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Steric hindrance dependence on the spin and morphology properties of highly oriented self-doped organic small molecule thin films†

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Introducing charge carriers is of paramount importance for increasing the efficiency of organic semiconducting materials. Various methods of extrinsic doping, where molecules or atoms with large/small reduction potentials are blended with the semiconductor, can lead to dopant aggregation, migration, phase segregation, and morphology alteration. Self-doping overcomes these challenges by structurally linking the dopant directly to the organic semiconductor. However, for their practical incorporation into devices, self-doped organic materials must be cast into thin-films, yet processing methods to allow for the formation of continuous and uniform films have not been developed beyond simple drop-casting. Whilst self-doped organic molecules afford the remarkable ability to position dopants with molecular precision and control of attachment mode, their steric bulk inevitably disrupts the crystallization on surfaces. As such, there is great interest in the development of processing modalities that allow deposited molecules to converge to the thermodynamic minimum of a well-ordered and highly crystalline organic thin film instead of getting trapped in local disordered minima that represent metastable configurations. By contrasting drop casting, ultrasonic deposition, and physical vapor deposition, we investigate the free energy landscape of the crystallization of sterically hindered self-doped perylene diimide thin films. A clear relationship is established between processing conditions, the crystallinity and order within the deposited films, the dopant structures and the resulting spin density. We find physical vapor deposition to be a robust method capable of producing smooth, continuous, highly ordered self-doped organic small molecule thin-films with tailored spin concentrations and well-defined morphologies.

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Introduction

Organic semiconductors (OSCs) can generally be subdivided into two major categories, *i.e.*, polymers and small molecules. The latter has attracted considerable attention from the semiconductor community because they possess many unique advantages over their polymeric counterparts. Chain length distribution, polymer architecture, local and global morphological ordering, and polymer microstructure are confounded by even small variations in monomer selection and synthetic procedures.^{1–3} Organic small molecules are more structurally homogeneous and synthetically modular than polymers, making them attractive for organic semiconductor applications.⁴ The intended use of a given small molecule OSC will dictate the specific properties it must possess. Some applications require

highly specific properties that may be noninterchangeable between platforms, such as particular orientation, electronic structure, or photophysical properties.^{3–13} There are, however, some general characteristics of functional small molecule OSCs that are generally commutable. Speaking in the broadest sense, a good OSC will have a substantial degree of preferential molecular organization and it will be effectively doped to account for their low charge carrier concentrations.¹⁴

Doping is an essential step in achieving any functional OSC regardless of its categorization.^{15,16} While several doping strategies have been employed for polymeric systems (*e.g.*, extrinsic doping, intrinsic doping, thermally activated *in situ* doping, *etc.*), small molecule OSCs are almost ubiquitously doped with other small molecules possessing desirable ionization potentials.^{15,17–26} Molecular n-type doping is achieved by mixing low ionization potential containing species with the OSC and subsequently optimizing solution-based processing conditions to obtain ordered thin-films. A number of debilitating issues typically arise when molecular doping is employed. For example, when a dopant is mixed with a host OSC, the solubilities of the respective species may be very

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different from one another.^{27,28} Solubility differences between the host and dopant results in inhomogeneous mixing. Phase segregation of the solvent orthogonal species and subsequent aggregation of the dopant during film fabrication have been the historically canonical hurdles in OSC development.^{22,29} Inhomogeneous mixing of dopants is detrimental because aggregation leads to local grain boundaries that decrease electron mobility values and stifle doping efficiency.^{30,31} Furthermore, phase segregation is known to occur at even modest doping concentrations (<0.1%).¹⁹ There is a wealth of literature solely dedicated to improving the miscibility between dopants and OSC hosts, owing to the great importance of achieving a homogeneous distribution. However, this process is time-consuming and may yield only limited results for a given pair. Furthermore, it has been demonstrated that entirely different morphological phases may arise when optimizing dopant concentration.^{32,33} In such scenarios, changes in the carrier concentration from doping are convoluted with changes to a material's altered electronic structure *via* morphological differences. This convolution makes it very difficult to precisely determine the source or nature of any material observable that is simultaneously sensitive to both carrier concentration and morphology (*e.g.*, electrical conductivity, electron mobility, *etc.*). Elevation or suppression of the observable can only be adequately described in a system where the morphology is primarily unchanged while the carrier concentration is modified or *vice versa*.^{13,29,34} Beyond intrinsic material parameters, the deconvolution of these properties is essential for the optimization of several electronic devices, such as organic thermoelectrics, where the figure of merit, *ZT*, is maximized by fine tuning the carrier concentration for a particular material quality factor.³⁴ Finally, the introduction of dopants modifies the density of states near the Fermi-energy such that populated states now exist at some energy relative to the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) of the OSC. Upon charge transfer, the energies of these states distort in ways that may be very difficult to predict, leading to a broadened density of states.^{15,35} The physical distribution of dopants within a host matrix directly affects the density of states, which is relevant for a number of applications.^{7,15,20} Self-doping intrinsically mitigates these issues (*vide infra*).

