very similar for each subsequent pulse. For each of the three analytes the responses from the three dendrimers were very similar as shown in Figure 2b with DMNB. This is somewhat surprising given that in solution G2 and G3 exhibited greater sensitivity than G1 to DNT and DMNB. This suggests that the interactions and binding between the analyte and the dendrimer molecules are different between solution and the solid-state.[23] It could also be a consequence of how the analyte vapors interact with and diffuse into the film, a process that will only occur in the solid-state but appears to play a first order role in the sensing performance.[22]

Additional quenching measurements for all three dendrimers with varying vapor concentrations of all three analytes were performed (the exposure time remained constant at 20 seconds) with the results summarized in Figure 3a. The PL quenching efficiency was calculated from the decrease in the PL intensity relative to the intensity before exposure. From the data it is clear that the three dendrimer generations behave similarly and that the differences observed are driven by the vapor pressures and electron affinities of the analytes. Of the three analytes, the electron affinity of DMNB is the lowest,[10] which is consistent with it having a low quenching efficiency despite its relatively high vapor pressure although it is also possible that there may be weaker binding with the dendrimers because it lacks the aromatic structure that would give rise to $\pi-\pi$ stacking. The quenching efficiency is strongly dependent on the vapor concentration, but from our measurements reported herein, we can deduce that concentrations of order 1 p.p.b. will generate a measurable response. The sensitivity of these dendrimer films is competitive when compared to previously reported fluorescent conjugated polymer films,[24-26] and porous silicon-based sensors,[27] although in the latter case a catalytic oxidation step was required in the detection process.
We also investigated the effects of varying the duration of the analyte exposure at low vapor concentrations from 1 to 400 seconds with the results plotted in Figure 3b. For each analyte the response reached saturation within 10 seconds. With the exception of G1 with DMNB all other dendrimer-analyte combinations gave a rapid response that was equal to at least 50% of the saturation response after just 1 second, which suggests that diffusion of the analyte vapors into the films is both fast and efficient. These measurements are a powerful demonstration of rapid trace detection of nitro-containing compounds. However, these measurements do not provide direct evidence for how the nitrated vapors interact with the dendrimer films and why the responses are similar between the different generations or how the absorbed vapors might be distributed within the film.

To probe the diffusion of nitroaromatic vapors into thin films of the dendrimers and their distribution at equilibrium we performed neutron reflectometry on the films. The reflectivity of a film of each dendrimer was measured in the as-cast state, at equilibrium with a saturated DNT atmosphere and after “removal” of the sorbed DNT, i.e., the “recovered” film. In order to achieve contrast between the dendrimers and the DNT vapor, deuterated DNT was used for the measurements, which has a significantly higher scattering length density (SLD) than the protonated films. Neutron reflectometry does not have the sensitivity to monitor the real-time sorption process of the analytes but measurements under saturated conditions provide an upper limit on the capacity of the film to absorb and retain analyte. The measured reflectivity profiles are shown in Figure 4 with fits based on the SLD profiles in the insets. The trend is the same for each dendrimer. The as-cast films can be described as a single layer with an SLD of \(1.67 \times 10^{-6}\) Å\(^{-2}\), corresponding to a mass density of 1.07, 1.03 and 1.01 g cm\(^{-3}\) for G1, G2 and G3, respectively. Under equilibrium with a saturated d-DNT atmosphere the films absorb the vapors,
swelling by ~5 % in the process. The fits to the data suggest that the d-DNT is close to uniformly distributed throughout the film with the exception of a thin region at the interface with the substrate. The results are consistent with quartz crystal microbalance (QCM) measurements performed on G1 with pNT,[22] which showed that nitroaromatic vapors propagate through the bulk of the film via Super-Case II diffusion. As stated earlier Super-Case II is a swelling-mediated process that causes an analyte front to accelerate through the film behind which the analyte concentration is uniform. The concentration of d-DNT vapor in the saturated films is listed in Table 1 and ranges from 0.25 ± 0.02 nm⁻³ in G1 to 0.38 ± 0.02 nm⁻³ for G2. In terms of the ratio of absorbed d-DNT to dendrimer molecules for each dendrimer there is an excess of d-DNT, which is consistent with the strong quenching of the fluorescence from the films. These observations provide a possible explanation for why the PL quenching behavior is similar between the dendrimers. The excess of analyte present in the films is likely to result in a very high PL quenching efficiency, regardless of binding site, and so the observed PL changes to analyte pulses will be determined by the front propagation. Given the structural similarities between the dendrimers the analyte diffusion is expected to be similar although we cannot verify this with neutron reflectometry. Despite the efforts to “recover” the films and remove the d-DNT vapor, a residual analyte concentration of ~0.1 nm⁻³ was found to be distributed throughout the films of each dendrimer. The presence of the residual analyte in the films is supported by the PL measurements, which show strong quenching in the “recovered” films even with the removal of a significant quantity of absorbed analyte.

