

Perylenes, Porphyrins, and Other Large Dye Molecules for Molecular Layer Deposition

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Molecular layer deposition (MLD) is an incredibly powerful and flexible tool for designing completely new materials with novel and unique properties. The low temperature layer-by-layer approach and the use of highly reactive reactants allows one to combine vastly different organic and inorganic species and construct nanostructures with subnanometer precision. If not limited by the volatility of the reactants involved, the possibilities will be endless. This is most notable for the organic building blocks where an overall low volatility severely limits the toolbox of large molecules with interesting optical and electrical properties such as red-ox activity and optical conversion. In this work, different strategies for molecular design of large molecules are investigated that allow vaporization while still having the necessary reactivity for MLD growth. Using these strategies, film growth with perylene and porphyrin derivatives, both molecules well known for their functional and optical properties are successfully achieved. With this knowledge, there is an opening to include much larger and more complex organic molecules into the world of vapor phase chemistry.

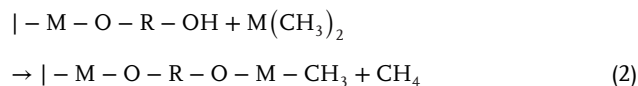
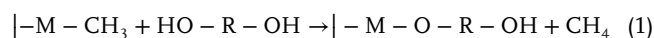
1. Introduction

Molecular layer deposition (MLD), called atomic layer deposition (ALD) when purely inorganic materials are deposited, is incredibly powerful and flexible for designing completely new materials. The low temperature layer-by-layer approach and time separated introduction of reactants is what gives this technique its edge. Depositions below 200 °C^[1] is common and even down to room

temperature is known.^[2] This allows use of more delicate substrates like fabrics and other fragile organic based materials. The low temperature also prevents most bulk diffusion processes in the deposited materials, allowing multilayers of different materials on nanometer^[3] and even sub-nanometer level^[4,5]. The sequential introduction of precursors on the other hand allows combinations of very reactive precursors without undesired reactions. As a result, MLD and ALD materials span the whole periodic table.^[6] In addition, the sequential operation also allows easy switching between different reactants, allowing even organic and inorganic materials to be combined in nano-composite material designs.^[7]

A simplified illustration of a regular two-component MLD reaction between a dimethyl-metal and an organic di-alcohol is given below. Three


important points are at work: (1) precursor A and B are reactive enough to react with each other, (2) they cannot react or bond to other molecules of the same type (i.e., no A-A or B-B reactions), and (3) they are introduced into the reaction chamber sequentially separated by a purge step that removes any surplus precursor in the atmosphere and all physisorbed precursors. Point 2 and 3 leads to the formation of a self-terminated monolayer of each precursor before the other precursor is introduced to react with it. For further explanations, the reader is referred to one of the many review papers on MLD and ALD.^[1,8,9]



MLD allows inclusion of organic species into hybrid or nanocomposite thin films, among other, potentially adding very strong optical absorption or optoelectronic properties. Organic molecules have an exceptional flexibility in design toward specific absorption and emission ranges. Unfortunately, the choice of organic components in MLD has historically been far more limited than inorganic components for ALD. The need to get these molecules into the vapor phase while also having sufficient reac-

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tivity reduces the practical range to fairly small molecules. Unfortunately, many of the molecules used in organic LEDs or organic electronics are quite large, often designed and optimized towards a liquid or solvent based deposition chemistry.

The organic building blocks explored for MLD chemistries^[8,9] so far are usually limited to a single aromatic ring or a short conjugated chain, with some examples of bi-aromatic species like naphthalene and biphenyl.^[10] To our knowledge, the largest molecules used in MLD today are curcumin^[11] and the dye IR-806^[12] with molecular weights of 368 and 775 amu, respectively. Such dye precursors require sublimation temperatures of ≈ 250 °C or even more, approaching the temperature where many organic molecules start to decompose or polymerize.

This work is aimed towards the MLD, ALD and vapor phase deposition communities. The focus is thus on practical aspects in thermal stability, reactivity, and volatility of large organic molecules. Thus, the goal is to establish some general strategies in selecting and designing large organic molecules to be compatible with vapor phase chemistries. Unlike physical vapor deposition (PVD) approaches, where a coating is made by sublimation and condensation, the MLD approach also requires a sufficient reactivity for subsequent reactions with the following pulse of co-reactants. However, this added reactivity also opens for additional pathways for polymerization or thermal decomposition during heating, which renders the molecule un-sublimable. However, volatilization of organic molecules is not new, as they have for long been applied in PVD processes, in particular in the field of molecular electronics.^[13] Our work builds on this, while focusing on the sub-selection of highly reactivity molecules.

How can we improve the volatility of an organic molecule? This is mostly about minimizing the intermolecular forces by reducing the possibilities of hydrogen bonds, dipole interactions, π - π stacking, in addition to reducing the possibilities of stable crystal structures by preventing dense packing of molecules through asymmetric or branched^[14,15] ligands. Aromatic structures are planar so while hydrogen bonds and dipole interactions depend on the choice of reactive groups and types of ligands, π - π stacking is a fundamental issue for sublimation. Thus adding bulky ligands to add volume to the molecule may reduce stacking efficiency, while ligands that lie on top of the planar aromatic surface may prevent the stacking more completely. It is commonly assumed that a higher molecular weight reduces volatility.^[16] However, in this work we show that this is a risky assumption as one may miss opportunities for drastic improvements in volatility by adding parts that addresses the first set of factors. In addition, the likelihood of thermal decomposition must be limited by reducing possibilities of internal polymerization, β -elimination reactions, dehydration, dehydrohalogenation, and other decomposition reactions. However, a high volatility and thermal stability is not sufficient for an MLD-type of precursor. It also needs to be reactive. Quite often large compromises to the requirements above will have to be made.

A class of interesting molecules for thin film depositions are the organic dyes, offering various types of optical activities. We have developed a set of strategies in our search for sublimable dye molecules: Our initial approach was to search among the commercially available dye molecules for those that may be sufficiently thermally stable to sublime, i.e., with reduced possibilities of polymerization, π - π interactions and decomposition by β -

elimination. The strategy is though limited by the fact that most, if not all, commercial dyes are not designed for sublimation, and any sublimation is largely a serendipity. That being said, our previous work on the deeply orange dye quinizarin in MLD was based on this approach.^[17] The next step was to redesign dye molecules to increase their volatility by adding functionality to the core structure to enable chemical reactivity and to reduce intermolecular forces. This approach is the focus of the current work.

We began our investigation by identifying two particularly interesting classes of dyes: perylenes and porphyrins. Both classes consist of quite thermally stable and sublimable core structures, that also allows for a large range of chemical modifications. In particular, both molecules allow adding functional groups without notably affecting their functional properties. This allows for separating the design for functional properties and the design for MLD compatibility, vastly simplifying the design process. The perylene tetracarboxylic dianhydride (PTCDA, named Per-C₂O₃ in this article) works as the simplest base structure. In luminescent perylene dyes (perylene diimides), the central oxygens in the carboxylic acid dianhydride units are replaced with N-R units (see Figure 4 for an example conversion reaction), where R has negligible effects on the core structure. Perylenes also offer functionality through the so-called bay positions on the perylene core structure itself. These positions will affect the perylenes functional properties and must be used with care. For porphyrins, the tetraphenylporphyrin (TPPH₂) acts as a well-known starting point where additional functional groups can be added to the phenyl groups with minor or negligible effects on the core structure. In addition, we have looked at alternative sources for these molecules, as such large molecules designed for research purposes are usually very expensive. We have obtained three different classes of dye molecules from an industrial dye producer, Sun Chemical, and successfully use these for MLD depositions.

2. Overview of Dyes in This Work

In this work we use the following abbreviations: Per for perylene; TPP, DPP and Por for 5,10,15,20-tetraphenylporphyrin, 5,15-diphenylporphyrin and porphine. All perylenes and porphyrins in this work consist of this core unit and different added functional groups. The free-base TPP itself is named TPPH₂ as this abbreviation is commonly used for this molecule. The two central hydrogens are unlikely to play a significant role in the MLD processes in this work. In addition, we have included several other large organic molecules that are relevant when exploring the barriers for vaporization and how to circumvent these. These include a corrole (Cor), BODIPY (BP) and two linear polyaromatic compound: naphthacenedione, and quinacridone (Quin) in two different polymorphs. All molecules are given short names to illustrate their base structure and their MLD relevant functional groups. This is summarized in Table S1 (Supporting Information) in addition to any other non-reactive functional groups they may have. The most important dyes are summarized in Table 1 here.

In addition to these 9 perylenes and porphyrins, 16 more molecules were investigated to form a broader understanding of the links between molecular structure and their sublimation and reaction properties. An overview of all dye molecules used

Table 1. Overview of the most important dye molecules used in this work and their abbreviations.

ID#	Short name	Reactive group	Functional group
1	Per-C ₂ O ₃ ^{a)}	C ₂ O ₃	
3	Per-COOH	COOH	
4	Per-X-C ₂ O ₃	C ₂ O ₃	O-PhC(CH ₃) ₃
5	TPPH ₂	^{b)}	
7	TPP-2COOH	COOH	
12	DPP-12arm		O(CH ₂) ₁₁ CH ₃
19	TPP-t-C ₂ O ₃ ^{a)}	C ₂ O ₃	O(CH ₂) ₁₁ CH ₃
20	TPP-c-C ₂ O ₃ ^{a)}	C ₂ O ₃	O(CH ₂) ₁₁ CH ₃

^{a)} C₂O₃ = Carboxylic acid dianhydride; ^{b)} The central hydrogen atoms may participate in bonding chemistry, but likely not allow for MLD-type film growth.

in this work is given in Figure S1 (Supporting Information). Despite such a long list of molecules, only a small selection resulted in well behaving MLD growth. However, the knowledge gained during this investigation shows a path for further explorations.

