

Uniform Approach to Bacteriochlorophyll-Based Monolayers on Conducting, Semiconducting, and Insulating Substrates

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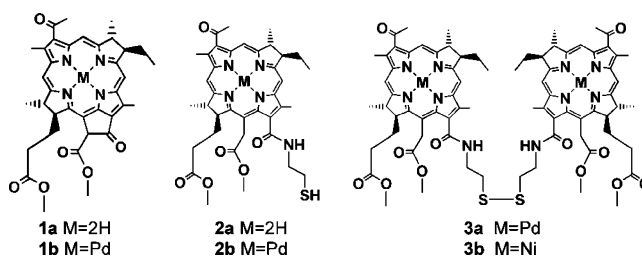
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A general approach is demonstrated for the formation of monolayers comprised of free-base and metalated Bacteriochlorophyll-based derivatives providing a new vehicle for studying photosynthetic motifs and chromophore thin-film interactions. Accessibility to covalent and self-assembled systems on conducting, semiconducting, and insulating substrates is realized utilizing identical molecular building blocks. The monolayers retain the optical features typical for the new systems in solution. Molecular organization of chromophore interaction motifs can be sequentially designed using preassembled building blocks in solution and expressed in the thin film optical properties. For instance, intramolecular π - π stacking is conserved for the dimeric Ni-based chromophores as deduced from the spectroscopic measurements of the monolayers and in solution.

The natural photosynthetic system is regarded as one of the most elaborate nanobiological machines and the subject of much ongoing interest.¹ It involves conversion of solar energy to electrochemical energy via a cascade of photoinduced energy and electron-transfer reactions between donors and acceptors in antenna complexes and reaction centers. Numerous studies on photosynthetic chromophores in Langmuir–Blodgett thin films have been reported.² However, the incorporation of photosynthetic pigments in self-assembled monolayers (SAMs) chemically bound on gold is rare.³ Furthermore, to the best of our knowledge, the formation of covalently bound thin films of photosynthetic chromophores, and Bacteriochlorophyll (BChl)-based monolayers in particular, has not been demonstrated. In sharp contrast, monolayers of porphyrins have been extensively studied.^{4–6a} The chemical sensitivity of BChls hampered formation of covalently bound thin films or SAMs as described here, utilizing natural photosynthetic pigments. Nevertheless, it is highly desirable to develop BChl-based versatile model systems to study the complex photosynthetic machinery as well as new avenues for utilizing the highly optimized photosynthetic chromophores. For instance, monolayers comprised of metalated and free-base BChl-derivatives may provide a new vehicle for studying natural donor/acceptor relationships in a well defined film matrix and present new opportunities for developing efficient synthetic solar energy devices. Recent synthetic progress allows the tailoring of structural and chemical modifications while retaining the unique spectroscopic and redox properties of BChls. The lower symmetry of BChl-based macrocycles as compared to porphyrins provides a highly informative electronic system as expressed in the responsive optical absorption bands. In particular, the microenvironment, ligation state, and charge density at the BChl core area can be probed.^{7–10}

Here we report a general approach toward the formation of covalently assembled thin films and SAMs consisting of donors, acceptor, and light-harvesting type pigments. The synthesis of functionalized free base (**2a**), metal (**2b**), and dimeric BChl-derivatives (**3a,b**) is demonstrated. Importantly, metal incorporation to the molecular building blocks can be used to model various photosynthetic chromophores or to control the BChl macrocycle stability toward oxidation or chemical modifications required for the film formation. Our approach grants accessibility to covalent and self-assembled systems on conducting, semiconducting, and insulating substrates utilizing identical molecular building blocks. The comprehensive approach enables systematic studies related to the monolayer microenvironment as a function of substrate, preassembled motifs and assembly pathways.

Compounds **2** and **3** were self-assembled on gold or covalently attached to benzyl-halide functionalized silicon, glass, and indium-tin-oxide (ITO) substrates. Compounds **2a,b** and **3a,b** were obtained by reaction of M-Bacteriopheophorbide (BPheid) methyl ester¹¹ (**1**; M = 2H, Pd) with an excess of 2-aminoethanethiol in CHCl₃/CH₃OH (2:1 v/v) resulting in aminolysis of the BPheid isocyclic ring.¹⁰ For **2a,b**, the reaction mixture was treated with excess dithiothreitol (DTT) to reverse disulfide formation. All compounds were purified by column chromatography and were characterized by ¹H NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and UV–vis spectroscopy (see the Supporting Information for details).



