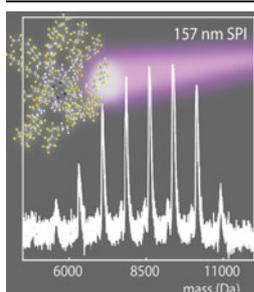


## RESEARCH ARTICLE

# Single-Photon Ionization of Organic Molecules Beyond 10 kDa

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**Abstract.** The volatilization and soft ionization of complex neutral macromolecules at low energies has remained an outstanding challenge for several decades [1]. Most volatilization techniques in mass spectrometry produce ions already in the source and most of them lead to particle velocities in excess of several hundred meters per second. For many macromolecules, post-ionization is inefficient since electronic or optical excitations can be followed by competing non-ionizing internal conversion, electron recapture, or fragmentation processes. Here, we explore the laser-assisted volatilization of neutral perfluoroalkyl-functionalized tetraphenylporphyrins as well as their single-photon ionization using vacuum ultraviolet (VUV) light at 157 nm. A systematic investigation of the ionization curves allows us to

determine the molecular velocity distribution and ionization cross sections. We demonstrate the detection of single photon ionized intact organic molecules in excess of 10 kDa from a slow molecular beam.

**Key words:** Single-photon ionization, VUV ionization, Slow molecular beams, Tailored porphyrin derivatives

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## Introduction

Many molecular beam experiments are concerned with the ability to generate and manipulate beams of organic molecules as well as to finally detect and identify them in, for instance, time-of-flight (TOF) or quadrupole mass spectrometry (QMS). In many applications, launch and ionization of the analyte molecules are coupled in a single step. This is, for instance, the case in matrix-assisted laser desorption (MALDI) [2] and electrospray ionization (ESI) [3], which have become routine tools of modern mass analysis [4].

While the presence of charged analytes is essential even for their volatilization in the case of electrosprays, laser desorption is known to produce more neutrals than ions in the first place [5]. A subsequent analysis would then profit from the availability of an efficient and soft post-ionization mechanism. This has also remained an important challenge for those investigations that aim at characterizing neutral molecules after collisions, deflection [6], spectroscopy, and advanced experiments on the foundations of quantum physics [7–9].

Our own studies are motivated by matter-wave experiments, which contribute to the discussions about possible limits of quantum delocalization in physics and chemistry [10, 11], and which enable new measurements of internal molecular properties [12]. A recent study already achieved showing that even molecules composed of more than 400 atoms could be delocalized as entire particles and still exhibit high-contrast quantum (de Broglie) interference [9]. Extensions of such experiments will profit from slow beams of neutral macromolecules, which are susceptible to single-photon ionization in UV/VUV standing light-wave nanogratings [13–15].

Slow molecular beams can, for instance, be generated by thermal sublimation or evaporation. A mass limit to this technique is, however, imposed by the particles' thermal stability. Complex biomolecules exhibit a high polarizability and often an electric dipole moment, which binds them to each other. They rather denature or fragment than evaporate or sublimate. This problem can be overcome by perfluoroalkyl-functionalization of a stable organic core. This may reduce their polarizability and raise their volatility [16]. But even then, the sublimation and evaporation enthalpy increases with the molecular mass. This necessitates increasing the heat transfer in the volatilization of more complex molecules, which also increases the probability of their thermal degradation.

Electrospray ionization avoids this problem and allows producing isolated organic molecules. High charge-to-mass ratios and high molecular beam velocities make this technique, however, inadequate for immediate use in applications such as neutral molecule spectroscopy or quantum interference experiments.

Thermal fragmentation can also be minimized in pulsed laser desorption because it limits both the interaction time and the exposed molecular sample in a well-focused nanosecond laser pulse. This strategy has contributed to the success of MALDI, which takes intact and mainly singly charged molecular ions into the gas phase, even at masses beyond 5 MDa [17]. In contrast, neutral particle experiments profit from the absence of acidic matrices, which favor charge transfer and can rely on direct laser desorption followed by a soft post-ionization detection scheme.

