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Electrostatic Self-Organization of Robust Porphyrin–Polyoxometalate Films

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Abstract

Strategies to create thin films using layer-by-layer methods use oppositely charged polymeric polyelectrolytes for both or at least one component to beneficially exploit multitopic electrostatic interactions between the deposited layers with opposite charges. In contrast, the electrostatic deposition of tetracationic 5,10,15,20-tetrakis(1'-methyl-4'-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP⁴⁺) with tetraanionic polyoxometalates such as EuPW₁₁O₃₉⁴⁻ or SiW₁₂O₄₀⁴⁻ onto charged substrates, such as mica, or polar substrates, such as glass and indium–tin oxide (ITO), demonstrates that the use of polymeric components is not a priori necessary. The use of molecules in sequential dipping approaches requires a careful balance in the interaction energies between the oppositely charged molecules, as demonstrated by the observation that a tetraanionic porphyrin such as 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin does not form layers with TMPyP⁴⁺. In the present case, these systems require several rounds of dipping to obtain films of uniform coverage and durability. The thin films deposited onto glass, quartz, ITO, and mica are surprisingly robust, since they are not removed by sonication in either organic solvents or 100 mM NaCl.

Introduction

Fabrication of robust thin films by layer-by-layer methods is accomplished by sequentially exposing a substrate to solutions containing oppositely charged polyelectrolytes, and the topic is well-reviewed.^{1,2} Polymeric polyelectrolytes are used to provide robust interactions between oppositely charged layers, wherein the detailed architecture of the self-organized material depends on the specific and nonspecific intermolecular interactions. These interactions are dominated by the electrostatics, but dispersion forces can play an important role as well. Oftentimes there is a significant degree of interdigitation of the oppositely charged polymers in the layers. The polyelectrolytes can be organic polymers, biopolymers, or inorganic materials. There are also some examples of materials made by layer-by-layer methods wherein one component is a small, charged molecule and the other is a charged polymer. There are a plethora of applications and potential applications of thin films fabricated by layer-by-layer methods, including photonics, coatings, and sensors.^{3–6}

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sulfate groups as the complementary component.²⁹ Constructs using phthalocyanines have also been reported.^{30,31} Porphyrins have been combined with derivatives of C₆₀, inorganic nanoparticles, and polyphenylenevinylene to create photonic films.^{32–34} Films of porphyrins have been made using polymers as complementary layers,³⁵ or cationic porphyrins have been placed between titania nanosheets using LB methods to create photoactive materials.³⁶ The deposition of cationic porphyrins and anionic POMs on modified glassy carbon electrodes produces organic–inorganic hybrid films^{37–39} that display electrocatalytic activity for the reduction of O₂ to peroxide or for hydrogen evolution from acidic water.³⁷ Films containing POMs and phthalocyanine show a third-order nonlinear optical response.⁴⁰ Most of these films are characterized by their chemical, electrochemical, or photophysical functions, but there is paucity of structural or organizational information because these are generally not highly ordered materials.

Herein we report the electrostatic formation of thin films by sequentially dipping a substrate into solutions of small, oppositely charged porphyrin and POM molecules. Tetracationic 5,10,15,20-tetrakis(1'-methyl-4'-pyridinio)porphyrin tetra(*p*-toluene-sulfonate) (TMPyP⁴⁺) and the zinc complex (ZnTMPyP⁴⁺) with acetate counterions are electrostatically matched by the tetraanionic polyoxometalates of the potassium salt of EuPW₁₁O₃₉⁴⁻ and SiW₁₂O₄₀⁴⁻ with hydrogen counterions (Figure 1). Though there is a reasonably linear addition of material for each dipping cycle, each cycle does not form a complete layer, which is consistent with previous observations,^{37–39} and this is likely true for other electrostatically assembled films made from small molecules. Thus, the term “layer-by-layer” for Por–POM films formed by sequential dipping into solutions of Por and POM is somewhat misleading. After a minimum number of dipping cycles, the films are remarkably robust, since they are removed neither by sonication in organic solvents nor by sonication in 100 mM NaCl. These films are fabricated using readily available compounds.