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SAMs on gold were prepared by immersing the substrates in a 0.5–1 mM solution of each compound in dry CH_2Cl_2 at room temperature for 24 h in a sealed vessel under N_2 with exclusion of light. Subsequently, the substrates were rinsed with copious amounts of CH_2Cl_2 , and dried under a stream of N_2 . Covalent binding of the identical compounds to Si, quartz, and ITO substrates was done in a consecutive manner. First, coupling layers (CL) were prepared from dichloroiodo(4-iodomethyl)-phenylsilane on freshly cleaned float quartz, Si(100), and ITO substrates.⁶ Subsequently, the CL functionalized substrates were fully immersed into a ~ 1 mM dry toluene solution of each of the compounds and heated for 72 h at 75 °C under N_2 using glass pressure tubes. The resulting films were washed and sonicated (5 min) with copious amount of toluene and CH_2Cl_2 and dried under a stream of nitrogen. The films can be stored under N_2 with exclusion of light at room temperature for at least three months. Exposure of the monolayers to light and air resulted in rapid film oxidation, typical for the BChl macrocycle. The films are strongly bound to the CL-functionalized substrates as they are stable toward prolonged heating in common organic solvents and cannot be removed with scotch tape.

All systems were characterized by a combination of transmission UV–vis spectroscopy, aqueous contact angle (CA) measurements, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). For example, XPS measurements on gold and ITO revealed the expected elemental composition, including the metal signals for **2b**, **3a,b** (i.e., $\text{Pd}(3d^{5/2}) = 338.7$ eV, $\text{Ni}(2p^{3/2}) = 855.3$ eV). Chemisorption on gold substrates was validated by XPS using the typical binding energy (BE) value for sulfur bound to gold, $\text{S}(2p^{3/2}) = 162$ eV.¹² The aqueous CA of **2a** (88°) and **2b** (91°) on 100 nm thick gold are nearly identical and comparable with values (90°–103°) reported for organized thiolated porphyrins SAMs on gold.¹³ The aqueous CAs of **3a,b** on 100 nm thick gold ($\sim 93^\circ$) are similar to the ones observed for the single thiolated compounds. The aqueous CA of **2a** and **2b** based monolayers on the CL-functionalized Si is $\sim 75^\circ$. Exposure of unreacted CL molecules may explain the higher wetting. Indeed, XPS measurements on ITO showed a 1:9 ratio for **2b**:CL, whereas the expected ratio for a fully formed film is $\sim 1:6$. The expected ratios are estimated based on the molecular dimensions obtained by molecular mechanics calculations (PM3) and the experimentally determined film thickness (vide infra). AFM measurements of monolayers **2a,b** on Si revealed a smooth surface with RMS roughness of 0.2 nm for $0.4\ \mu\text{m} \times 0.4\ \mu\text{m}$ scan areas. AFM imaging of the 100 nm thick gold on mica showed a typical surface with average terraces diameter varying between 15 and 25 nm (see the Supporting Information). Examination of the gold surface after adsorption of **2b** showed a somewhat island pattern. “Digging” experiments on SAMs **2a,b** revealed a film thickness of ~ 2 nm, in reasonable agreement with the XPS-derived thickness on gold and ITO (~ 1.6 nm). Considering the molecular dimensions, the molecular orientation with respect to the substrate surface may therefore be interpreted as ranging between an essentially vertical (2 nm thick) and a somewhat tilted orientation (1.6 nm) for **2a,b** based films. Prolonged reaction times for the monolayer formation did not result in any further changes in the optical absorbance, contact angle, and XPS elemental ratios.

The monolayers retain the optical features typical for the BChl systems (Table 1). Notably, the Q_y band, which is highly sensitive to macrocycle conformation and aggregation, shows a distinct broadening of 10–20 nm with respect to the solution value. This broadening may indicate the presence of intermo-

TABLE 1: Transmission UV–vis Data of **2a,b and **3a,b** in CH_2Cl_2 (~ 0.5 mM), on Semitransparent Gold and on CL-Quartz (in Parentheses)**