3. Experimental Section

The dyes were sublimed in an in-house built vacuum sublimator while being filmed, as illustrated in **Figure 1**. A white alumina plate was placed in a colder area. A camera continuously takes pictures of the dye and the alumina plate, monitoring changes happening in the dye powder and color changes on the alumina plate. The RGB and corresponding grey values (WRGB, W = white level) of a selected area of the pictures were plotted as a function of the heater temperature. These values were relative to the WRGB values of the alumina plate in the first pictures, i.e., $R(T) = R_T/R_0$ where R_T was the R value at temperature T and R_0 was the R value for the alumina plate. The heating rate of the finger was $\approx 2 \text{ }^\circ\text{C min}^{-1}$.

The films were deposited in a F120 reactor (ASM Microchemistry). Nitrogen purging gas was supplied from a Schmidlin Sirocco5 generator producing 99.9995% (N₂) and maintained at a flow rate of 500 cm³ min⁻¹. Pulse and purge times were kept constant at 2/1/3/1 s for the Ln(thd)₃ / purge / dye / purge cycles, with the following exceptions: (1) For the porphyrin acid anhydrides synthesized in this work 3/3/5/3 s was used, (2) for depositions using TMA (trimethylaluminium) or TiCl₄ the 2 s Ln(thd)₃

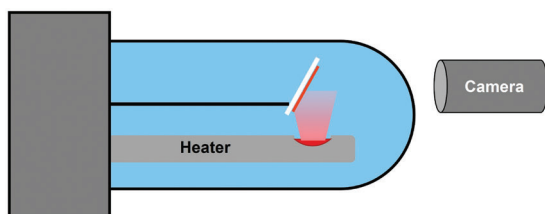


Figure 1. Illustration of our camera-based sublimation setup. The precursor powder is placed in a recess in the heating finger, while the camera monitors both the precursor and the white plate. The changing color of the plate resulting from subliming precursor condensing onto it is then converted to WRGB values and plotted as a function of heater temperature.

pulse was replaced by a 1 s metal pulse, and (3) all pulses and purges were 3 and 1 s, respectively, for perylene depositions that include glycine. The number of cycles were varied between 500 and 2000. The deposition temperature was kept at 400 °C except for all Per-X-C₂O₃ depositions, which were deposited at 350 °C.

The growth of perylene based films was investigated in more detail using quartz crystal microbalance (QCM), using 6 MHz AT-cut quartz crystal mounted in custom holders. Standard pulse parameters during these cycles were 2 and 1 s for pulse and purge times during Eu(thd)₃ + Per-COOH depositions, and 3 and 2 s for pulse and purge times during Y(thd)₃ + glycine + Per-X-C₂O₃ + glycine depositions. The films thickness and corresponding growth rate per cycle (g, Å/cycle) was characterized with spectroscopic ellipsometry using a Woollam Alpha-SE ellipsometer. UV-Vis transmission was measured on a Shimadzu-3600 UV-Vis-NIR photospectrometer.

For the synthesis of the perylene carboxylic acid precursor (Per-COOH), solid state NMR, FTIR and UV-Vis spectroscopy were performed to characterize the product. The NMR analysis was conducted on a Bruker 500 MHz instrument and the software used was Topspin 3.0. Magic angle spinning (MAS) = 10kHz. The powders (≈ 0.1 g) were encapsulated in 4 mm zirconia rotors. Simulations of the predicted spectra were performed through an online NMR simulator^[18] building on a tool developed by Binev et. al.^[19] FTIR measurements were performed on a Bruker VERTEX 70 FTIR spectrometer in reflection mode on the back side of a QCM crystal on which the precursor had been sublimed. The results were analyzed with OPUS. Absorption measurements of the precursor powders were performed by an Ocean Insight USB2000+ spectrometer with a D₂ lamp. Ba₂SO₄ was used as the reference.

For the porphyrin synthesis of the two acid anhydride dyes **19** and **20**, the following instruments were used. ¹H NMR spectra were recorded on Bruker Avance NEO spectrometers operating at 500 or 400 MHz and available at the PACSMUB-WPCM technological platform, which relies on the “Institut de Chimie Moléculaire de l’Université de Bourgogne” and SATT SAYENS “TM”, a Burgundy University private subsidiary. All NMR shift values were expressed in ppm. UV-vis spectra of the synthesized compounds were recorded on a Varian Cary 50. Quartz cells with optical path lengths of 10 mm were used. ESI mass spectra were recorded on a LTQ Orbitrap XL (THERMO) instrument for HR-MS spectra and on an AmaZon SL (Bruker) instrument for the LRMS spectra or on a Bruker Microflex LRF MALDI Tandem TOF mass spectrometer using dithranol as the matrix.

While some dyes were obtained commercially, about half were synthesized. An overview of which dyes were of commercial origin and the synthesis routes for the others were given in the supplementary information.

4. Results and Discussion

4.1. Dye Sublimation Experiments

As mentioned in the introduction, in order for a molecule to be suitable for MLD reactions, it has to be sufficiently volatile. We have chosen to investigate this using our sublimation setup in combination with image analysis due to its robustness and ability to function in dynamic vacuum. This gives conditions most near

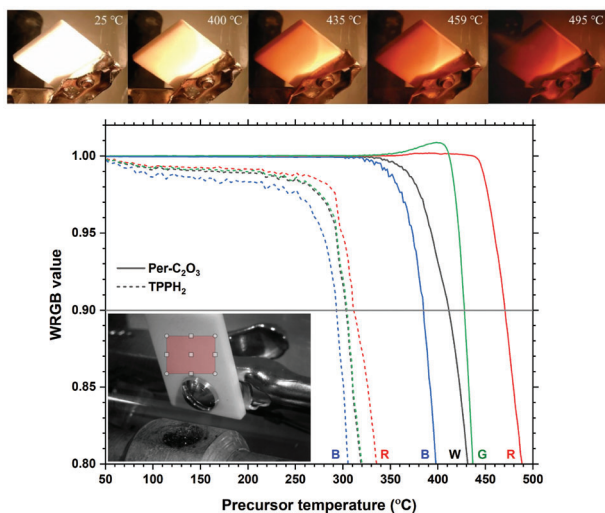


Figure 2. WRGB values as a function of dye temperature during sublimation experiments of TPPH₂ and Per-C₂O₃. The inset shows one of the photos in the temperature series for TPPH₂. The white alumina plate is seen mounted above the precursor, and the red rectangle is the area used for RGBW values. The five images above show the evolution of the plates color as the precursor heats up and starts to sublime for Per-C₂O₃.

to realistic deposition conditions. Our aim with this investigation is to identify those parameters that affect volatility the most. Our setup is illustrated below.

The large organic molecules in this work were chosen due to their strong visible absorption, i.e., dyes. Organic dyes can have very non-homogeneous absorption across the visible spectrum. This is particularly well exemplified with porphyrins, which have a fairly narrow but exceptionally strong absorption in the blue range (the Soret band) and broader and relatively weaker absorption bands across the green and red range (the Q bands). Even though the absorption spectrum varies between dyes, they are all strongly absorbing and to calculate the white value of their absorption to some extent averages out these differences. When using this approach to characterize other types of materials, one should plan the experiments according to the color of the precursor and choose a back plate with a contrasting color. As an initial approximate value of onset of dye sublimation at a rate sufficient for MLD, we use the temperature where we reach $W = 0.9$ for our heating rate of 2 °C min^{-1} . This value ($W = 0.9$) was chosen based on sublimation experiments of other more common MLD and ALD precursors that we have experience with, and $W = 0.9$ matched well with the actual precursor temperatures we use for these. This is illustrated with Per-C₂O₃ and TPPH₂ in **Figure 2**, showing how all four RGBW values change as the precursor heats up and how $W = 0.9$ is found. A summary of all WRGB = 0.9 values for all dyes investigated in this work is given **Figure 18**.

The actual precursor temperature used will depend on other factors as well, such as base pressure, carrier gas flows, how large dye surface is available (fine powders sublime more readily than a solid lump) and the amount of dye powder. Thus, the aim of these sublimation experiments is to determine an approximate temperature for sublimation during similar vacuum conditions as in an MLD reactor, while using a small amount of dye powder.

4.2. Perylenes

Figure 3 shows three of the perylenes used in this work, along with their molecular masses and the sublimation temperature corresponding to $W = 0.9$. It is clearly shown that even though Per-X-C₂O₃ is the heaviest molecule (865 vs 506 and 392 amu for Per-COOH and Per-C₂O₃), it sublimates at $\approx 120\text{ °C}$ lower. The most important point to note here is that the sublimation temperature is not directly dependent on the molecular mass itself, but rather depends on the intermolecular forces, as stated in the introduction. For Per-X-C₂O₃, the four -OR bay-position groups point out-of-plane due to the angled oxygen bonds and hinders effective π - π stacking between the otherwise flat perylene molecules. This example shows that it is in fact possible to increase the molecular mass quite a bit without increasing the sublimation temperatures, as long as this reduces the strongest intermolecular forces (π - π in this case) and does not introduce any new bonding types.

The two acid anhydride perylenes (Per-C₂O₃ and Per-X-C₂O₃) are commercially available and they both sublime without leaving residues. This allowed us to obtain sufficient amounts to investigate their MLD growth in more detail. Per-COOH can be synthesized wet chemically by reacting Per-C₂O₃ with RNH₂.^[20,21] This is illustrated in **Figure 4**, where R is a carboxylic acid (glycine), producing the perylene diimide carboxylic acid Per-COOH.