Experimental Section

Materials.

All reagents and solvents were of analytical grade and used without further purification. The water was passed through a Barnstead NANOPure water purification system and filtered using a Nalgene PTFE 0.2 μm filter. The 5,10,15,20-tetrakis(1'-methyl-4'-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP⁴⁺), silicotungstic acid hydrate (SiW₁₂O₄₀⁴⁻), and *meso*-tetraphenylporphyrin sulfonate (TPPS⁴⁻) were purchased from Aldrich.

Zn(II)TMPyP⁴⁺ was prepared as follows. 5,10,15,20-tetrapyridylporphyrin was refluxed with zinc acetate in dichloromethane/ methanol (6:1) for 3 h. The resulting crystals were purified by a water/dichloromethane extraction, whereupon the dried crystals were then dissolved in a dichloromethane/methanol mixture (50:1) with an excess of methyl iodide and left stirring at room temperature overnight. The recovered purple microcrystals are soluble in water and characterized by the UV–visible spectrum and mass spectrometry.⁴¹

EuPW₁₁O₃₉⁴⁻ was prepared according to literature procedures.⁴² The mica (muscovite form) was purchased from SPI supplies and freshly cleaved using Scotch tape before use.

The indium–tin oxide (ITO) coated slides (70–100 ohm resistance) were purchased from Aldrich, glass slides were purchased from Fisher, and quartz slides were purchased from SPI supplies. The glass, ITO, and quartz substrates were cleaned in an ozone cleaner for 30 min, rinsed with copious amounts of NanoPure water, dried, and used within 0.5 h. The nanolithographic methods to place patterns of polymer insulated gold nanowires on mica were reported previously.⁴³

Physical Measurements.

A Varian Cary Bio-3 spectrophotometer was used for UV–visible spectroscopy, in double-beam mode. Steady-state fluorescence spectra were taken on a Fluorolog-3, with excitation at the maximum UV–visible absorbance (Soret band). Atomic force microscope (AFM) measurements were made with a Nanoscope III Multi-mode (Veeco Metrology, Sunnyvale, CA). Images were acquired in air using commercial silicon tips (MikroMasch, Portland, OR) in both contact mode (CSC21/AIBS lever A & B) and tapping mode (NSC15/AIBS) with a typical tip curvature radius of less than 10 nm (CSC21, force constant = 0.12 N/m, resonant frequency = 12 kHz; CSC21-B, force constant = 2.0 N/m, resonant frequency = 0.2 kHz; NSC15, force constant = 40 N/m, resonant frequency = 325 kHz). The *z* scale was calibrated using commercial calibration grids (MikroMasch, Portland, OR). Nanoshaving data were obtained with a minimum of three nanoshaving experiments per sample for a minimum of two samples.

Fabrication of Multilayer Films.

Films were prepared at room temperature by soaking the solid substrate (mica, glass, quartz, ITO) in a 0.5 mM aqueous solution of porphyrin for 1 min, followed by dipping the substrate three times in unbuffered NANOPure water to remove the excess, nonbound porphyrin solution from the substrate. Subsequently, a layer of polyoxometalates was added by soaking the substrate for 1 min in a 0.5 mM aqueous solution of polyoxometalates and rinsed three times by dipping in NANOPure water. The procedure was repeated until the desired film thickness was obtained. The amount of the material deposited is affected by the drying procedure. After each rinsing, the samples were dried by keeping the substrate vertical and blowing a gentle stream of nitrogen gas at a ca. 45° angle to drive the drops of solution on the surface off the lower part of the substrate. The films on the glass side of the ITO substrate were physically removed by gently wiping with a cotton Q-tip moistened with H₂O, followed by a Q-tip moistened with ethanol. Material is deposited on both sides of the glass, quartz, and mica substrates, and since removal of the material from one side may be incomplete, the samples were used as made. Thus, the UV–visible spectral data (Supporting Information), the fluorescence (Figure 3), and the photos (Figure 4) represents the material deposited on both sides of these substrates. To compare the amount of material on one side of these substrates to the ITO, the absorbance values for glass, quartz, and mica in Figure 2 are divided by two.