**Conclusion**

In summary, we have shown that films of carbazole dendrimers are capable of rapid and consistent detection of nitrated vapors, including the explosive components DNT and DMNB at
concentrations as low as 4 ppb. Repeated exposures show that the film becomes sensitized by the first exposure to nitrated vapor, which increases the sensitivity towards any following exposures. Fluorescence quenching responses were very rapid even at low vapor concentrations with saturated responses achieved within 10 seconds. Neutron reflectometry showed that the dendrimers have a large capacity to absorb analyte, with an excess of analyte under saturated conditions. Lastly, although the different dendrimer generations had been previously found to exhibit different sensitivities to the analyte in solution, these differences did not translate to the solid-state. Performance for each analyte was very similar across all three generations, which we attribute to the similar diffusion behavior of the analyte vapors with the dendrimer films. Whilst these results demonstrate the ability of our material system to detect sub-saturation levels of DMNB, DNT and pNT reversibly in the solid-state – which is a critical for developing practical sensing materials - these results also highlight the need to characterize the quenching behavior in the solid-state and the importance of understanding the mechanism of analyte diffusion.

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Biographies
Safa Shoai is a PDRF at the Centre for Organic Photonics & Electronics (COPE), School of Chemistry and Molecular Biosciences, The University of Queensland, Australia. She received her PhD from Imperial College London, UK, in 2010 on the topic of charge generation in bulk heterojunction organic solar cells. Her research interests lie in the application of optoelectrical measurements and optical spectroscopy to understand the properties of organic semiconductor devices and the development of sensing technology based on fluorescent compounds.

Simon Chen graduated with a First Class Honors degree in Chemistry from The University of Queensland in 2008. This was followed with a PhD at The University of Queensland on the effects of structure on the optoelectronic and charge transport properties of dendrimers, which he was awarded in 2013.

Hamish Cavaye graduated with a First Class Honors degree in Chemistry from the University of Oxford. He then joined The University of Queensland to do a PhD on dendrimer-based sensors for the detection of explosives, using neutron reflectometry to probe the diffusion of organic vapors into thin films. He was awarded a PhD in 2012.

Arthur Smith obtained a First Class Honors degree in Chemistry from The University of Queensland, which he followed with a PhD on the properties of materials for OLEDs with the application of neutron reflectometry to probe inter-diffusion between the organic layers. He was awarded his PhD in 2012.

Paul Burn is Professor of Chemistry and Head of the Centre for Organic Photonics & Electronics at The University of Queensland. He received his PhD from the University of Sydney before moving to Cambridge University during which he held the Dow Research Fellow at Christ's College, Cambridge. In 1992 he moved to the University of Oxford and then in 2007 moved to The University of Queensland as an Australian Research Council Federation Fellow. His research focuses on the development of organic optoelectronic materials and their application in technologies. He is a Fellow of the Australian Academy of Science and Royal Society of Chemistry.