BChl	medium	λ_{max} (nm)			
		Q_y	Q_x	B_x	B_y
2a M=2H	solution	750	519	382	356
	surface	750(748)	520(519)	382(381)	353 (353)
2b M=Pd ^a	solution	750	519	387	333
	surface	747(749)	518(520)	389(388)	--- (335)
3a M=Pd ^a	solution	750	518	387	333
	surface	747(750)	518(518)	386(386)	--- (335)
3b M=Ni	solution	787	536	398	344
	surface	787(790)	530(530)	395(398)	--- (344)

^a A band ($\sim 10\%$) at $\lambda = 645$ nm is formed due to partial oxidation of the chromophores on CL-Quartz and ITO substrates.

lecular π – π interactions; however, there are no strong excitonic interactions. Typically, aggregation of photosynthetic complexes in solution results in large shifts and enhanced absorption of the Q_y transition as a result of dominant intermolecular interactions.^{8,14} Similarly, J-type aggregation in porphyrin-based SAMs result in large red shifts and broadening of both Soret and visible region bands.^{3,5,6a} The optical spectra of the SAMs on gold show an extended absorption in addition to the BChl electronic band structure. This effect is attributed to the changes induced by monolayer formation on the thin gold films.¹⁵

UV–vis spectra of compounds **3a,b** on gold vs CH_2Cl_2 solutions are shown in Figure 1 exhibiting the typical absorption bands observed in monomeric solution. For the Pd dimer and monomer, **3a**, and **2b**, respectively, the Q_y band show similar broadening upon film formation, indicating that the molecular setup for the dimer and monomer based films is similar. In sharp contrast to **3a**, the solution UV/vis spectrum of **3b** shows intramolecular π – π interactions which are most apparent as an additional shoulder at $\lambda = 745$ nm and a nonsymmetric Q_x band. Interestingly, these optical features are also present in the SAM of **3b** on the gold surface, implying that the intramolecular π – π stacking is conserved. The stacking is related to the nature of the metal center and the short disulfide linkage. The Ni center induces a highly ruffled macrocycle

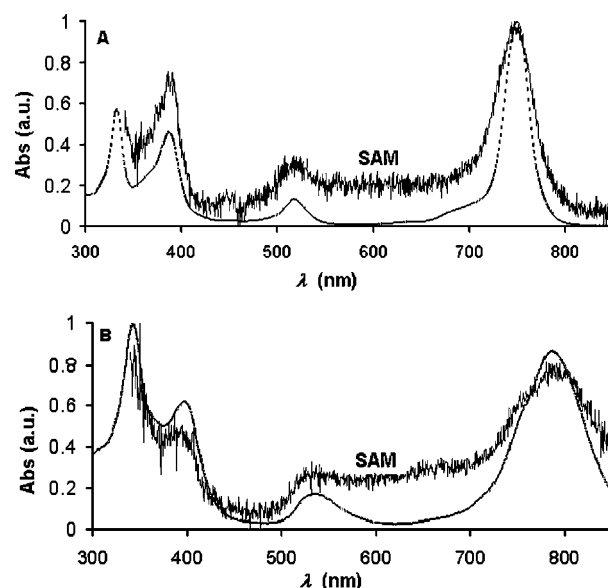


Figure 1. Transmission UV–vis spectra of compounds (A) **3a** and (B) **3b** on semitransparent gold substrates. SAMs vs solution spectra (CH_2Cl_2 , ~ 0.5 mM).

conformation, whereas the Pd (**2b,3a**) and 2H (**2a**) derivatives are planar.¹⁶ The intramolecular chromophore–chromophore interaction is preserved indicating that competing packing interactions in the monolayer do not alter the preassembled molecular setup.

In conclusion, we have demonstrated the synthesis and building up of a platform of organized BChl derivatives allowing conservation of intramolecular interactions and characteristic spectroscopic features. The broad scope of surface chemistry ranging from covalent attachment to self-assembled systems made accessible to the natural related BChl derivatives is critical for controlling chromophore environment and thin film properties. The molecular organization of the thin film motifs can be sequentially designed using preassembled macrocyclic building blocks in solution. Remarkably, the low redox-potentials of BChl as compared to porphyrin macrocycle are strongly affected by the nature of the metal center,⁷ enabling unprecedented control and engineering of monolayer properties including metal–ligand coordination, covalent modifications, and molecular interactions.

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Supporting Information Available: Synthesis and characterization data of compounds **2a,b** and **3a,b**. AFM images of gold substrate and SAM of **2b** on gold (Figures S1,S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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