Per-C₂O₃, Per-COOH and Per-X-C₂O₃ were used for MLD depositions. **Table 2** summarizes the growth rates obtained for these depositions along with the compositions of selected films and their ideal stoichiometry (marked with grey). Per-C₂O₃ resulted in a very low growth rate per cycle, even though repetitive depositions showed that the perylene did not decompose. It is possible that the reaction between the acid anhydride group and Y(thd)₃ is slow. It is possible to hydrate the acid anhydride to form carboxylic acid groups under the right circumstances. Thus, we added a water pulse before and after the Per-C₂O₃ pulse to determine if this would increase the growth rate. This resulted in more than doubling of the growth rate from 0.09 to 0.23 Å cycle^{-1} . However, UV-vis measurements and visually inspecting the sample indicated that adding H₂O pulses caused a brown film with an optical absorption more indicative of partially decomposed organic species. The UV-vis data and a photo of the sample with water pulses is shown in **Figure 6**. Thus, it was concluded that adding H₂O to hydrate the acid anhydride groups was

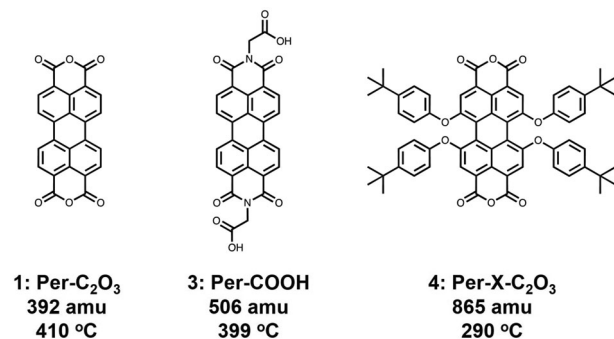


Figure 3. Three of the perylene dyes used in this work, along with their molecular masses and $W = 0.9$ temperatures.

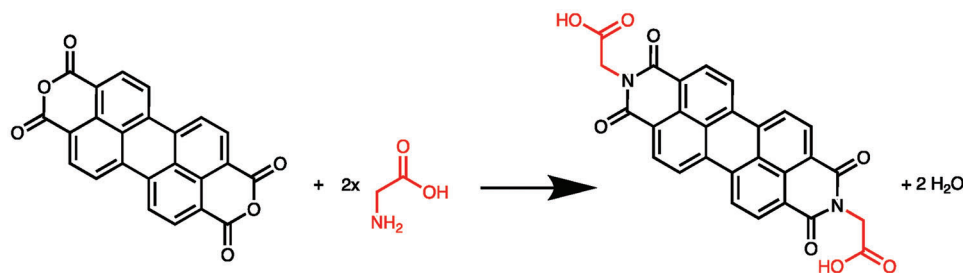


Figure 4. Synthesis route of 3 Per-COOH from 1 Per-C₂O₃ and glycine.

not a viable strategy, at least at this high deposition temperature (400 °C). A film with Y and Per-C₂O₃ (i.e., without water pulses) was characterized with XPS to determine its chemical composition. As given in Table 2, this film corresponds very well to the ideal stoichiometric Y₂(Per-C₂O₃)₃. This shows that Per-C₂O₃, which is a relatively cheap compound, can be used in MLD and produce even films with the expected stoichiometry although the deposition temperature must be very high.

Depositions with Per-COOH showed more promise. The growth rate with both Y(thd)₃ and Eu(thd)₃ was an order of magnitude larger than that of Per-C₂O₃. In addition, the films color and UV-vis transmission (Figure 6) showed clear red films with absorption similar to that of the perylene acid anhydride. One Eu film was characterized with XPS, showing a stoichiometry close to that of an ideal Eu₂(Per-COO)₃ compound. However, as with the porphyrin carboxylic acids, Per-COOH was also not stable at the sublimation temperature used. Subsequent depositions resulted in reduced growth rate, and all film depositions showed gradients. Per-COOH may too be useful in MLD if it is introduced into the reactor with care.

Per-X-C₂O₃ was the most successful dye in this work as it can be sublimed at a reasonably low temperature while also having re-

active groups. Depositions together with Y(thd)₃ resulted in blue colored films that were fairly even in the gas flow direction (10% thickness difference over 8 cm) while still showing gradients towards the reactor walls. The growth rate is 0.38 Å cycle⁻¹, which is higher than that of Per-C₂O₃, but still low considering the large size of the dye molecule. The high growth rate of Per-COOH, low sublimation temperature of Per-X-C₂O₃ and its relative ease of wet chemical conversion to diimide carboxylic acid (Figure 4) lead us to try to convert the perylene acid anhydride into perylene diimide carboxylic acid in situ by reacting with glycine in the gas phase. These depositions followed an A-B-C-B and A-C-B sequence, where A, B and C is Y, glycine and Per-X-C₂O₃, respectively. This approach circumvents the temperature sensitivity issue when including carboxylic acid groups directly on the precursor dye molecule. The A-B-C-B depositions will, ideally, convert all Per-X-C₂O₃ into a diimide (commonly called PDI's) terminated with carboxylic acid and thus in practice be equivalent to an A-B reaction between Y(thd)₃ and Per-COOH. Following a cycle starting from a Y terminated surface, |Y(thd)_x will react with the carboxylic acid of glycine leaving the surface amine terminated. Per-X-C₂O₃ can then react with the amine and form a one-sided imide with the surface being terminated with the other acid anhydride group. The acid anhydride group will react with the amine group of the next glycine pulse, leaving the surface terminated with carboxylic acid which is a good reactive group towards Y(thd)₃. This is illustrated in Figure 5. Note that the surface bonded perylene unit in the third step in this figure, i.e., the second glycine pulse, is asymmetrical in that it has one imide group bonded to the surface while the other side only contains oxygen. This illustrates how MLD actually is quite well suited to create both symmetrical diimides and acid anhydrides in addition to unsymmetrical monoimides.

Leaving out one of the two glycine pulses will let Y(thd)₃ and the acid anhydride groups react directly, which the previous results with Eu(thd)₃ and Per-C₂O₃ show that they do. One A-B-C-B film was also characterized with XPS for chemical composition (Figures S6 and S7, Supporting Information). These films have a substantial over-stoichiometry of nitrogen, oxygen and yttrium compared to carbon. This can indicate that there is an under-stoichiometry of perylene. The large size of Per-X-C₂O₃ could explain this as it might be very difficult to fit three molecules around an yttrium ion, even with the glycine linker between them. The result could be a film closer to chain-like structure where one of the three glycines around Y is unreacted (i.e., has intact glycine R-NH₂ group attached to it): |-[PDI-Y(gly)]_x-, where PDI is the Per-X-C₂O₃ with a glycine attached on each side. The resulting stoichiometry of this Y(Gly)(PDI) would be YC₇₀N₃O₁₄H₆₄,

Table 2. Summary of growth rates (GPC, nm per cycle) and film composition (at.%) of perylene films. The ideal film materials and their stoichiometries are marked in grey.

MLD precursors	GPC [nm cycle ⁻¹]	Ln	C	N	O
Per-C ₂ O ₃					
Ln ₂ (Per-C ₂ O ₃) ₃		2.2	78.2	0	19.6
Y	0.09	2	77	0	21
H ₂ O + Y + H ₂ O	0.23				
Per-COOH					
Ln ₂ (Per-COO) ₃		1.8	71.7	5.3	21.2
Eu	1.6	1	72	5	22
Eu 2 nd run	0.58				
Y	0.96				
Per-X-C ₂ O ₃ , glycine					
Y ₂ (gly) ₆ (Per-X-C ₂ O ₃) ₃	0.8	82.3	2.4	14.5	
Y(Gly)(PDI)	1.1	79.5	3.4	15.9	
Gly + Y + gly	1.4	2	72	7	19
Gly + Y	1.3				
Gly + Y 2 nd run	1.7				
Y	0.38				

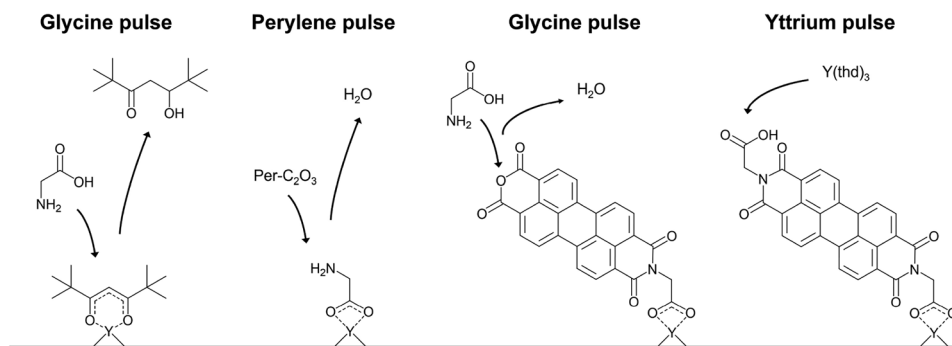


Figure 5. Illustration of A-B-C-B reactions using $Y(\text{thd})_3$, glycine and $\text{Per-C}_2\text{O}_3$, starting from an $Y(\text{thd})_x$ terminated surface. This illustration uses $\text{Per-C}_2\text{O}_3$ instead of $\text{Per-X-C}_2\text{O}_3$ simply because $\text{Per-X-C}_2\text{O}_3$ is quite a bit larger and the reaction mechanisms is better illustrated with the “clean” $\text{Per-C}_2\text{O}_3$.

compared to $Y\text{C}_{102}\text{N}_3\text{O}_{21}\text{H}_{90}$ for ideal $Y_2(\text{gly})_6(\text{Per-X-C}_2\text{O}_3)_3$ or $\text{C}_6\text{N}_3\text{O}_6\text{H}_6$ for $Y(\text{gly})_3$. Although this chain-like structure is relatively higher in N and O and lower in C, the differences is even larger in the measured sample. Unsymmetric A-B-C reactions were also explored. These will ideally give perylenes that have one imide end that is connected to Y through the glycine component, while the other end is still oxygen terminated (i.e., $-\text{C}_2\text{O}_3$) and is directly connected to Y. This ideally is a very simple way of creating unsymmetrical perylene molecules by using different B species in A-B₁-C-B₂ reactions or by omitting B₂ completely, one can open for novel explorations into perylene’s physical properties. In our case we omitted B₂ and the films showed similar optical characteristics as A-B-C-B reactions, **Figure 6**. In addition, the growth rate of A-B-C depositions were similar to and even a bit higher than A-B-C-B depositions.