Furthermore, perylene diimides (PDIs) with covalently-bound amino functional groups, such as those depicted in Fig. 1A, have been shown to form stable radical anions at room temperature and have demonstrated great promise in many applications including photovoltaic transport layers, n-type thermoelectrics, battery cathodes, WORM memory devices, biological and chemical sensing, as well as chromic and thermotropic liquid crystals for thin-film polarizers.^{36–49} However, any future incorporation of these materials into practical next-generation functional devices will require a robust processability method for producing high-quality thin-films. Despite the rising interest, attempts to fabricate thin-films have been limited to drop-casting from chloroform solutions (or water after methylation of the amine), which often produces rough and discontinuous films with little to no control over thickness.^{37,46,50} As such, drop-casting is usually not amenable

to large scale processing and is seen as an inferior method of thin-film production. Here, we report a robust physical vapor deposition fabrication process capable of yielding highly oriented, uniform, and continuous self-doped organic thin-films. We believe this method can be extended to the fabrication of other self-doped organic small molecule thin-films that are not amenable to solution processing.

Results and discussion

Self-doping, a process known by several names in the small molecule literature including “intrinsic doping,” or “push-pull,” can be generally understood to mean an n-type organic semiconductor that has been doped by a covalently bound electron source.^{36,51–54} Fig. 1 depicts the series of self-doped organic molecules (perylene diimides, PDIs) that were synthesized and fully characterized (Fig. S1–S6, ESI[†]) using a simplified method developed in our laboratory (#4 was purchased directly from Sigma Aldrich without further purification). Experimental details are available in the supporting information. Very little is known about the impact of self-dopant architecture on the doping process. Regarding PDIs, previous reports have been limited to tertiary and quaternary methylamines, yet there are several reasons one may choose to modify this architecture.^{36,37,46,47} Dimethylamines attached to chromophores are known to undergo a photoinduced electron transfer process to generate the PDI radical anion PDI^{•−}.^{55–57} However, the precise variables affecting the reactivity or subsequent stability of the resultant radical amines R'-NR2^{•+} are unclear. Some architectures are prone to degradation of the amine moiety while others exhibit pronounced stability.^{50,58,59} However, since there are no clearly established self-dopant design

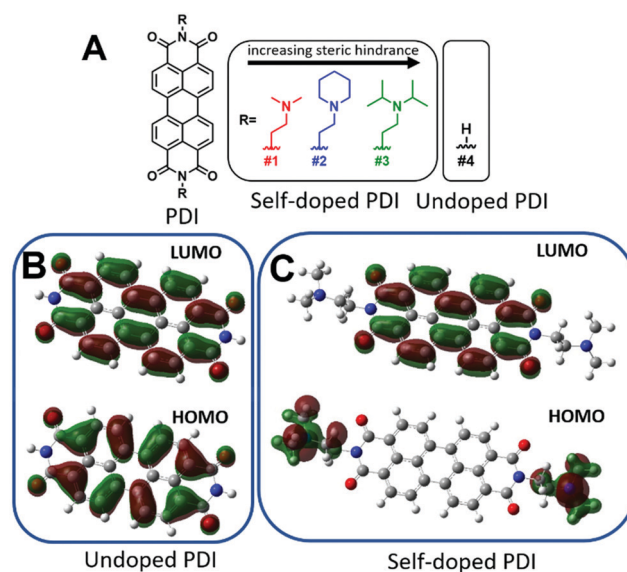


Fig. 1 (A) Chemical structures for self-doped and undoped PDIs. The self-doped PDIs are ordered as a function of increasing steric hindrance. Gaussian simulated molecular orbitals for undoped and self-doped PDIs in their charge neutral forms. (B) HOMO and LUMO depictions for undoped PDI. (C) HOMO and LUMO depictions for self-doped PDI.