Several experimental groups have tackled the post-ionization of large molecules: most biomolecules have vertical ionization energies in excess of 8 eV [18–21] with ionization yields saturating close to energies around 20 eV [22]. Single-photon ionization (SPI) then requires light sources with wavelengths shorter than available in commercial lasers (i.e., shorter than 157 nm).

In contrast, multiphoton ionization (MPI) has been shown to work well for a variety of small molecules [21]. The lack of photoionization data for massive oligomers has been explained [21] by an enhanced fragmentation rate in polar oligomers. For less polar structures MPI was successfully extended to jet-cooled perfluorinated polyethers with masses up to 7 kDa [23].

Also, the use of ultra-short laser pulses has proven to be beneficial for a number of small molecules [24], as they can lead to ionization even before the onset of non-radiative relaxation. However, this idea has not yet led to the systematic extension of soft-ionization to high-mass molecules.

More recently, it has been suggested that the tagging of large biomolecules with light chromophores can facilitate their detection [25]. This idea has also been corroborated in our own studies on the photo-detection of large neutral amino acid and nucleotide clusters [26]. We here extend it to larger and covalently bound organic molecules.

Tetraphenylporphyrin (TPP) and its derivatives have already been studied in various experiments [27, 28]. Both UV multi-photon [29] and VUV single-photon [30] ionization are possible for an ionization potential of about 6 eV [31]. This raises the question how to integrate TPP into a larger molecule to realize the soft laser desorption (LD) of these tailor-made compounds as slow particle beams as well as to optimize their efficient and soft single-photon ionization.

We here follow the idea that the attachment of highly fluorinated side chains will leave the ionizing TPP core unperturbed. The functionalization will add mass and reduce the intermolecular binding such that it becomes possible to release the particles at lower energy and lower velocity from

a bulk sample. At the same time, these side chains will not modify the non-polar character of TPP. This is beneficial for the desorption and ionization process [21] as well as for certain future quantum experiments [32]. In the following we describe the molecular synthesis, neutral laser desorption of slow beams, as well as the single-photon ionization of tailor-made particles in excess of 10 kDa.

## Experimental

### Materials

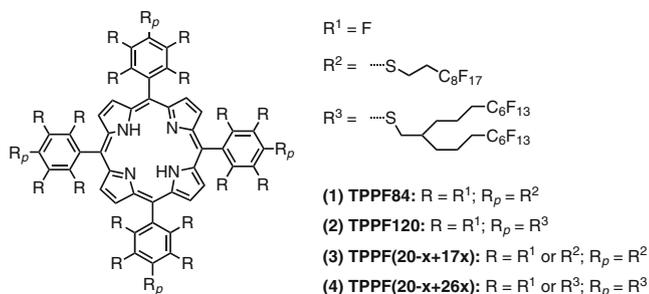
The molecules of our study are TPPF84 (**1**), TPPF120 (**2**), TPPF(20-x+17x) (**3**), and TPPF(20-x+26x) (**4**), as sketched in Figure 1. Compounds (**1**) and (**2**) are monodisperse and chemically pure samples, whereas the structures (**3**) and (**4**) were synthesized as molecular libraries (i.e., mixtures of molecules with the same core but with a different number of side chains). All porphyrin derivatives were synthesized by the attachment of highly fluorinated thiols to meso-tetra(pentafluorophenyl)porphyrin in nucleophilic aromatic substitution reactions. The 4-fold substituted derivative TPPF84 was assembled using commercially available 1H,1H,2H,2H-perfluorododecane-1-thiol as nucleophile. Under the applied reaction conditions, which are described elsewhere, the substitution takes place mainly at the activated *para*-position of the pentafluorophenyl moieties [13]. To obtain TPPF120, a branched fluorinated thiol precursor was synthesized in seven reaction steps prior to the attachment to the porphyrin [17]. Both compounds were obtained as monodisperse and pure samples after purification by column chromatography. The libraries TPPF(20-x+17x) and TPPF(20-x+26x) were obtained by the reaction of meso-tetra(pentafluorophenyl)porphyrin with a large excess of 1H,1H,2H,2H-perfluorododecane-1-thiol and the tailor-made branched thiol, respectively, and under harsher conditions compared with 4-fold substituted derivatives. The isolated product mixtures were used without further separation for the volatilization and ionization studies.