Results and Discussion

Solution Phase Interactions.

Solution-phase experiments were done to garner information on the interactions between the two components, but the hierarchical organization of the molecular components in the films is likely quite different from the structures in the solution. UV–visible spectra of 10 μM solutions of TMPyP^{4+} titrated with $\text{EuPW}_{11}\text{O}_{39}^{4-}$ or $\text{SiW}_{12}\text{O}_{40}^{4-}$ in water show well-resolved isosbestic points until 1 equiv of the POM has been added to the aqueous solution. This indicates that the two molecules interact in water due to strong electrostatic interactions to form an ion pair that does not precipitate for several hours. The 422 nm Soret slightly blue shifts by 2 and 518.5 nm and Q-band slightly red shifts by 3 nm as the POM is titrated into the porphyrin solution. However, when more than 1 equiv of the POM is added to the porphyrin solution, e.g., an excess of 0.2 equiv, there is a change in the electronic spectrum manifested by a deviation from the isosbestic points and the formation of a brown precipitate over ca. 1 h. Under these conditions, the association constant for the 1:1 complex is about 10^4 L M^{-1} , but this can only be considered an estimate, since further aggregation leading to precipitation is occurring. Solutions containing a 2:3 porphyrin:POM ratio have significantly different UV-visible spectra, indicating further aggregation prior to the rapid precipitation. The fluorescence intensity of the porphyrin decreases linearly, reaching ca. 70% of the initial value when 1 equiv of the POM is added. The quenching can be due to electron or energy transfer to the POM species and/or due to the heavy atom effect and enhanced intersystem crossing to the triplet state. The last is likely the predominant pathway, because neither the characteristic porphyrin radical anion or cation electronic bands nor photosensitization of Eu luminescence is observed. The characteristic blue color of the reduced POM is also not observed upon illumination with a 50 W halogen lamp in the presence of 2-propanol.⁴⁴

Films. UV–Visible Characterization.

The film growth can be monitored by UV–visible spectroscopy as each deposition of POM or porphyrin is added. The 434 nm Soret absorption peak of the porphyrin in the multilayer film shows a red shift of approximately 12 nm and a significant broadening of the absorption bands compared to the spectra in solution. The red shift and broadening of the optical spectra of the films are likely ascribed to porphyrin–POM aggregates, as observed to a lesser extent in the solution spectra, and to the absorption of the chromophores onto surfaces as previously observed.⁴⁵ Significant porphyrin–porphyrin interactions are not indicated because the well-known spectral signatures for J and H aggregates of these chromophores are not observed. Also, the lack of observable energy transfer in experiments with the zinc and free base derivative in alternating layers contraindicates significant electronic communication between chromophores. UV–visible spectra show that very little of the porphyrin is removed during the deposition of the POM.

The O to W charge-transfer band of the POM is at ca. 250 nm, so deposition of these films onto quartz substrates allows one to monitor the increasing absorbance due to the addition of the POMs. Since the porphyrin pyridyl groups also absorb in this region, a plot of the absorbance at 255 nm is a convolution of the two molecular components, but it remains

linear (Supporting Information). There are no significant shifts in the UV–visible spectra for the POM in the films compared to solution.

