

Assembly of a Zn(II)-Porphyrin–Bipyridinium Dyad and Au-Nanoparticle Superstructures on Conductive Surfaces

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Received August 31, 1998

The chemical modification of surfaces with functionalized monolayers or thin films attracts extensive recent research effort directed to the miniaturization of devices to nanoscale dimensions.¹ Functionalization of electrodes with ordered arrays of redox-active components has yielded assemblies revealing vectorial electron transfer and rectifier functions² and sensoric activities.³ The modification of electrodes with photoisomerizable, redox-active monolayers has enabled the organization of systems for the electronic transduction of recorded optical information.⁴ The assembly of ordered metal nanoparticles on solid supports attracts substantial research efforts as a consequence of their unique electronic and optical properties.⁵ The assembly of Au- or Ag-colloid monolayers on glass or conductive glass supports has been accomplished by the self-organization of the metal particles onto aminosiloxane or thiol siloxane layers associated with the solid supports.⁶ Three-dimensional superstructure arrays of Au- or Ag-nanoparticles or Au–Ag composite arrays have been reported by the use of dithiols or diamino bipyridinium as molecular cross-linkers for the 3D-nanostructures.⁷ The combination of metal nanoparticles and molecular photoactive or electroactive components could lead to integrated nanoscale assemblies or nanodevices of unique functions. Recently, it was demonstrated that the nanometer-scale organization of metal colloids is of high value in the engineering of nanodevices. Au-

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(1) (a) Drexler, K. E., Ed. *Nanosystems, Molecular Machinery, Manufacturing and Computation*; Wiley: New York, 1992. (b) Carter, F. L.; Siatowsky, R. E.; Woltjen, H., Eds.; *Molecular Electronic Devices*; Elsevier: Amsterdam, 1988. (c) Finklea, H. O. In *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19, pp 109–335. (d) Willner, I.; Willner, B. *Adv. Mater.* **1997**, *9*, 351. (e) Willner, I.; Willner, B. *J. Chem. Mater.* in Press.

(2) (a) Smith, D. K.; Lane, G. A.; Wrighton, M. S. *J. Phys. Chem.* **1988**, *92*, 2616. (b) Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (c) Vining, W.; Surridge, N. A.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2281. (d) Doron, A.; Portnoy, M.; Lion-Dagan, M.; Katz, E.; Willner, I. *J. Am. Chem. Soc.* **1996**, *118*, 8937. (e) Katz, E.; Heleg-Shabtai, V.; Willner, I.; Rau, H. K.; Haehnel, W. *Angew. Chem.* in Press.

(3) (a) Hickman, J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *Science* **1991**, *252*, 688. (b) Schierbaum, K. D.; Weiss, T.; Thorden van Zelzen, E. U.; Engbersen, J. F. G.; Reinhoudt, D. N.; Göpel, W. *Science* **1994**, *265*, 1413.

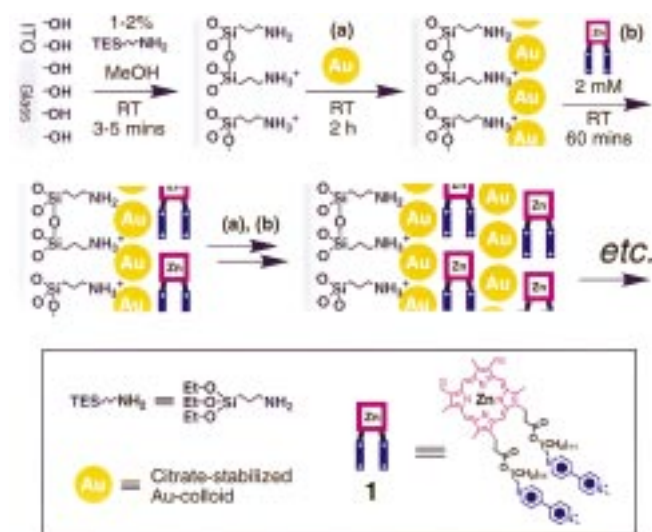
(4) (a) Daub, J.; Salbeck, J.; Knöchel, T.; Fisher, C.; Kunley, H.; Rapp, K. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1494. (b) Doron, A.; Katz, E.; Tao, G.; Willner, I. *Langmuir* **1997**, *13*, 1783. (c) Willner, I.; Lion-Dagan, M.; Marx-Tibbon, S.; Katz, E. *J. Am. Chem. Soc.* **1995**, *117*, 6581. (d) Doron, A.; Katz, E.; Portnoy, M.; Willner, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1535. (e) Willner, I.; Blonder, R.; Katz, E.; Stocker, A.; Bückmann, A. F. *J. Am. Chem. Soc.* **1996**, *118*, 5310.

(5) (a) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1658. (b) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457. (c) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41. (d) Weller, H. *Adv. Mater.* **1993**, *5*, 88. (e) Weller, H.; Eychmüller, A. *Adv. Photochem.* **1995**, *20*, 165. (f) Alivisatos, A. P. *Science* **1996**, *271*, 933. (g) Brus, L. E. *Appl. Phys. A* **1991**, *53*, 465.