Figure 6 shows a photo of the A-B-C-B depositions. The films were very uniform throughout the reaction chamber. The UV–vis spectra show the visible absorption from the perylene dye. The A-C depositions and the A-B-C-B deposition, i.e., zero-imide and diimide both show distinct absorption spectra. This is expected as replacing the central oxygen with nitrogen has some impact on the energy level structure of the molecule. However, the films that are most different are the asymmetric A-C-B depositions. This shows that in these depositions, the perylene is clearly and strongly affected by the chemistry of the film due to the differences in cycle sequence. Asymmetric perylenes usually refer to differences in the R component at the imide position or differences in the bay and *ortho* positions of the perylene core unit. Mono-imides, like what the A-C-B depositions ideally would result in, are less explored. This is likely due to the fact that perylene diimides have superior optical and luminescent properties. But it is also that monoimides are more difficult to prepare. Our A-C, A-C-B, and A-B-C-B depositions show that it is in fact uniquely simple to design different asymmetric perylene units with MLD by either having different functionalities on the B molecules, i.e., B₁ and B₂, or by omitting one of the B pulse entirely.

Figure 7 shows the XPS results of a $Y(\text{thd})_3 + \text{Per-C}_2\text{O}_3$ film. The Y, C, and O peaks show the different bonding types expected to be found in this perylene acid anhydride film, showing that the perylene unit is intact. This also proves that the film contains Y. Equivalent spectra of $\text{Eu}_2(\text{Per-COO})_3$ and $Y_2(\text{Gly})_6(\text{Per-X-COO})_3$ is shown in Figures S6 and S7 (Supporting Information).

Due to the successful depositions with perylene dyes, the processes when combining $\text{Ln}(\text{thd})_3$ with Per-COOH and glycine/ $\text{Per-X-C}_2\text{O}_3$ /glycine were investigated with QCM. **Figure 8** shows the QCM results for $\text{Eu}(\text{thd})_3$ and Per-COOH . The $\text{Eu}(\text{thd})_3$ pulse saturates rather quick with respect to pulse time, indicating a self-saturating MLD growth. This also indicates that there is no CVD component during the lanthanide pulse. The Per-COOH pulse, however, does not saturate to the same level. There is a clear difference in growth for the first 0.5 s, but after that, it appears as a linear growth with exposure time. This is likely due to polymerization reactions between the acid groups on surface-bound perylene molecules and on incoming perylenes from the pulse. Another cause is the likely porous nature of these hybrid materials and that some $\text{Eu}(\text{thd})_3$ diffuse into the already deposited structure. If so, this bulk- $\text{Eu}(\text{thd})_3$ will likely be free to react with the next perylene pulse. Both may play a role. However, a CVD-like polymerization growth should give a growth that is linear with time, similar to what we observe. Purge times (not shown) showed little effect on the growth to support such a hypothesis.

Figure 9 shows the QCM results of A-B-C-B depositions. The length of both glycine pulses does not affect the growth much. The $Y(\text{thd})_3$ pulse behaves similar as the $\text{Eu}(\text{thd})_3$ in **Figure 8**. If the explanation of $\text{Eu}(\text{thd})_3$ filling up some of the voids within the already deposited hybrid film structure is correct, then this effect should also be present for the A-B-C-B depositions in **Figure 9**. On first inspection, the $\text{Per-X-C}_2\text{O}_3$ pulses looks unusual. For pulses longer than about 1 s, the growth is fairly stable. But for shorter pulses, the growth increases with decreasing perylene pulse. QCM of such three-component A-B-C-B depositions are not common in literature, and to understand this unusual increase we need to consider the two glycine pulses. The acid groups on glycine will readily react with $Y(\text{thd})_3$. The resulting $Y(\text{thd})_{3-x}(\text{gly})_x$ is very unlikely to be sublimable and will thus lead to a deposition of dye-free Y-hybrid material. Glycine is much smaller the $\text{Per-X-C}_2\text{O}_3$, so if the growth is dominated by $Y(\text{thd})_3$ and glycine then it is logical that the overall growth rate increases with decreasing amount of perylene pulse.

Figure 10 shows detailed QCM responses during A-B-C-B cycles with normal and long pulse and purge times. The glycine pulses are shown to rapidly saturate for both normal and long parameters, in accordance with **Figure 9** showing that pulse lengths

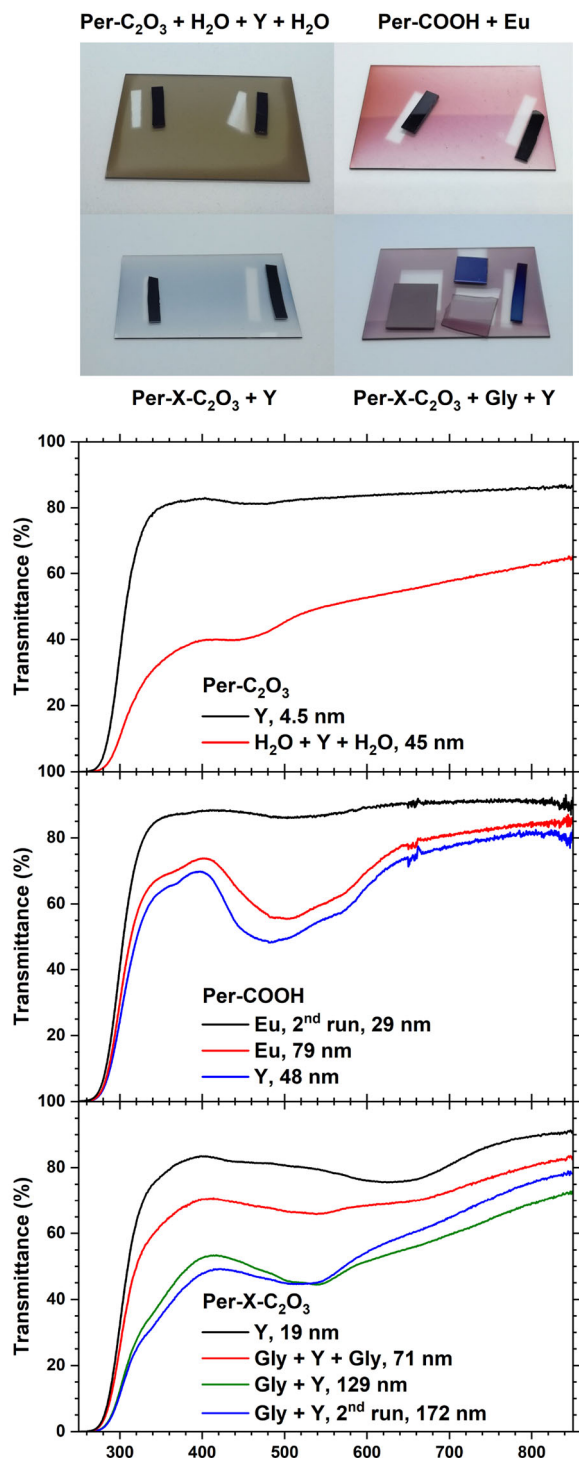


Figure 6. Photos and UV-vis spectra of selected perylene films.

of glycine have little effect on the overall growth rates. The long pulse times indicate that the Per-X-C₂O₃ pulse also saturates. The Y(thd)₃ pulses on the other hand show a more continuously increasing QCM response through the pulse for both normal and long pulse times.

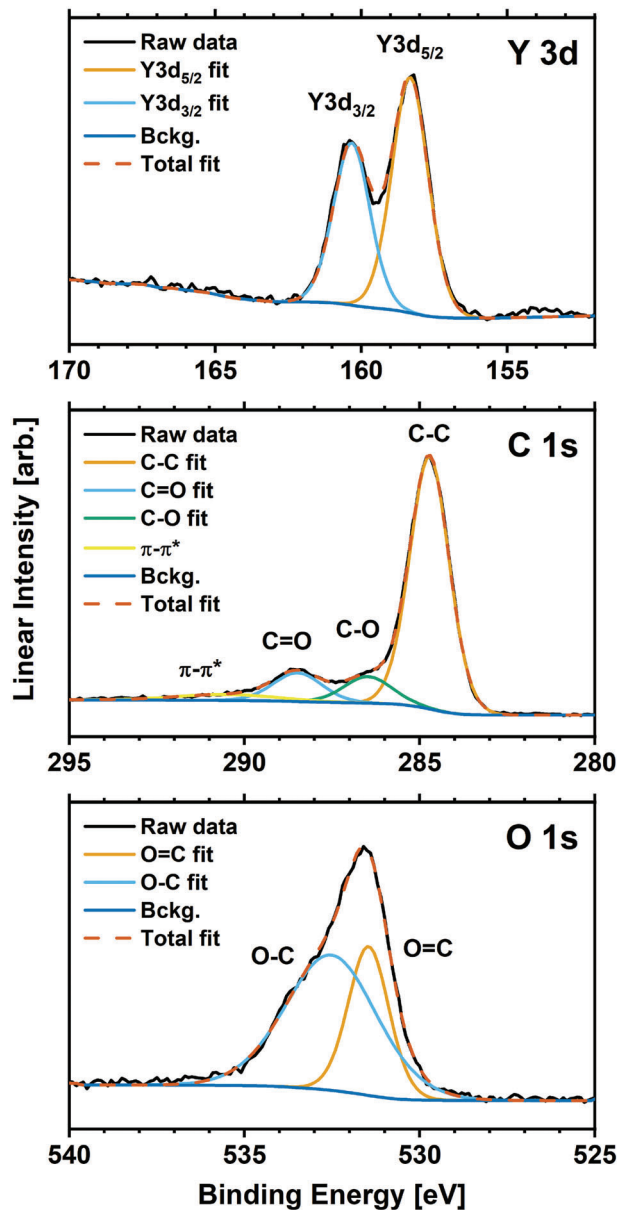


Figure 7. XPS result from Y(thd)₃ + Per-C₂O₃.