The plot of the absorbance as a function of the number of layers for the deposition on different substrates shows the influence of the substrate on the multilayer film formation (Figure 2). Because the surface energetics change during the first few dipping cycles due to screening of surface energy/charge, the initial part of the plots are not a priori linear, but the deposition process does not yield enough data to accurately fit a nonlinear curve. The second part of these plots should be linear, since this represents the regime where the surface energy/charge no longer changes. Thus, we broke the curves into two linear parts to more accurately assess and compare the different systems. Our hypothesis is that the initial part of these curves is affected more by the surface properties, and the second linear portion depends more on the compounds used to make the films. See the detailed discussion by Koenig and Martel on plots of optical spectral intensities versus deposition in layer-by-layer systems.⁴⁶ The initial slopes and the number of deposition cycles in the first region of the plots depend on the magnitude of the surface charge/energy. While the charge density (lattice charge) of mica is well-known (2.1 negative charges/nm²),⁴⁷ the glass charge density depends on the type of glass and the method of cleaning, but in general, the number of negative sites on mica is considerably greater than the number of charged sites on glass,⁴⁸ which is greater than that on ITO. The surface energies of the three different substrates are quite different; for mica at room temperature in air, this is 375 mJ/m² and the value is 180 mJ/m² in a water vapor atmosphere,⁴⁹ while for glass it is 82.5 mJ/m²⁵⁰ and for ITO after ultrasonic degreasing the surface energy is 56 mJ/m².⁵¹ Note that the magnitude of the slopes of the initial lines in Figure 2 are in the same order: mica > glass > ITO. On mica, we estimate that the surface density of the initially deposited TMPyP⁴⁺ from one dipping cycle is ca. 1 porphyrin per 5 nm² using the extinction coefficient of the Soret band of $2.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and assuming that the macrocycles lay flat on the surface. The initial surface density is less on the other substrates. Thus, on mica four or five deposition cycles are required to reach the point where the surface energetics are screened, while on glass and ITO it takes one or two deposition cycles.

The second line for the mica (slope 0.0063) data represents the remaining layers, and the slope is similar to those of glass (0.0059), quartz (0.0060), and ITO (0.0056), indicating that the surfaces are essentially similar. The greater error for the mica data compared to ITO and glass is likely due to imperfections and greater variation in the baseline due to the multiple planes in the mica. Atomic force microscopy (AFM) of the ITO surface shows that it is not atomically smooth and has a surface rms (root means square) roughness of 1.5 nm on 1 μm^2 scans (glass rms = 0.74 nm, mica rms = 0.29 nm). Thus, the increased surface area and perhaps the deposition of more material in the valleys may effect the deposition. Annealing the films at 120 °C up to 24 h does not result in any change of the film morphology or thickness. For the SiW₁₂O₄₀⁴⁻/TMPyP⁴⁺ system, the slope of the lines is similar, even after 60 deposition cycles on ITO and 30 deposition cycles on glass.

The molar absorptivities of the Soret band of Zn(II)TMPyP⁴⁺ ($\epsilon = 2.04 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$)⁴¹ is ca. 10% less than the free base TMPyP⁴⁺ ($\epsilon = 2.26 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$),⁵² so the UV spectra indicate that when Zn(II)TMPyP⁴⁺ is used, more material is initially deposited on ITO

compared to the free base (Figure 2). When the porphyrin layers alternate between the free base and the metalloporphyrin derivatives, the amount of material deposited is in between those of the individual compounds. The Zn(II) ion in the porphyrin has no propensity to bind oxygen ligands, and there is no evidence of free base protonation; thus, the increased slope may be due to small electrostatic or solubility differences of the metalloporphyrin compared to the free base. The deposition of TMPyP^{4+} using $\text{SiW}_{12}\text{O}_{40}^{4-}$ as the counterion material on glass produced films that are similar to those obtained using $\text{TMPyP}^{4+}/\text{EuPW}_{11}\text{O}_{39}^{4-}$ on the same substrate, but with a greater amount of material deposited in each cycle, as judged by the slope of the Soret absorption band maximum versus deposition cycle (0.010). This confirms that the net charge and size of the porphyrin and POM are important determinants of film formation.

Fluorescence Properties of the Films.