### Soft Laser Desorption and Post-Ionization

Our beam line is shown in Figure 2. Laser desorption is followed by photoionization in the extraction volume of a linear TOF-MS further downstream. The sample is prepared on a stainless steel plate from pure analytes, using a dried-droplet technique: for that we dissolve the compounds in acetone, for (**1**) and (**2**), or ether, for (**3**) and (**4**) without any additional matrix.

The molecular beam is formed by desorption of the pure analytes using a nitrogen laser at 337 nm (VSL-337, Laser Innovations). Its pulse energy of 250  $\mu$ J is focused onto the sample.

Two deflection electrodes in front of the mass spectrometer are set to  $\pm 60$  V to deflect a charged fraction from the molecular beam and to null the mass spectrometer signal.



**Figure 1.** Structure of the fluorinated porphyrin derivatives explored in the experiments. The central part of the molecule—the tetraphenylporphyrin structure—stays identical, while the number and composition of side chains attached (denoted by R) to the phenyl ring varies. **(1)** TPPF84 with the sum formula  $C_{84}H_{26}F_{84}N_4S_4$  and an average molecular weight of 2815 Da; the four  $R^2$  side chains are attached to the *para*-positions. Compound **(2)** TPPF120= $C_{124}H_{38}F_{120}N_4S_4$  with a molecular weight of 3991 Da contains the side chain  $R^3$ . Mixtures **(3)** TPPF(20-x+17x)= $C_{44}H_{10}F_{20-x}N_4(S(CH_2)_2C_8F_{17})_x$  and **(4)** TPPF(20-x+26x)= $C_{44}H_{10}F_{20-x}N_4(SCH_2CH((CH_2)_3C_6F_{13})_2)_x$  represent two different molecular libraries with varying numbers of the side chains  $R^2$  **(3)** and  $R^3$  **(4)**. The components of **(3)** appear most probably with  $x=14$  (7417 Da). Library **(4)** was present with  $x=9-12$ , with a most probable  $x=11$  (9363 Da)

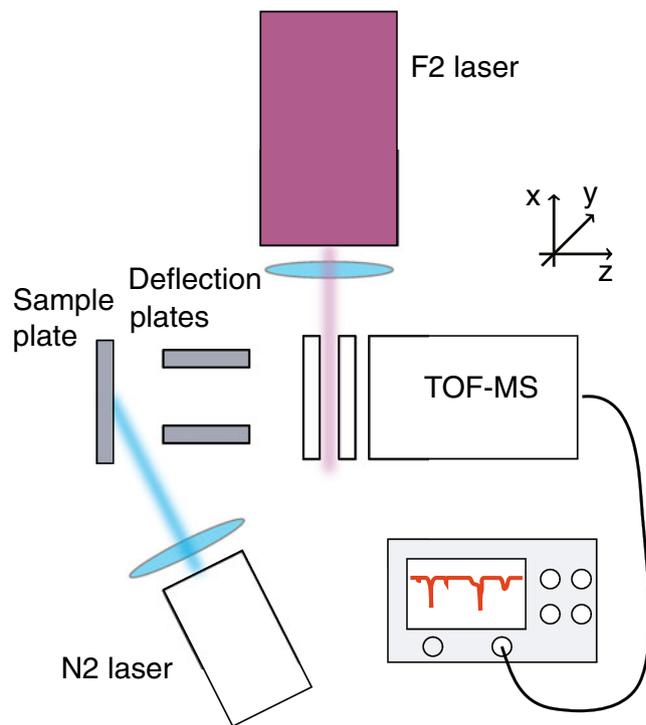
The neutral molecules are photoionized by the pulsed radiation of an  $F_2$  excimer laser (EX5; GAM Inc., Orlando (FLorida) USA 157.6 nm) with a pulse duration of 5 ns and a maximal pulse energy of 1.5 mJ. The photo-ions are detected by a linear TOF-MS (Kaesdorf,  $m/\Delta m=100$ ,  $U_{acc.}=18$  kV). We average over 16 to 30 laser shots, with a fresh sample spot exposed for every optical pulse. By varying the delay time between the desorbing and the ionizing laser pulse, we assess the different velocity classes.