un-heated samples of compounds 1–3 in both air and under a nitrogen atmosphere (Fig. S13–S15, ESI†). No structural degradation was observed in samples equilibrated to air or nitrogen, nor was any sample degradation observed upon heating to 120 °C up to 7 days in nitrogen. However, in air, compound #2 showed clear signs of sample degradation in both the aromatic (120–140 ppm) and aliphatic (20–60 ppm) regions of the SSNMR spectrum (Fig. S14, ESI†). This demonstrates that subsequent reactivity of $R'-NR_2^{\bullet+}$ radical cation requires the presence of atmospheric oxidants, and involves a dealkylation mechanism that requires a specific construct of the dopant. Interestingly, this effect did not seem to be related to sterics of $R'-NR_2^{\bullet+}$, and instead may be related to the presence of longer hydrocarbon chains or an abundance of hydrogen in the alpha position.^{50,55} Moreover, this data demonstrates that $R'-NR_2^{\bullet+}$ radical cations are likely present in our systems rather than undergoing any further reaction under inert conditions.

Given that the PVD fabrication process allows for the systematic control of the morphology of our self-doped PDI thin films, we performed quantitative EPR measurements to investigate the impact that the addition of aliphatic head groups has on the generation of charge carriers. Fig. 5A shows the EPR spectra for undoped and self-doped PDIs. Compounds 1 and 3 have a first derivative Lorentzian line shape while compound 2 is a Gaussian–Lorentzian mixture due to dipolar broadening. The spin concentrations reported are defined as the number of radicals (*i.e.* EPR active states) present per 1 mole of sample. TEMPO, a widely known stable organic radical containing 1 spin equivalent per molecule, was used to construct a standard calibration curve. We then use this calibration curve to obtain the total number of spins, or unpaired electrons, in the samples. As depicted, the undoped PDI is not EPR spin active. However, upon the addition of aliphatic head groups which serve as dopants to the PDI molecules, we observe radical formation and an increase in spin concentrations. The average spin concentrations for self-doped PDIs are provided in Fig. 5B. We determined that even modest increases in the steric hindrance of the electron source results in a ten-fold decrease in doping efficiency, an observation which is consistent between both EPR and absorption studies (10^{21} to 10^{20} spins per mole when going from PDI self-doped with moiety #1 to #3, respectively). From EPR alone a ~ 1 –0.1% doping efficiency for 1–3 is obtained. However, the absorption spectra of the respective thin films (Fig. S4, ESI†) are indicative of a much higher concentration of the radical anion $PDI^{\bullet-}$, pointing to a larger true doping efficiency ($> 5\%$). This discrepancy could plausibly be explained by the presence of spin-paired states which result in a magnetic moment of zero, and are thus EPR silent. We have already demonstrated that $R'-NR_2^{\bullet+}$ radical cations are present within our doped systems, leading us to propose that $R'-NR_2^{\bullet+}$ couples to $PDI^{\bullet-}$ following electron transfer, some of which are spin-paired. This coupled state is known as a heteroexcimer or exciplex, which imparts stability to what would otherwise be unstable radicals. Exciplexes have been demonstrated in similar constructs of tertiary amines covalently attached to chromophores.^{65–68} The fluorescence