The fluorescence analysis of film formation (Figure 3) shows that the TMPyP^{4+} fluorescence ($\lambda_{\text{ext}} = 432 \text{ nm}$, porphyrin Soret) is slightly quenched when deposited on quartz due to anisotropy. The fluorescence is further quenched by the deposition of the POM due to the heavy atom effect from the tungsten in the POM. The fluorescence intensity reaches a steady ca. 20% of the initial value after four deposition cycles, which is when the films reach a consistent composition (vide infra). This demonstrates that the porphyrin–POM material has inherent fluorescence properties. The fluorescence properties of the films suggest that not all porphyrins have POMs directly stacked on the top of the macrocycle, which would likely completely quench the fluorescence by heavy atom effects, so there is a fraction of porphyrins wherein the POMs are held away from the porphyrin by the pyridinium groups. Because the pyridinium groups are orthogonal to the macrocycle, this architectural arrangement less effectively quenches the fluorescence by the heavy atoms in the POM.^{15,16}

Metalloporphyrins.

Consistent with the reduced fluorescence of zinc porphyrins relative to the corresponding free bases, the fluorescence of films made by 12 dipping cycles on ITO with ZnTMPyP^{4+} is ca. 20% of the films formed from the free base. In order to probe the degree of energy transfer between porphyrins in these materials, both the free base TMPyP^{4+} and the metalated ZnTMPyP^{4+} were alternately used in the deposition cycles, i.e., $\text{TMPyP}^{4+}/\text{EuPOM}/\text{ZnTMPyP}^{4+}$. It is well-established that supramolecular constructs containing both zinc and free base porphyrins can exhibit energy transfer from the metalloporphyrins to the free base macrocycles, which is often demonstrated by observing an increase in the free base fluorescence when the metalloporphyrin is selectively excited.^{15,16} Fluorescence studies of these films on glass show that both the free base and the zinc porphyrin fluoresce, but there is little observable indication of energy transfer from the zinc complex to the free base. This likely means that the porphyrins are generally not close enough, or electronically coupled via the POM, to allow efficient energy transfer. An alternative explanation, that the POMs quench the excited-state of the porphyrins by rapid electron transfer or energy reactions, is not indicated by these steady-state experiments for the same reasons they are not observed in the solution-phase studies.

Oppositely Charged Porphyrins.

Mixtures of TMPyP^{4+} and TPPS^{4-} porphyrins and similar derivatives have been extensively studied in terms of the formation of a plethora of aggregate structures.^{8,9} We find that sequential dipping of a substrate into aqueous solutions of TMPyP^{4+} and TPPS^{4-} does not result in multilayer films and no subsequent materials are deposited after the first dipping cycle. This is in contrast to films made with tetrapyrrolylporphyrin appended with four cationic ruthenium complexes^{29,30} and TPPS^{4-} , and electrostatically assembled porphyrin/phthalocyanine films.³¹ Though TPPS^{4-} bears the same number of negative charges and is of similar size as the polyoxometalates, it is likely that the TMPyP^{4+} and the TPPS^{4-} interact so strongly that the ion pair formed has little affinity for the substrate. The interactions between these oppositely charged species are further stabilized by hydrophobic interactions between the aromatic macrocycles. This demonstrates that there must be a careful balance between the intermolecular interactions, the molecular interactions with surfaces, and geometries of the component molecules.

Stability.

The stability of the POM–porphyrin films in toluene, water, and 0.1 M NaCl was investigated. The films formed from 12 deposition cycles on the three different substrates were immersed in toluene, water, and 0.1 M NaCl. UV–visible spectra were taken of samples soaked in the solvent after 1 h, 24 h, and 24 h followed by 1 min of sonication (Figure 4). The UV–visible spectra of the films do not show significant absorption decreases after treatment in these solvents (<10%), and this is confirmed by the optical spectra of the soaking solutions. One might expect that the salt ions screen the charges on the molecules and, therefore, decrease the interaction energies between the component molecules and between the film and the surface. Thus, the electrostatically self-organized films are remarkably robust to solvent-induced disassembly or delamination. The films are stable independent of the type of substrate used. Sonication does not seem to accelerate the delamination process, but the film can be mechanically removed by wiping with a solvent-soaked Q-tip.

Film Morphology.