The perylene investigations shown here illustrate two important points: (1) Although carboxylic acid groups are much used in MLD due to their high reactivity toward common metal precursors, they also provide degradation routes when high temperatures are used. (2) Adding large and bulky groups to a molecule can in fact cause a quite dramatic reduction in sublimation temperature.

4.3. Porphyrins

A similar approach was conducted with porphyrins. However, unlike the perylenes there are no commercially available acid anhydride variants of porphyrins. Also, unlike the perylenes, the TPPH₂ molecule does not have any reactive groups, so additions

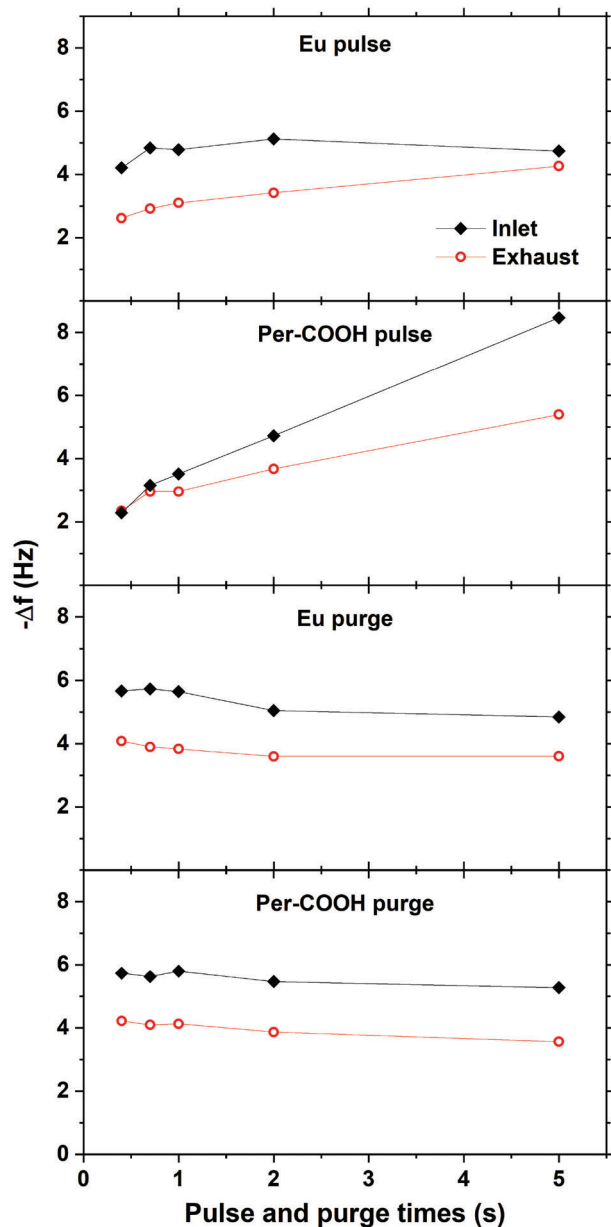


Figure 8. QCM results at $T_{\text{dep}} = 400^\circ\text{C}$ for $\text{Eu}(\text{thd})_3$ and Per-COOH depositions.

must be made to this molecule before it can be used for MLD. We selected TPP-2COOH along with the two specially designed TPP-t- C_2O_3 and TPP-c- C_2O_3 for MLD depositions. This design was based on the reduction in sublimation temperature obtained when the porphyrins have alkane chains going backwards above and below the main porphyrin ring structure. These and the free-base TPPH₂ is shown in Figure 11. In addition, porphyrin identical to TPP-12arm with shorter alkyl groups, TPP-8arm, was investigated.

While having acid anhydride groups that may show reactivities in the same range as carboxylic acids, these two porphyrins sublime at roughly the same temperature as TPPH₂. Note that these two porphyrins are thick and nearly solid liquids which form a

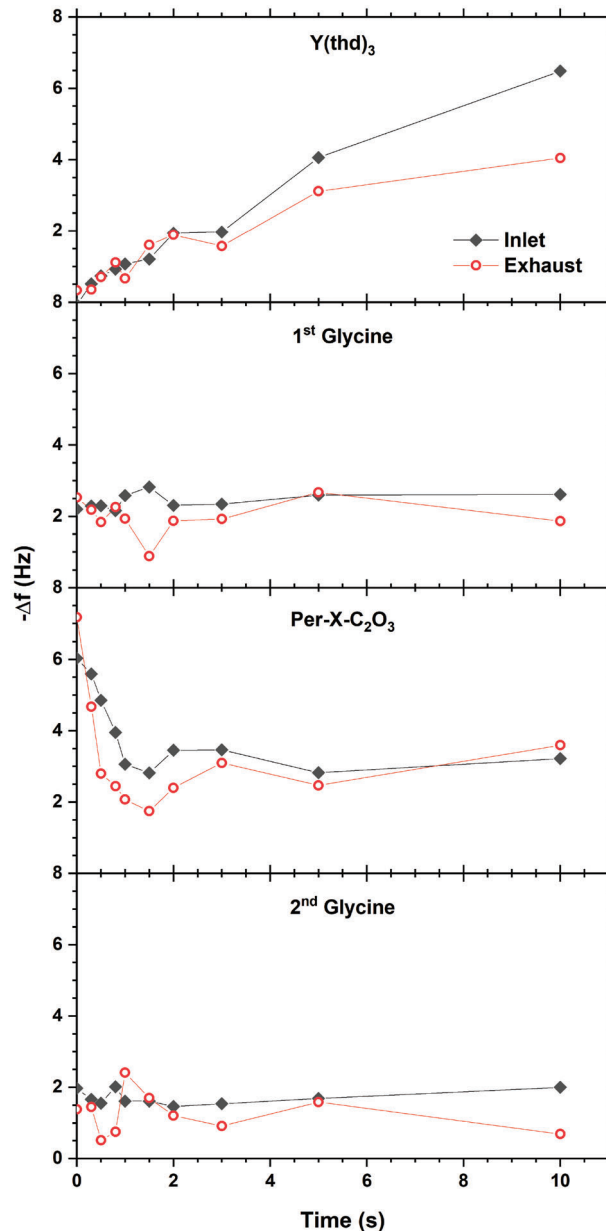


Figure 9. QCM results of $\text{Y}(\text{thd})_3$ – glycine – Per-X- C_2O_3 – glycine depositions.

smooth surface and intimate contact with the heater. This is a significant difference from all other dyes in this work which are powders and also never melted or showed significant densification during the heating experiments. Dyes 19 and 20 therefore have significantly less surface area, which decreases the sublimation rate compared to a powder. Nevertheless, the sublimation temperature is even lower than the base TPPH₂ porphyrin.

Sublimation experiments showed that TPP-2COOH stops subliming after some time similar to Per-COOH. 1000 cycles of $\text{Y}(\text{thd})_3$ and TPP-2COOH resulted in 14.8 nm film and a growth rate of only $0.148 \text{ \AA cycle}^{-1}$. The film was yellow due to the very strong Soret band absorption and gradients were clearly seen (photo, Figure 12). A second deposition with the same precursor

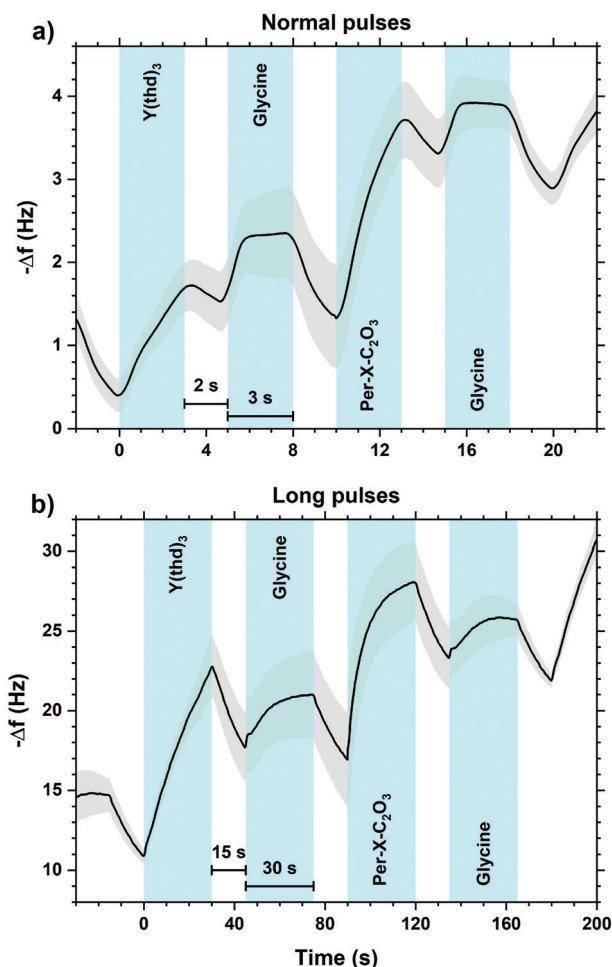


Figure 10. Detailed QCM response during normal and long MLD cycles of A-B-C-B depositions. Note the differences in both x-scale and y-scale.

powder resulted in no film. The porphyrin clearly stopped subliming at some point during the first deposition, likely gradually. This means that TPP-2COOH is not well fit for MLD with the current precursor delivery system. However, it also proves that this precursor is volatile and shows good reactivity. Provided a precursor delivery system with a lower thermal budget can be used, i.e., liquid injection, TPP-2COOH and likely also TPP-4COOH can be useful MLD precursors. Figure 12 shows the UV-vis transmission of this film deposited on a silica substrate. Even though the film is only 14.8 nm, the Soret band causes >10% absorption. It is clear that the dye is included in this film, as porphyrins are particularly easy to identify with UV-vis spectroscopy due to the unique and very intense Soret band.