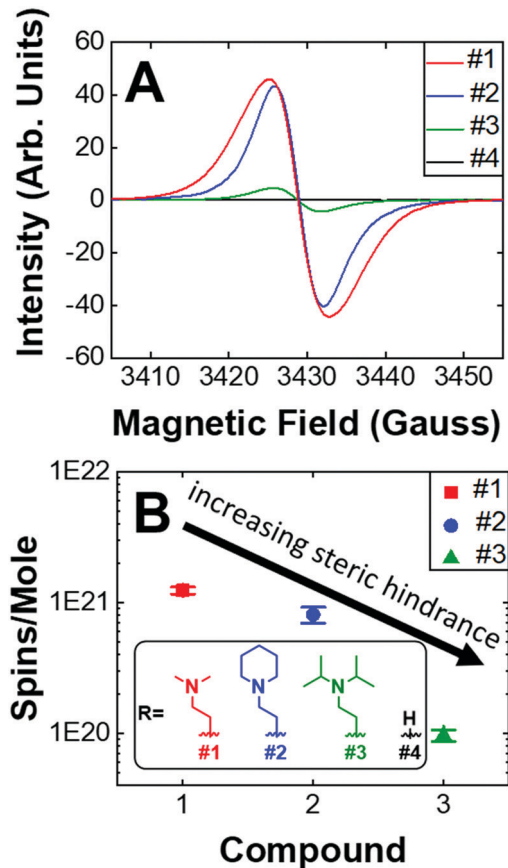


Fig. 5 (A) Raw EPR spectra. Maximum intensities of compounds 1–4. (B) Average spin concentrations of compounds #1–3. Compound 4 is not spin active. (inset) Dopant structures and control compound #4.

signal for compounds 1–3 thin films were also fully quenched, consistent with the formation of exciplexes, and leads us to propose that these and other self-doped PDIs may be ideally suited to organic light emitting diode (OLED) applications.⁶⁹ We also note the possibility that spin pairing between $PDI^{\bullet-}$ and $PDI^{\bullet-}$ is also plausible if $R'-NR_2^{\bullet+}$ were to act as a reversible photoacid, or undergo some other reversible transformation.

We also investigated the air stability self-doped PDI thin films. Fig. S16 (ESI†) shows the EPR spectra for compounds 1–3 which were measured under both a nitrogen atmosphere and after 3 days of air exposure. We observed that the spin concentration of #1 decreased by 60%, #2 decreased by 32%, and #3 decreased by 12% following air exposure. The more hindered amines are thus the most resistant to oxidation, which is a major challenge in n-type systems. The addition of carbonaceous substituents about the nitrogen source on the one hand increases the distance between donor and acceptor thus decreasing electron transfer efficiency, while on the other hand the same also imparts stability by shielding the radicals from oxidation. It remains to be seen how the incorporation of other heteroatoms, such as phosphorus, oxygen, or sulfur, may impact self-dopant performance in PDIs. It is anticipated that steric hindrance will play a key role in future work to establish dopant design principles and structural optimization.



Conclusions

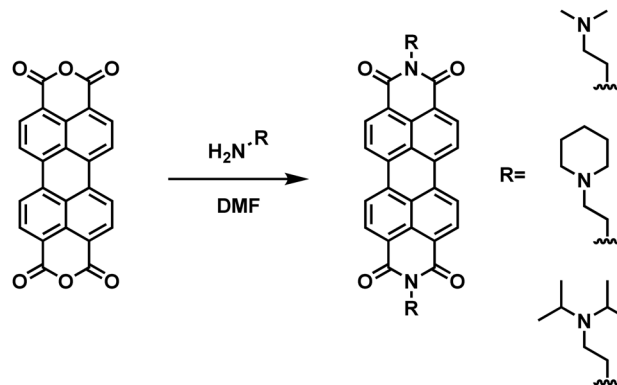
To summarize, self-doping is a compelling doping strategy for PDIs and other small-molecule organic semiconductors that has recently emerged because it intrinsically mitigates phase segregation, dopant aggregation, and the need for host/dopant miscibility investigations. Self-doping also induces the increase in charge carrier concentrations in organic small molecules. For practical purposes, however, these materials must be easily processable into high-quality thin-films for them to be viable in functional devices. Self-doped PDIs have shown great promise in many applications, yet previous attempts at making thin-films have been limited to drop-casting from chloroform or water yielding poorly controlled morphologies. Here, we improve on earlier methods for thin-film production of self-doped materials. The elimination of host/dopant mixing enables us to utilize vapor deposition during film fabrication. We compare this method with two solution processing methods, namely drop-casting and ultrasonic spraying. We demonstrate that ultrasonic spray can be used to produce more homogeneous films than drop-casting without drastically altering the structures of the crystallites that form upon solvent evaporation. More importantly, we have demonstrated that physical vapor deposition is a robust method for fabricating smooth, continuous, and crystalline thin-films of self-doped perylene diimide derivatives with high spin carrier concentrations. We have also demonstrated that the elevated temperatures present during PVD film fabrication do not hinder the self-doping process in organic thin-films. This has allowed us to conclude that the introduction of bulky dopant structures deleteriously impacts the spin concentrations in self-doped organic thin films while simultaneously imparting stability to atmospheric oxidation of both the radical anion and cation. We propose that $R'-NR_2^{*+}$ couples to $PDI^{\bullet-}$ to form transient exciplexes whose lowered energy imparts improved n-type stability, and is amenable to a variety of applications including OLEDs. We believe our work may enable the fabrication of other self-doped organic thin-films with controllable morphology and high spin carrier concentrations.