The film morphology and thickness were analyzed by AFM using both tapping and contact mode. For example, tapping mode images of the films after eight deposition cycles on mica (Supporting Information) show a uniform coverage of the surface that has a granular look with a rms roughness of 2.6 nm. The rms varies somewhat with the number deposition process (4 cycles = 1.8 nm, 12 cycles = 1.6 nm) on $1\ \mu\text{m}^2$ scans. Contact mode AFM studies on films from eight deposition cycles on mica reveal that some of the topmost material can be moved by the scanning probe tip, even with the minimum force between the tip (CSC21-A) and the surface. We refer to this part of the film as the *mobile layer*. To determine the total thickness of the film, a small square section was nanoshaved using contact mode AFM. These nanoshaving experiments (Figure 5) indicate that the film on mica has a total film thickness of 23 ± 3 nm consisting of a lower *nonmobile* layer of 15 ± 3 nm and an upper mobile layer (thickness 7 ± 2 nm). Table 1 summarizes the thicknesses of the films after different numbers of deposition cycles were determined by nanoshaving experiments. The

film prepared with 12 deposition cycles shows a total thickness of approximately 29 nm, but no significant mobile layer. The initial layers can be characterized by AFM on mica substrates, but not on ITO or glass because of the surface roughness. We propose that on mica the first few depositions result in an underlying nonmobile layer until the surface energy is effectively screened by the film. Above this, the mobile layer represents a part of the film that is neither densely packed nor strongly interacting with the surface, and may be ca. 7 nm aggregates. Additional deposition cycles increase the thickness of the upper, mobile part of the film and fill in the defects to make it more compact (see Figure 11 in Supporting Information). Thus, a robust film emerges after 12 deposition cycles. This also explains the difference in roughness between the samples with eight and 12 layers, and is consistent with the UV–visible data.

AFM analysis shows that the morphologies of films resulting from 12 deposition cycles on glass and ITO are similar to those on mica. However, nanoshaving experiments (using a small contact mode cantilever followed by imaging using a tapping mode tip) reveal a film thickness of 9.5 ± 2 nm on glass and 8 ± 2 nm on ITO. The films on glass and ITO are ca. 3-fold thinner than the corresponding 29 nm films on mica, but the UV–visible data indicate that the amount of material deposited on glass and ITO is only ca. half of that of the films on mica. The discrepancy between measured film thicknesses and the optical data is attributed to denser packing of porphyrins and POMs on the glass and ITO substrates, to the wider variations in the surface roughness, and to errors in the measurements. UV–visible measurements of the mica films are hampered by light refraction on mica planes and micrometer imperfections on the surface.

Preliminary cyclic voltammetry studies indicate that the ITO surface has a small effect on the potentials measured for the TMPyP^{4+} and $\text{SiW}_{12}\text{O}_{40}^{4-}$, which are similar to those found using glassy carbon electrodes.^{53,54} The half-wave potentials observed for the $\text{TMPyP}^{4+}/\text{SiW}_{12}\text{O}_{40}^{4-}$ film correspond to each molecular component of the film, but are somewhat shifted from those of the porphyrin or the POM measured in solution under the same conditions. As expected, the measured currents increase with the number deposition cycles (Supporting Information). Detailed electrochemical analysis will be the subject of a future publication.

Patterns of Porphyrin–POM Films.

The use of thin films of photonic materials often requires the formation of patterns of the material on appropriate surfaces. We recently reported a new nanolithographic method that yields polymer insulated gold nanowires on a variety of ceramic substrates.⁴³ Stamped arrays of gold nanowires insulated with polycarbonate on mica provides an ideal platform to further organize the porphyrin–POM film into patterns, because these molecules have high affinities for the mica substrate and low affinities for the polycarbonate polymer. Thus, the sequential dipping of a mica substrate bearing a pattern of gold nanowires encapsulated in polycarbonate into the POM and porphyrin solutions results in a thin film residing on the exposed mica. AFM analysis of these photonic films (Figure 6) reveals that they are somewhat thicker than the films on bare mica, likely due to the accumulation of materials in the valleys of the pattern.