## Results and Discussion

### Mass Spectra

In Figure 3a–d, we show the mass spectra for compounds **(1)** and **(2)** as well as the libraries **(3)** and **(4)**. They were all recorded at the highest pulse energy of both the desorption and the ionization laser. The delay times between desorption and ionization differ for compounds **(1)–(4)**, since their peak intensities depend on the velocity. In Figure 3a, the cation of the intact molecule is indicated by  $M1^+$  and several fragments are visible as  $M1-(R1-S), \dots, M1-4 \cdot (R1-S)$ . The relative peak height of the precursor and product ions varies with the delay time between desorption and ionization. At shorter delays, corresponding to the arrival of faster molecules, we observe predominantly molecular fragments. At long delays (i.e., for slower molecules) the intact precursor molecule dominates.

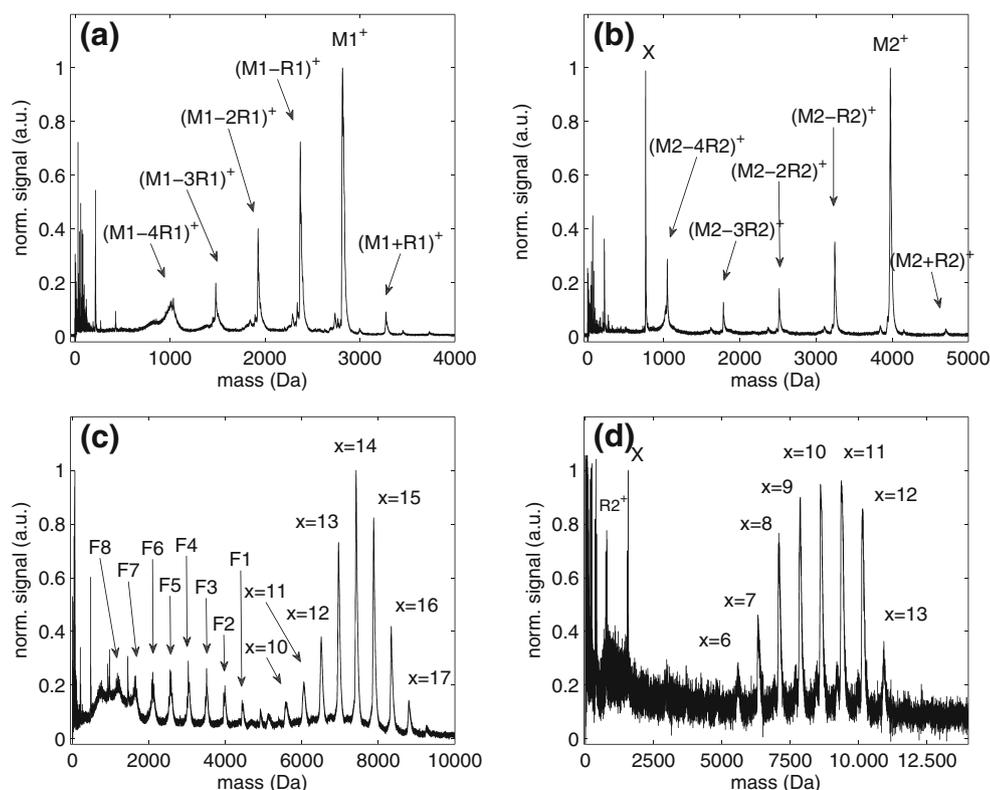
We interpret this as an indication for thermally induced fragmentation of the precursor particles. Fast molecules



**Figure 2.** Laser-desorption and photoionization of high-mass TPP derivatives. The desorption plume passes through a pair of deflection electrodes to remove the charged content. The remaining neutral molecules enter the ionization region in the extraction TOF-MS volume. The  $F_2$  laser emits pulsed radiation at 157 nm, which is guided to the mass spectrometer in an enclosure purged with dry nitrogen. The focal parameters of the  $N_2$  laser were  $f=+1000$  mm,  $w_y=0.95$  mm,  $w_x=1.2$  mm for compounds **(1)–(3)** and  $f=+300$  mm,  $w_y=0.63$  mm,  $w_x=1.55$  mm for molecule **(4)**

originate in hotter parts of the desorption plume. When the internal and external degrees of freedom are correlated, fast molecules are expected to exhibit a higher internal temperature and more fragmentation than the slow ones.