We had only a very limited amount of acid anhydride porphyrin to experiment with, and were able to perform only one test deposition of each. A proper MLD investigation would require a significant scale up of the synthesis. Both precursors resulted in thin films with the easily identifiable Soret band, **Figure 13**. Repetitive use of the same precursor resulted in thinner films. This might indicate that these porphyrins are also temperature-sensitive. However, the result also indicates that the acid anhydride group provides enough reactivity for porphyrin depositions.

4.4. MLD Using Other Molecules

In addition to the perylenes and porphyrins, we investigated a selection of other dye molecules that are potentially MLD compatible. These are shown in **Figure 14** and will be discussed in turn.

BP-COOH, a BODIPY dye, shows interesting sublimation properties in having both a low sublimation temperature of 250 °C and two carboxylic acid groups at opposite ends. Unfortunately, the repeated sublimation with the same dye show that this dye degrades fast at the sublimation temperature. There are dicarboxylic acids that sublime well in the 225 – 250 °C range without significant degradation.^[10,22] We attempted MLD depositions with BP-COOH and Y(thd)₃, but we got no film. Likely, this dye is quite sensitive to temperature even though we could evaporate it in the sublimation experiments.

4-Ring-OH has by far the lowest sublimation temperature and also have two hydroxy groups that are well suited for MLD. In addition, this molecule did sublime to completion. We have recently investigated a very similar molecule, quinizarin^[17], and show it is highly compatible with MLD in the TMA + quinizarin system. Thus, due to the high similarity between 4-Ring-OH and quinizarin, we do not investigate it any further in this work apart from noting that the 4-Ring-OH molecule should be highly applicable for MLD.

The two polymorphs of the quinacridone dye, β -Quin and γ -Quin, deviate from this trend. Although even larger than 4-Ring-OH, the main difference is the reactive group and position of carbonyl groups. It is interesting to note that both quinizarin (3-Ring) and 4-Ring-OH have similar and very low sublimation temperatures, while β -Quin requires a full 200 °C more to sublime. Neither β -Quin nor γ -Quin sublimed to completion. As amines are generally much less reactive than hydroxy or carboxylic acid groups towards the common cation precursors used in MLD, we used the highly reactive TMA as the cation precursor in these depositions. **Figure 15** show UV-vis transmission spectra of two films deposited using different sublimation temperatures for β -Quin. New dye was used in each deposition as the sublimation experiments showed that β -Quin precursor likely would at least partially degrade during an MLD deposition. Films produced were deeply colored and quite even throughout the reaction chamber. The thickness differences between the inlet and exhaust side of the chamber was \approx 6%. γ -Quin showed similar sublimation properties as β -Quin and in the gas phase they will have the same reactivity. Thus, we did not conduct additional MLD tests with γ -Quin. A disadvantage of this molecule compared to perylenes and porphyrins is that it is not possible to add new functional groups to the molecule without also strongly affecting the aromaticity and thus optoelectronic properties.

4.5. Porphyrins: Other Reactive and Functional Groups

In addition to dyes presented so far, we have investigated other functional groups to affect the sublimation temperature in addition to three other possible reactive groups. This investigation was mainly based on porphyrins due to the relatively large range of commercially available variants.

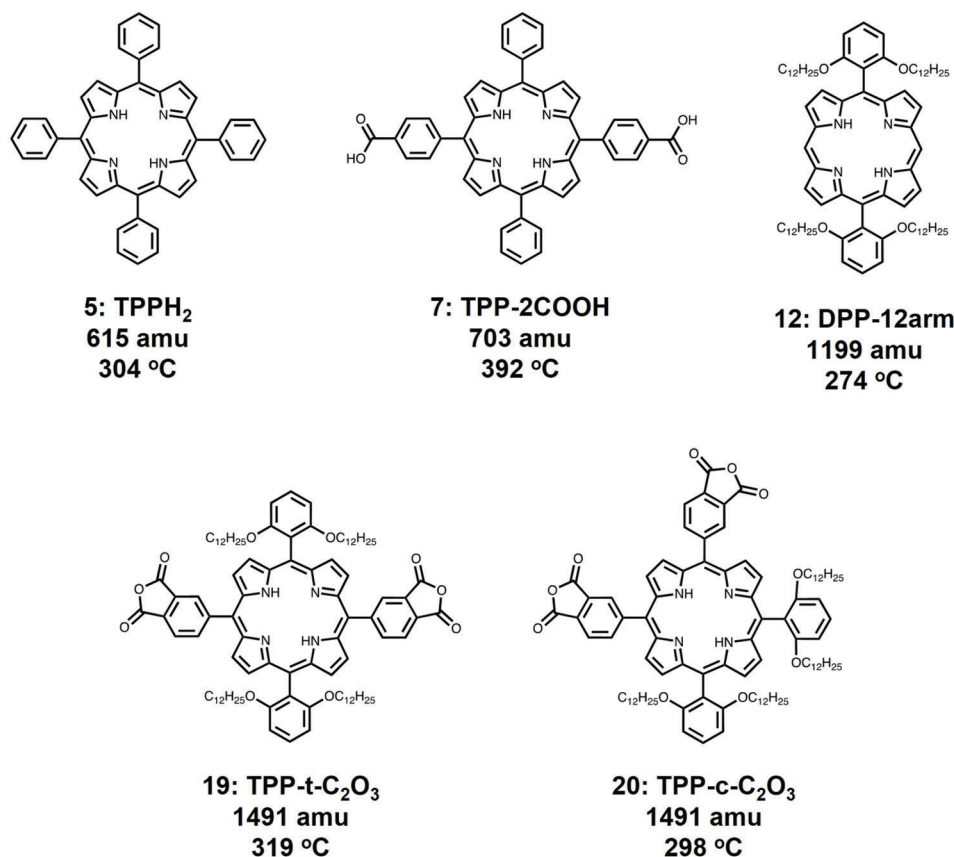


Figure 11. Five of the porphyrins used in this work, along with their molecular masses and $W = 0.9$ sublimation temperatures.

First, other reactive groups are explored, namely alcohols, amines and a trimethylsilylethynyl porphyrin where both the ethynyl and silyl groups could be available for reaction. These are shown in **Figure 16**. It is clear that the number of acid groups

(TPP-2COOH vs TPP-4COOH) or type of hydrogen containing reactive groups (alcohol and amine) results in insignificant differences in sublimation temperature. In addition, they all degrade similarly upon the onset of sublimation. Common for these dyes

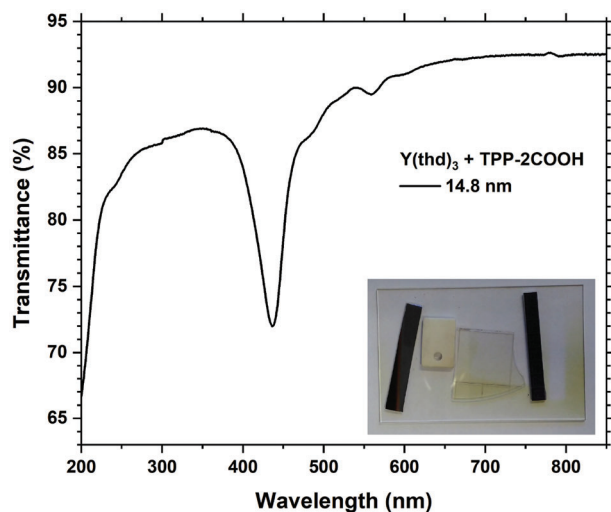


Figure 12. UV-Vis spectrum of a film deposited on silica substrate by Y(thd)₃ and TPP-2COOH.

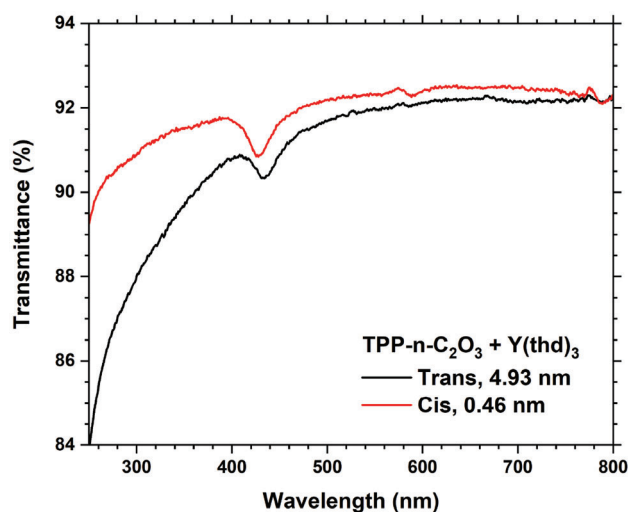


Figure 13. UV-Vis transmission spectra of two films deposited with porphyrin acid anhydrides and Y(thd)₃.