Experimental section

All reagents were purchased directly from commercial sources and did not require further purification. 3,4,9,10-Perylene tetracarboxylic dianhydride was purchased from Acros Organics, 3,4,9,10-peryene tetracarboxylic diimide was purchased from Combi-Blocks, and 2-aminoethyl diisopropylamine was purchased from Alfa Aesar. Both *N*-(2-aminoethyl)piperidine and 2-dimethylaminoethylamine were purchased from Sigma Aldrich.

Synthesis

Compounds **1**, **2**, and **3** were synthesized and purified according to a simplified method developed in our laboratory (Scheme 1). Briefly, 4 equivalents of 1,1-dimethylethylenediamine (compound **1**, 2 mmol), 2-piperidinoethylamine (compound **2**, 2 mmol), or



Scheme 1 Reaction scheme for the synthesis of self-doped PDIs.

N,N-diisopropylethylenediamine (compound **3**, 2 mmol) were added to 1 equivalent of perylene-3,4,9,10-tetracarboxylic dianhydride (0.5 mmol) suspended in DMF (20 mM) in a round-bottom flask equipped with a condenser and stirred overnight at 120 °C. Upon cooling to room-temperature, 50 mL of acetone was added to the mixture and allowed to stand for 10 minutes. The slurry was then transferred to a centrifuge tube and centrifuged at 6000 rpm for 2 minutes and the supernatant was decanted. To remove unreacted starting material during the synthesis of compound **3**, the product was treated with 30 mL of 0.1 M aqueous NaOH and washed with water. All solids were subsequently re-suspended and centrifuged 3 times with both acetone and diethyl ether (50 mL each wash).

Nuclear magnetic resonance

Proton NMR experiments were performed on a 500 MHz VXR-class spectrometer. All peaks are reported in units of δ and ppm relative to residual internal $CHCl_3$ (7.26 ppm).

Compound **1** 1H NMR: (500 MHz, chloroform-*d*) δ 8.69 (d, J = 7.9 Hz, 4H), 8.62 (d, J = 8.0 Hz, 4H), 4.37 (t, J = 7.0 Hz, 4H), 2.70 (t, J = 7.0 Hz, 4H), 2.37 (s, 12H).

Compound **2** 1H NMR: (500 MHz, chloroform-*d*) δ 8.64 (d, J = 7.9 Hz, 4H), 8.55 (d, J = 8.1 Hz, 4H), 4.40–4.36 (m, 4H), 2.73–2.67 (m, 4H), 2.58 (s, 8H), 1.63–1.58 (m, 8H), 1.48–1.43 (m, 4H).

Compound **3** 1H NMR: (500 MHz, chloroform-*d*) δ 8.71 (d, J = 8.0 Hz, 4H), 8.66 (d, J = 8.1 Hz, 4H), 4.21 (t, J = 7.8 Hz, 4H), 3.12–3.06 (m, 4H), 2.75 (t, J = 7.8 Hz, 4H), 1.07 (d, J = 6.5 Hz, 24H).

Solid state NMR (SSNMR) spectra were collected on a chemagnetics spectrophotometer operating at 50.3 MHz ^{13}C . The samples were loaded into a 5 mm rotor and data were collected at room temperature while spinning at 6 kHz and referenced to the methyl signal of an external sample of hexamethylbenzene. Room temperature samples were equilibrated in a nitrogen glovebox environment and in open air for several days, while heated samples were annealed at 120 °C for 7 days in air and nitrogen prior to analysis.