For molecule **(2)**, the spectrum of Figure 3b shows again an intact precursor peak  $M2^+$  together with its fragments  $(M2-R^2)^+$  to  $(M2-4 \cdot R^2)^+$ . The peak denoted by X is consistent with  $CH_2CH((CH_2)_3C_6F_{13})_2^+=[R^3-S]^+$  (e.g., a single side chain without the sulphur atom attached). Mixture **(3)** represents the molecular library TPPF(20-x+17x): all molecules have the same TPP core but a varying number of side chains  $R^2$  attached to it, with the different abundances due to the synthesis process. This is reflected in the mass spectrum of Figure 3c. These peaks represent the ionized intact TPP derivatives, differing in mass by the weight of a single side chain minus the fluorine atom. Peaks F1–F8 differ by about  $478 \pm 40$  Da. This is consistent with the clustering of side chains without any coordinating TPP. Mixture **(4)** originates from the molecular library TPPF(20-x+26x), by the addition of  $R^3$  side chains to the TPP core.



**Figure 3.** Mass spectra of different perfluoroalkyl-functionalized TPP compounds. **(a)** Compound (1). We identify the intact precursor ion, molecular fragments as well as a well-defined splitting at the sulfur bond. The hypothesis of partial fragmentation in the source is corroborated by the observation of  $(M1+R1)^+$ : since the initial sample contains neither this mass nor any one higher than this, it can only be explained by molecular decomposition in the source and cluster formation in the desorption plume. Waist of the F2 laser in a–c:  $w_x=8$  mm,  $w_z=0.6$  mm; d:  $w_x=10.2$  mm,  $w_z=0.4$  mm. **(b)** Compound (2). The explanation is similar to (a). The relative peak height is determined by the relative time delay between desorption and ionization. **(c)** Library (3). The mass spectrum reveals the components of the molecular library, denoted as  $x=10\dots17$  with  $x=14$  as the most probable number of side-chains. The peaks F1 ... F8 correspond to clusters of side chains without the TPP core. **(d)** Mixture (4). The detected number of side chains ranges from 6 to 13 with  $x=11$  being most prominent. Laser desorption and soft photoionization is even possible for masses in excess of 10 kDa, here for  $x=12$  and  $x=13$ , respectively

### Slow Beams of Neutral Macromolecules up to and Beyond 10 kDa

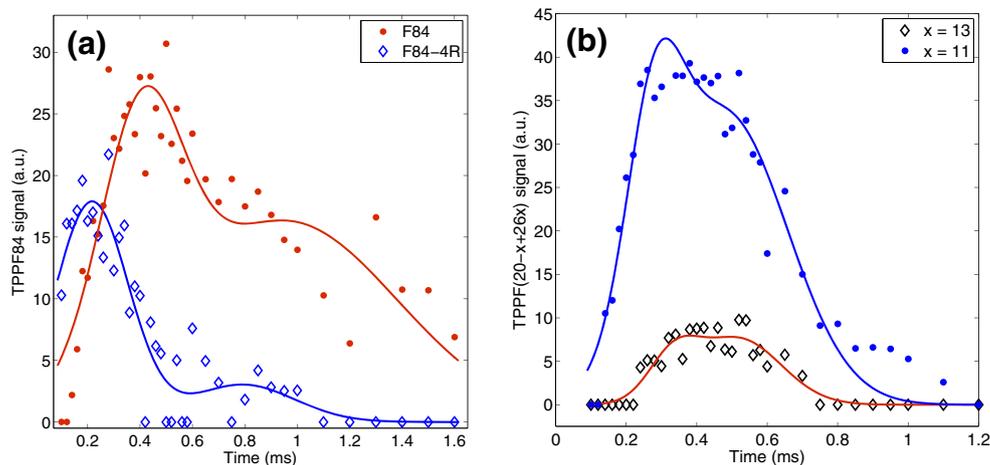
Slow molecular beams are important in many experiments. We associate, for instance, a de Broglie wavelength of  $\lambda_{dB}=400$  fm to a molecule at 10 kDa and 100 m/s, which would be still compatible with existing molecule interferometers [10]. Also in electric or magnetic molecule deflectometry [33–35], the maximal shift of the molecular beam is inversely proportional to the square of the particle velocity and a larger shift enables measurements of higher precision.