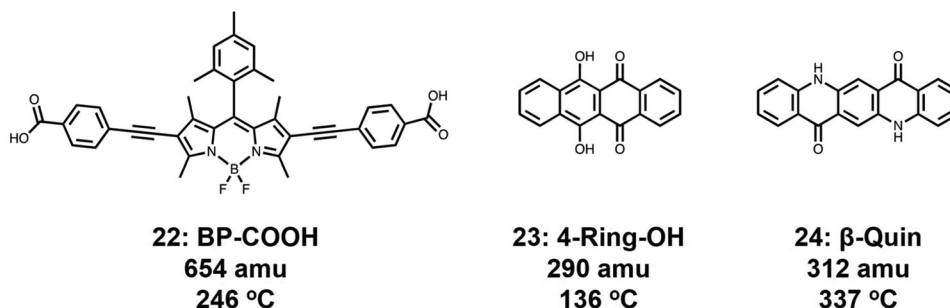
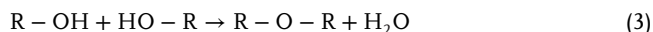


Figure 14. BODIPY carboxylic acid, naphthacenedione and anthraquinone dyes, along with their molecular masses and $W = 0.9$ sublimation temperature. Note that quinizarin^[17] is the same as 4-Ring-OH if the left ring is removed, i.e., the four leftmost carbon atoms.

(-OH, -COOH and -NH₂) is that they have the potential to polymerize as in reaction (3) below, or similar reactions for amides with NH₃ as a leaving molecule. The trimethylsilylethynyl porphyrin on the other hand stands out with a substantially lower sublimation temperature. However, also this porphyrin degraded rapidly upon the onset of sublimation. Thus, our conclusion is that all of these reactive groups are difficult to use at these high temperatures.



Capping the alcohol with methyl to form methoxy groups lowers the sublimation temperature significantly. Methoxy groups are much less reactive than alcohol groups, and to our knowledge there are no reports of MLD or ALD reactions involving methoxy groups. Nevertheless, we attempted to react TPP-OMe with more reactive TMA and TiCl₄. These MLD runs did not result in any film deposition. Comparing TPP-COOMe with TPP-4COOH however, show no improvement in sublimation temperature even though the -OH group is capped.

Second, we investigated other modifications and functional groups to the porphyrin base structure and their effect on sub-

limation: capping the alcohol and acid with methyl, additional fluoride and nitro groups. In addition, a fluoro-nitro corrole^[23] was investigated, which has a slight structural difference to porphyrins. These are illustrated in **Figure 17**. Fluorination can in some cases cause a drastic reduction in sublimation temperature as it is much less polarizable and thus reduces intermolecular forces. Tetrafluoroterephthalic acid has been used in MLD using a sublimation temperature of 145 °C, which is 55 °C lower than regular terephthalic acid (200 °C).^[22]

Comparing TPPH₂ (304 °C) with the four fluoro-nitro porphyrins shows a significant reduction in sublimation temperature for only two of them. Thus, we conclude that adding such groups *can* be beneficial, but the design is less straight forward than the bulky groups of Per-X-C₂O₃ and TPP-12arm. The structural difference of the corrole along with its fluoro and nitro groups show no clear benefit.

4.6. Summary of Sublimation Properties

The WRGB values of all dyes investigated in this work is shown in **Figure 18**. We have added a stapled line for TPPH₂ $W = 0.9$ for easy comparison with the other dyes. The grey color is simply an eye guide to see the groups of dye types. The yellow color is the two special-designed carboxylic acid anhydride porphyrins synthesized for MLD in this work. There is a large variety of sublimation temperatures in this set, and as we have discussed there is also a very large range of molecular masses which does not seem to directly relate to sublimation properties. Thus, we plotted all $W = 0.9$ temperatures as a function of the molecules mass. This is shown in **Figure 19**. It is clear that there is no direct relationship between molecular mass and sublimation temperature. By comparing Per-COOH and TPP-c-C₂O₃, the porphyrin is nearly four times heavier and still sublimates at over 100 °C lower than the perylene.

4.7. Guidelines for Large Molecules in ALD/MLD

From the sublimation and MLD results in this work we have constructed some general guidelines when searching for large organic molecules compatible with MLD:

- 1) Reactive groups that can participate in polymerization reactions should be avoided, including R-OH, R-COOH and R-NH₂ particularly when both of these are included together

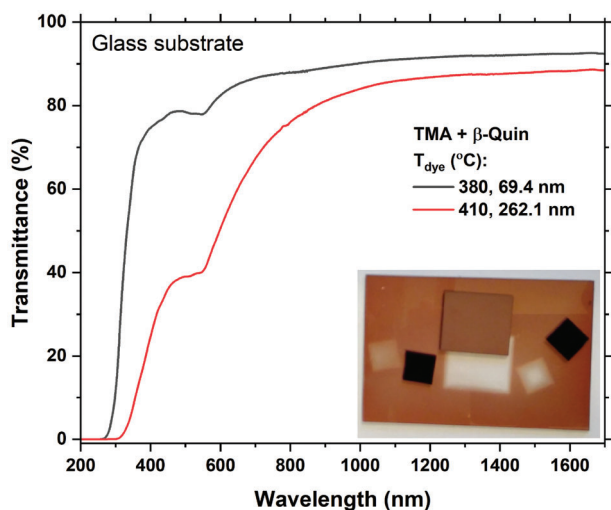


Figure 15. UV-vis spectra of two films deposited using TMA and β -Quin on glass substrates, along with a photo of the thickest sample.

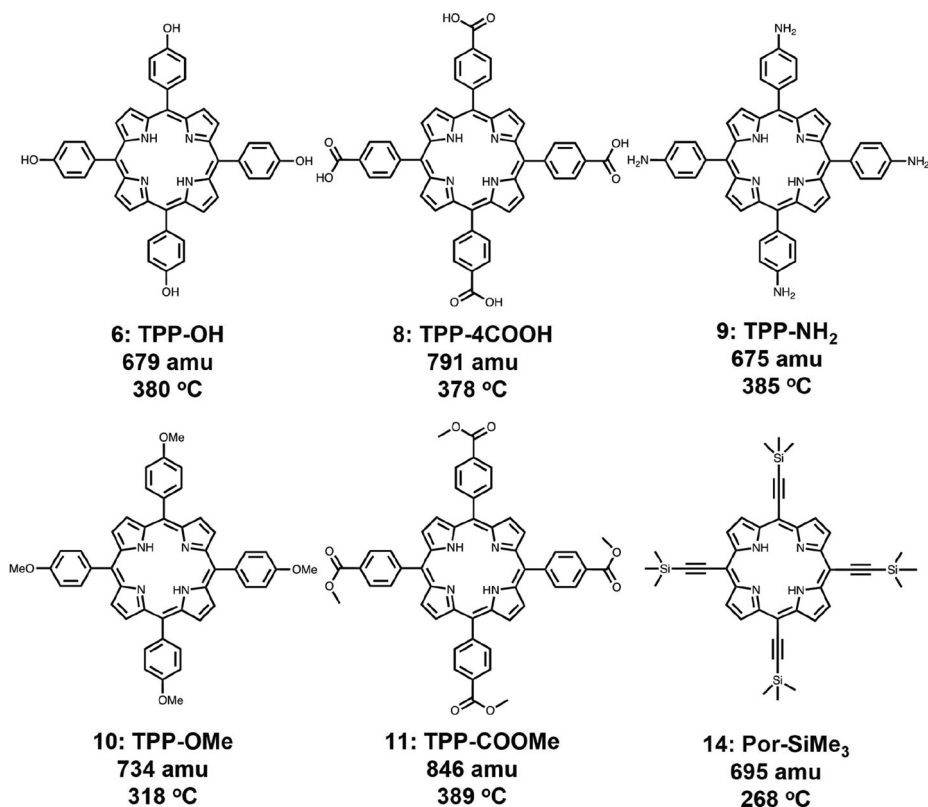


Figure 16. Porphyrins with other reactive groups, along with their molecular masses and $W = 0.9$ sublimation temperature.

as for example $R-NH_2$ and $R-COOH$. Instead, prioritize non-hydrogen terminated reactive groups like $R-OMe$, $R-OOME$ or $R-C_2O_3$.

- 2) If the deposition temperature is low enough, multi-step sequences, i.e., A-B-C sequences, are possible routes to successful MLD.
- 3) The molecular weight should not be given too much importance. Increasing molecular weight by additional ligands have a small effect on sublimation compared to the additional positive or negative effects the new ligands bring.
- 4) Reducing π - π stacking can significantly reduce the sublimation temperature. Reducing or controlling the number and strength (type) of intermolecular forces is far more important than the sometimes significant increase in molecular weight.
- 5) Substitutions with for example fluorine can lead to some reduction in sublimation temperature. A possible reason is a reduction in molecule packing efficiency.

Additional note: The combination of $R-OH$ and $R = O$ in quinzarin and 4-Ring-OH brings exceptionally low sublimation temperatures alongside good reactivity. The sublimation temperature in these two cases is low enough to avoid the issues in point 1.

Many of the common reactive groups used in MLD fall into point 1 and will severely limit the maximum temperature that the precursor can be maintained at during deposition. There are exceptions though, and previous work has shown that glycine can be safely sublimed for MLD at 200 °C without such

degradation.^[24] The groups in point 2 are safer in this respect. The methyl terminated groups are generally much less reactive though and it may be difficult to find uncatalyzed reactions suitable for surface-vapor MLD chemistry. The acid anhydride $R-C_2O_3$ is sufficiently reactive and should be investigated further when designing large MLD compatible molecules. The transfer of acid anhydride chemistry to porphyrins was partially successful, and further exploration of acid anhydride porphyrins may lead to stable MLD chemistries.