Conclusions

The sequential dipping of a variety of ceramic substrates into aqueous solutions of a tetracationic porphyrin and tetraanionic POM results in remarkably stable nanoscaled films. There are a minimum number of layers needed to fabricate robust films, which depends on the surface energetics of the substrate, but films are readily deposited onto glass, quartz, and ITO, in addition to a charged mica surface. Both the nanolithographic method and the electrostatic formation of the thin films described herein demonstrate that control of surface energetics can be beneficially used in the fabrication of nanomaterials. The film thickness or optical density can be exquisitely controlled by the number of deposition cycles. The chemical properties of the two molecular components, the substrate, and the balance of the intermolecular and molecule–surface interactions dictate the ability to form these films in analogy to the widely studied layer-by-layer methods. The functionality of these films can be modulated by the metal ions in either the porphyrin or lacunary POMs. These thin films are luminescent and can be patterned by dipping substrates bearing nanoscaled arrays of polymers for which the water-soluble molecules have little affinity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Left: 5,10,15,20-tetrakis(1'-methyl-4'-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP⁴⁺) (H = light blue, N = Yellow, C = brown). Right: polyoxometalate (POM) EuPW₁₁O₃₉K₄ (O = red, W = blue, Eu = green, P = pink) The counterions are left out for clarity.

Figure 2.

Absorbance at the Soret band (434 nm) is plotted as a function of the number of layers for the deposition on different substrates and using different porphyrins. Deposition of TMPyP^{4+} and $\text{EuPW}_{11}\text{O}_{39}^{4-}$ on mica (black), on glass (blue), and on ITO (red). Deposition of ZnTMPyP^{4+} and $\text{EuPW}_{11}\text{O}_{39}^{4-}$ on ITO (green) and alternating between porphyrins $\text{TMPyP}^{4+}/\text{EuPW}_{11}\text{O}_{39}^{4-}/\text{ZnTMPyP}^{4+}$ on ITO (pink). The plot for the deposition on quartz is not shown for clarity, since it is nearly the same as that on glass (see Supporting Information). In the case of the glass and mica, the measured absorption is divided by two to account for the deposition of material on both sides of these substrates. Error bars represent ± 1 standard deviation from the mean.

Figure 3.

The fluorescence intensity of the strong emission band at 660 nm of TMPyP⁴⁺ is plotted as a function of deposition cycle, where the closed circles represent spectra taken after porphyrin deposition and the open circles spectra after EuPW₁₁O₃₉⁴⁻ deposition on a quartz substrate. Error bars represent ± 1 standard deviation from the mean.

Figure 4. Stability of the films formed by 12 deposition cycles of TMPyP^{4+} and $\text{EuPW}_{11}\text{O}_{39}^{4-}$ on ITO, glass, and mica. The samples shown are after being soaked for 24 h followed by 1 min sonication in water (W), toluene (T), and 100 mM NaCl.

Figure 5. AFM analysis of a film formed after eight deposition cycles of TMPyP⁴⁺ and EuPW₁₁O₃₉⁴⁻ on mica shows that there are two components of the film, a top ca. 7 nm mobile layer and a bottom ca. 15 nm nonmobile layer.

Figure 6.

Top: contact mode AFM topography of mica patterned with gold nanowires encapsulated in polycarbonate. Bottom: contact mode AFM topography of a different part of the substrate after eight deposition cycles of TMPyP^{4+} and $\text{EuPW}_{11}\text{O}_{39}^{4-}$ shows that the thin film resides on the exposed mica, and nanoshaving experiments indicates a thickness of ca. 40 nm.

Table 1.AFM Analysis of Film Thickness on Mica^a

	thickness, nm		
	4 deposition cycles	8 deposition cycles	12 deposition cycles
total deptd	14 ± 2	23 ± 3	29 ± 3
mobile film	7 ± 2	7 ± 2	none
non-mobile film	7 ± 2	15 ± 3	29 ± 3

^aThe mobile and nonmobile layers were assayed by AFM and nanoshaving experiments. The latter used a cantilever with a higher force constant (CSC21-B). The total thickness of the film deposited on mica increases nonlinearly as indicated by the electronic spectra.