Recent experiments on laser desorption/VUV postionization [36] showed that higher desorption energies can even lead to lower translational temperatures in amino acid beams. This can be attributed to the influence of high plume densities and more collisional cooling of the emerging molecules. Our own experiments also explore the velocity distributions in laser desorption of pure, neutral, and matrix-free macromolecules with an emphasis on slow rather than

cold beams. In Figure 4 we compare in particular the lightest **(1)** and the most massive molecule **(4)** and their fragments.

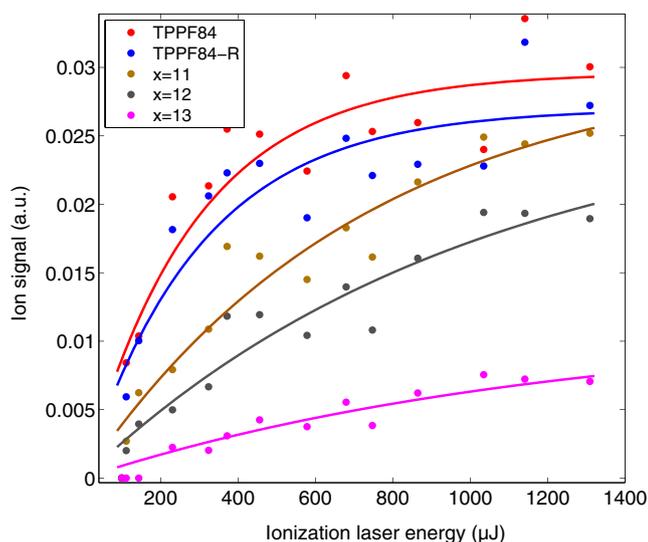
The data of TPPF84 shows a non-thermal, bi-modal flight time distribution. A best fit to the data is obtained by the sum of two Gaussians with the most probable velocities of  $\hat{v} = 76$  m/s and  $\hat{v} = 179$  m/s. In Figure 4a, the broad tail of the flight time distribution shows that relative strong signal intensities even for velocities smaller than 100 m/s can be reached. The lightest fragment of this molecule, TPPF84-4R, displays a similar spread in velocity compared with the intact precursor ion, but shifted to minor flight times. This experimental data set is fit best by the sum of two Gaussians as well. Here, the two most probable velocities are  $\hat{v} = 91$  m/s and  $\hat{v} = 333$  m/s, respectively.

Figure 4b shows a non-thermal flight time distribution of the  $x=11$  and  $x=13$  compound of TPPF(20- $x$ +26 $x$ ), which is again best fit by the sum of two Gaussians. A numerical fit yields most probable velocities  $\hat{v} = 149$  m/s,  $\hat{v} = 259$  m/s, and  $\hat{v} = 139$  m/s,  $\hat{v} = 216$  m/s ( $x=11$  and  $x=13$ , respectively).