Mass spectrometry

MALDI mass spectrometry was performed on a Maldi micro MX ToF instrument with 1 mg mL $^{-1}$ samples in chloroform.



Absorption spectroscopy

Absorption studies were carried out with a 300 W xenon lamp and silicon photodetector attached to a monochromator in transmission geometry.

Thermogravimetric analysis (TGA)

TGA was performed on a TA Instrument Q500 series equipped with an evolved gas furnace. Samples were placed in an aluminum pan and heated under atmospheric pressure at $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $500\text{ }^{\circ}\text{C}$ under continuous 10 mL min^{-1} nitrogen flow.

Thin film preparation

All glass substrates were cleaned and washed in a sonicator bath for 15 minutes with Alconox detergent, deionized water, acetone, and isopropyl alcohol and dried with a nitrogen gun prior to film fabrication. Drop-cast and sprayed films were prepared from 1 mg mL^{-1} chloroform solutions. Spray coated films were prepared using an MTI MSK-SP-01A ultrasonic power supply (40 KHz, 0.5 amps) equipped with a cone-shaped spray nozzle. The distance between the substrate and nozzle was fixed to 10 cm. An EQ-300SP-LD digitally controlled infusion syringe pump was used to control the dispense rate at 2 mL min^{-1} . Substrates were heated to $60\text{ }^{\circ}\text{C}$ during the spray deposition process. Vapor deposited films were prepared in an MTI OTF-1200X tube furnace. 15 mg of fresh self-doped PDI was used for each sample batch. Sample boats were placed in the center of the tube furnace heating zone and substrates were placed 1 cm outside the heating zone. A vacuum level of 4.0×10^{-4} Torr and an argon flow rate of 60 sccm were set before the furnace heating cycle was initiated. The furnace temperature was ramped at $10\text{ }^{\circ}\text{C min}^{-1}$ until final temperatures were reached and held constant for 30 minutes. Final temperatures of $305\text{ }^{\circ}\text{C}$, $295\text{ }^{\circ}\text{C}$, and $310\text{ }^{\circ}\text{C}$ were set for compounds **1**, **2**, and **3** respectively. Under vacuum, these materials are expected to be considerably more stable. The film thickness could be controlled by the amount of material loaded into the sample boat as well as the deposition time.

Gaussian simulations

All calculations were completed using the Gaussian 09 software package. Optimized geometries and frequencies of the neutral species were computed at the DFT level using the B3LYP functional and a 6-311G** basis set.

Atomic force microscopy and scanning electron microscopy

AFM images were collected on a Bruker dimension icon atomic force microscope in tapping mode. SEM images were obtained on a FEI Nova NanoSEM 630 that was equipped with a field emission gun and operated at a 10 keV accelerating voltage.

Grazing incidence wide-angle X-ray scattering

GIWAXS samples were all collected at the D1 station of the Cornell High Energy Synchrotron Source. The X-ray beam energy was 13.0 keV with synthetic multilayer optics (Mo/B4C, 30 Å *d*-spacing), and the sample to detector distance (SDD) was

190 mm. The incident angle for all GIWAXS patterns was 0.14° . Scattered intensity was collected on a two-dimensional CCD detector comprising 1024×1024 pixels with a size of $46.9\text{ }\mu\text{m}$ each. All images were background corrected and processed using the GIXSGUI graphical user interface. Mosaicity factors were calculated using the Shekiefactor.m matlab code.

Electron paramagnetic resonance (EPR) spectroscopy

EPR experiments were performed on a Bruker EMX X-band rectangular cavity CW instrument. All samples were measured at room temperature. The instrument was calibrated for quantitative EPR measurements using TEMPO, a widely known stable organic radical, to construct a standard calibration curve. Samples were prepared in triplicate, weighed, and transferred to 5 mm quartz EPR tubes. Special care was taken to reduce static electricity in the weighing environment for error minimization with the aid of an anti-static wristband, fan ionizer, and an alpha ionizing cartridge. Thin film samples were prepared by cleaving quartz microscope slides into substrates sized to fit inside a 5 mm EPR tube. Substrates were cleaned (same procedure as glass slides) and weighed.

Conflicts of interest

There are no conflicts to declare.

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