The combination and mutual positioning of $R-OH$ and $R = O$ in quinzarin and 4-Ring-OH is quite exceptional. The sublimation temperatures of these molecules are far below the other dyes tested in this work and have reactive groups that are well suited for MLD. Searching for and designing other molecules that contain similar combinations is likely to successfully lead to novel MLD chemistries. With respect to point 4, we have shown in this work that it is possible to deposit films of perylene diimides by building the diimide in situ from acid anhydrides. Using a diimide carboxylic acid directly as a precursor leads to the dye degrading, hindering further film growth. The perylene acid anhydride, glycine and $Y(thd)_3$, on the other hand, can safely be kept for prolonged times at the sublimation temperature without degrading.

5. Conclusion

In this work, we have investigated several classes of large organic dye molecules for MLD. We have developed strategies for

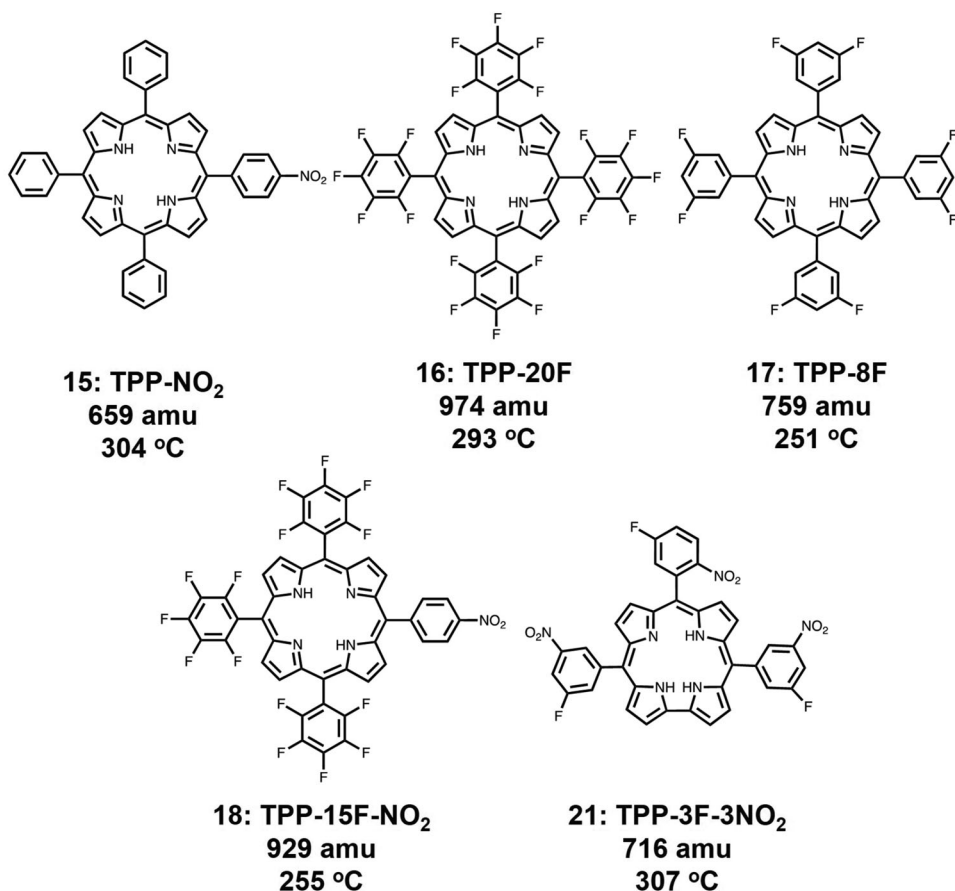


Figure 17. Porphyrins with other functional groups and with the corrole structure, along with their molecular masses and $W = 0.9$ sublimation temperature.

how to select or design molecules with respect to thermal stability, reducing sublimation temperatures and maintaining sufficient reactivity for MLD chemistries. For reducing sublimation temperatures, we show that reducing molecules possibilities for efficient π - π stacking is a much larger factor than the increase in molecular mass. We also show that dicarboxylic acid anhydride groups ($-C_2O_3$) provide sufficient reactivity for MLD chemistry, while avoiding the risk of sublimation hampering through polymerization reactions with carboxylic acids ($-COOH$) and hydroxyls ($-OH$). With this knowledge, we designed two porphyrin molecules for reduced sublimation temperature and good reactivity. The molecule that was most successful for MLD in this work, however, was a commercially available perylene that has carboxylic acid anhydride reactive groups in addition to bulky groups that prevent efficient π - π stacking. Even with a molecular mass of 865 we were able to successfully use the Per-X- C_2O_3 perylene for MLD at a sublimation temperature of 320 °C and reaction temperature of 350 °C. Per-X- C_2O_3 can be reacted directly with a metal cation precursor ($Ln(thd)_3$ in our case), and the relatively modest reaction temperature also allowed successful A-B-C-B reaction with glycine as B precursor. This effectively turned the Per-X- C_2O_3 into a diimide with carboxylic acid ($-COOH$) reactive groups. Thus, it is possible to in situ form “B-C-B” molecules with different reactive end groups by attaching amines ($R-NH_2$).

This also allows in situ formation of unsymmetric “B₁-C-B₂” molecules by using two different R-NH₂ amines or by emitting one of the B pulses entirely for direct $-C_2O_3$ metal reactions.

With this work, we show that MLD using large organic molecules is feasible with careful design and selection of the organic molecule, its π - π stacking prevention groups and reactive groups.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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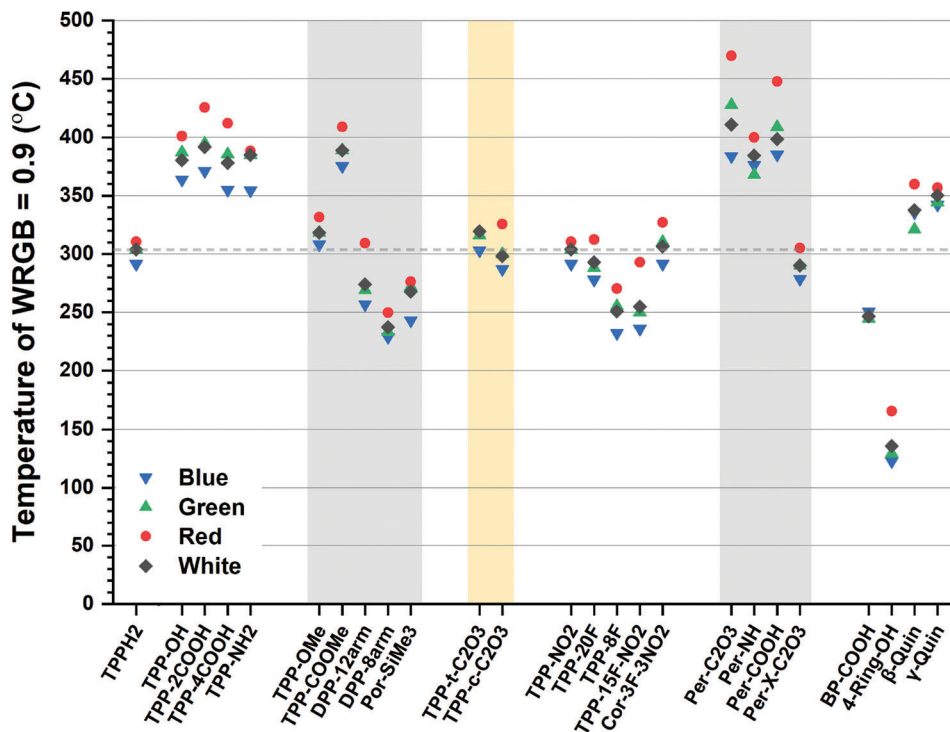


Figure 18. Summary of temperatures for WRGB = 0.9 for all dyes in this work. Grey columns are simply guides to the different groups of dyes, while the yellow columns indicate the two porphyrins specially designed for MLD synthesized in this work.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.-A.H. contributed in conceptualization, investigation, and writing – original draft, supervision. S.H.S. contributed in investigation. C.P.G. contributed in supervision, review, editing, and project administration (French partner). N.D. contributed in supervision of the porphyrin and corroles synthesis, review, editing. O.N. contributed in supervision, review, editing, and project administration (Norwegian partner).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

atomic layer deposition (ALD), molecular layer deposition (MLD), perylene, porphyrin, thin films

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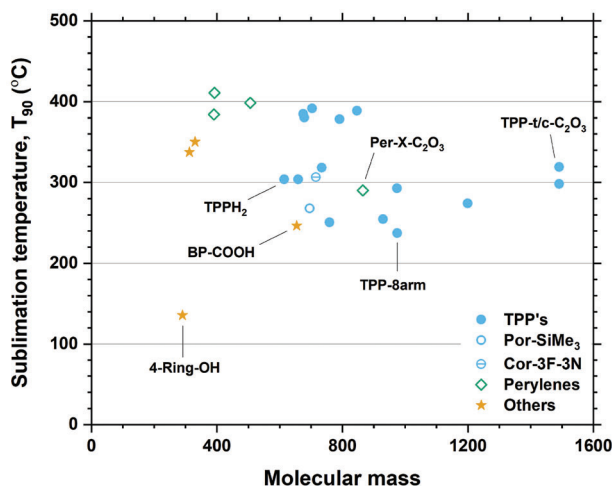


Figure 19. Summary of temperatures for W = 0.9 for all dyes in this work as a function of the dyes molecular mass.

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