**Figure 4.** Flight time distribution of neutral TPPFx compounds. Post-ionization signal as a function of the molecular flight time of (a) TPPF84 (intact molecule and lightest fragment) and (b) TPPF(20-x+26x),  $x=11$  as well as  $x=13$ . The data in (a) were fitted by a sum of 2 Gaussians (shown as lines). Significant signal can still be achieved for velocities slower than 100 m/s. The data of the high-mass library (b) were fit by a sum of two Gaussians as well

When comparing the speeds of the different components within the molecular library TPPF(20-x+26x), we observe a size-dependent velocity slip for the compounds  $x=9$ ,  $x=10$ ,  $x=11$ ,  $x=12$ , and  $x=13$  (not all data shown). Especially for the larger molecules the fast part of the velocity distribution is slowed. Similar to TPPF84, significant part of the peak intensity can be observed at velocities smaller than 130 m/s.



**Figure 5.** VUV ionization cross sections of perfluoroalkyl-functionalized TPP compounds. A plot of the ion yield versus laser energy allows the determination of the ionization cross section. Here, only several molecules of compounds 1 and 4 are presented. The points represent measured data, while the lines are fits according to Equation 1

### VUV Ionization Cross Sections

We have seen that large TPP-derivatives can be ionized by 157 nm light. For applications in future quantum coherence studies, we additionally require that they undergo single-photon ionization with a cross section in excess of  $5 \times 10^{-17} \text{ cm}^2$  to fit our quantum interferometers [15]. In order to determine the ionization cross section we measure the ion signal as a function of the VUV laser intensity at a fixed delay (i.e., a fixed molecular velocity (175 m/s)). We find a functional form, which is consistent with the saturation of a single-photon process [37].

$$S(P_L) = S_{sat} [1 - \exp(-\sigma \frac{P_L}{hv} \Delta t)] \quad (1)$$

**Table 1.** Ionization cross section for TPPF84 and TPPF(20-x+26x). The measured ionization laser energy dependence allows us to extract the ionization cross sections for the two molecular compounds. With increasing complexity of the molecular structure the ionization cross section decreases

Molecule	$\sigma$ ( $10^{-17} \text{ cm}^2$ ) (90 % Confidence bounds)
TPPF84	
TPPF84	18 (9/28)
TPPF84-R	17 (8/27)
TPPF84-2R	14 (5/21)
TPPF84-3R	9 (1/2)
TPPF84-4R	4 (-3/11)
TPPF(20-x+26x)	
$x=9$	2 (0/6)
$x=10$	5 (2/8)
$x=11$	7 (3/11)
$x=12$	5 (1/9)
$x=13$	5 (0/10)

Here,  $S_{\text{sat}}$  denotes the saturation signal,  $P_L$  the laser power density,  $\Delta t$  the pulse duration of the ionizing laser and  $\sigma$  the ionization cross section.

The data in Figure 5 follow a saturated single-photon absorption curve and all molecules exhibit an ionization cross section of  $\sigma_{\text{ion}} \geq 5 \times 10^{-17} \text{ cm}^2$ , as shown in Table 1.

Any ionization process in mass spectrometry is only as useful as it preserves the initial molecular distribution. While electron ionization is known to generate substantial fragment peaks [38, 39] and multi-photon ionization is often accompanied by new compounds [40], single-photon ionization may take the electron into the continuum with little internal heating. Figure 5 shows an overall increase of all mass signals with growing ionization energy with only little fragmentation. The molecular fragments in Figure 3 are therefore dominantly caused by the desorption process.

## Conclusions

We have shown that a new class of large perfluoroalkyl-functionalized TPP molecules is well suited for laser desorption and single-photon ionization. While earlier experiments showed the efficient two-photon, multiphoton ionization [21, 23] or the use of dye tagging for the enhanced single photoionization [41] of large molecules, they were performed with particles entrained in a supersonic expansion. In contrast, our self-seeded molecular beam exhibits a velocity distribution with a substantial fraction slower than 100 m/s the single-photon ionization of intact organic molecules beyond 10 kDa.

The combination of low velocities and non-destructive ionization is relevant for applications in molecule deflectometry and quantum studies. It is an interesting challenge to further explore the concept of molecular functionalization or decoration and its possible mass or complexity limits. Future particles could, for instance, be based on compound (4) and be extended by a second order dendritic layer. But also the coloring of nanocrystals with photosensitive dyes will be a worthy challenge for chemical synthesis and subsequent molecular beam experiments.

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