Ian Gentle is Professor of Chemistry in the School of Chemistry and Molecular Biosciences and Associate Dean (Research) in the Faculty of Science, The University of Queensland. A PhD graduate in Physical Chemistry from the University of Sydney, he has been at The University of Queensland since 1993. During 2008-2010 he was seconded to the Australian Synchrotron in Victoria, Australia’s largest user scientific facility, as the Head of Science. His research is based on interfacial processes with applications in organic optoelectronics, energy storage and catalysis.
Paul Meredith is a Professor of Materials Physics and Australian Research Council Discovery Outstanding Researcher Award Fellow at the University of Queensland School of Mathematics and Physics. He is also co-Director of the Centre for Organic Photonics & Electronics. He received his PhD from Heriot Watt University and was a PDRF at Cambridge University’s Cavendish Laboratory before spending six years as a product development scientist with Proctor and Gamble. He joined the University of Queensland in 2001 and his research interests focus on sustainable advanced materials for applications such as solar energy conversion, sensing, light emission, electronics and bioelectronics.

Paul Shaw received his PhD in Physics from the University of St Andrews in 2009 on the topic of exciton diffusion in conjugated polymers. Since then he has worked as a postdoctoral research fellow at The University of Queensland and his currently a Queensland Advanced Fellow. His research interests lie in the application of optical spectroscopy to understand the properties of organic semiconductor and the development of sensing technology based on fluorescent compounds.
Figures

Scheme 1. Schematic diagram of the photoluminescence quenching experimental setup.

Scheme 2. Chemical structures of the three generations of carbazole dendrimer: G1, G2 and G3.
Figure 1. Normalized absorbance and PL spectra for films of the G1, G2 and G3 dendrimers.
Figure 2. PL quenching and recovery of films of a) G1 after quenching at fixed vapor concentration of 4 ppb (DNT), 60 ppb (DMNB) and 80 ppb (pNT) for 20 seconds. During the recovery phase the films under a stream of nitrogen. b) PL quenching and recovery of dendrimer films with DMNB.
Figure 3. Photoluminescence quenching efficiency of G1 (red), G2 (black) and G3 (blue) films during exposure to vapors of DNT, DMNB and pNT, a) at a fixed exposure time of 20 s subject to different concentrations and b) at fixed vapor concentration of 4 ppb (DNT), 60 ppb (DMNB) and 80 ppb (pNT) for different exposure times.
Figure 4. Neutron reflectivity profiles of as-cast, d-DNT saturated and recovered films of a) G1, c) G2 and e) G3. The profiles have been offset for clarity. The corresponding PL spectra are included in the respective insets. The SLD profiles corresponding to the fits to the reflectivity data are shown for b) G1, d) G2 and f) G3.
Table 1. Summary of the characteristics of the dendrimer (Gx) films as measured by neutron reflectometry in their as-cast, d-DNT saturated and recovered states

<table>
<thead>
<tr>
<th></th>
<th>Mass density g.cm⁻³</th>
<th>Film thickness (as cast) nm</th>
<th>DNT concentration (saturated) nm⁻³</th>
<th>DNT concentration (recovered) nm⁻³</th>
<th>Gx:DNT ratio (saturated)</th>
<th>Gx:DNT ratio (recovered)</th>
<th>Swelling (saturated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>1.07</td>
<td>89.4±0.1</td>
<td>0.25±0.02</td>
<td>0.08±0.01</td>
<td>1:1.16±0.07</td>
<td>1:0.37±0.01</td>
<td>4.0%</td>
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<tr>
<td>G2</td>
<td>1.03</td>
<td>89.3±0.1</td>
<td>0.38±0.02</td>
<td>0.10±0.01</td>
<td>1:3.89±0.22</td>
<td>1:0.97±0.01</td>
<td>5.6%</td>
</tr>
<tr>
<td>G3</td>
<td>1.01</td>
<td>87.9±0.1</td>
<td>0.32±0.02</td>
<td>0.10±0.01</td>
<td>1:6.72±0.41</td>
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