(6) (a) Freeman, R. G.; Graber, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629. (b) Freeman, R. G.; Hommer, M. B.; Graber, K. C.; Jackson, M. A.; Natan, M. J. *J. Phys. Chem.* **1996**, *100*, 718. (c) Doron, A.; Katz, E.; Willner, I. *Langmuir* **1995**, *11*, 1313.

(7) Blonder, R.; Sheezy, L.; Willner, I. *Chem. Commun.* **1998**, 1393.

Scheme 1. Stepwise Assembly of the Three-Dimensional Array of the Bis-bipyridinium–Porphyrin Dyad and Au-Nanoparticles on a Conductive ITO Support



clusters were persuaded to behave as a tunnel resonance resistor⁸ and a Au-cluster was used as a single-electron tunneling transistor.⁹ Also, three-dimensional Au-colloid superstructures, cross-linked by a bipyridinium cyclophane and assembled on conductive supports, were reported to act as tunable sensing interfaces for hydroquinone-derived compounds.¹⁰

Photosensitizer–electron-acceptor dyads or triads have been examined as model systems for the photosynthetic reaction center.¹¹ Effective intramolecular photoinduced electron transfer proceeds in these supramolecular systems, resulting in redox intermediates. Here we report on the assembly of layered 3D-superstructures consisting of the bis-bipyridinium–Zn(II)-protoporphyrin IX, (1),¹² as photosensitizer–acceptor dyad and nanosize (15 ± 1 nm) Au-particles.

The superstructure of Au-nanoparticles cross-linked by 1 was assembled on an ITO electrode as outlined in Scheme 1. The cleaned conductive support was first functionalized with (3-aminopropyl)triethoxysilane, and then a first layer of citrate-stabilized Au-particles (15 ± 1 nm) was assembled on the ammonium-functionalized surface. The resulting Au-colloid layer was treated with an aqueous solution of 1 (2 mM, 1 h), followed by standing in water for 1 h) and subsequently with the Au-particle solution (0.05 g·L⁻¹) to generate the second Au-layer. By stepwise treatment of the assembly with the cross-linking component 1 and the Au-nanoparticle solution, three-dimensional arrays consisting of a controllable number of layered cross-linked

(8) Simon, U.; Schön, G.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 250.

(9) (a) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifengerger, R. *Science* **1996**, *272*, 1323. (b) Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. *Nature* **1997**, *389*, 699.

(10) Shipway, A. N.; Lahav, M.; Blonder, R.; Willner, I. *Chem. Mater.*, in press.

(11) (a) Connolly, J. S.; Bolton, J. R. In *Photochemical Electron Transfer, Part D*; Fox, M. A. Chanon, M., Eds.; Elsevier: Amsterdam, Section 6.2. (b) Gust, D.; Moore, T. A. *Top. Curr. Chem.* **1991**, *159*, 103. (c) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849. (d) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (e) Gust, D.; Moore, T. A.; Moore, A. L.; Seely, G.; Liddell, P.; Barrett, D.; Harding, L. O.; Ma, X. C.; Lee, S. J.; Gao, F. *Tetrahedron* **1989**, *45*, 4867. (f) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435. (g) Willner, I.; Willner, B. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., Von Bünau, G., Eds.; Wiley: London, 1995; Vol. 20, p 217.

(12) Saito, T.; Hirata, Y.; Sato, H.; Yoshida, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1925.

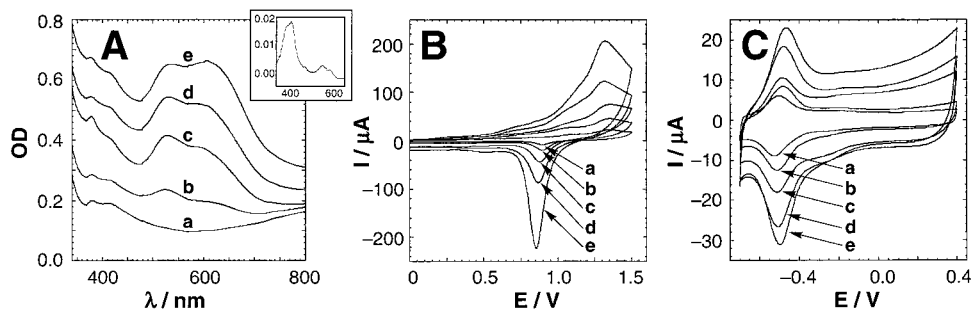


Figure 1. (A) Absorbance spectra of the layered receptor–Au-colloid superlattice: (a) one Au-layer (b) two Au-layers (c) three Au-layers (d) four Au-layers (e) five Au-layers. (A, inset) Change in the absorbance spectrum of an electrode functionalized with a monolayer of gold upon treatment with the porphyrin “cross-linker” component. (B) Cyclic voltammograms of the layered Au-colloid assemblies corresponding to the electrochemical oxidation and reduction of particle surface: (a) to (e) correspond to one up to five layers of Au-particles. Carried out in 1.0 M H₂SO₄, scan rate 50 mV·s⁻¹. (C) Cyclic voltammograms corresponding to the redox activity of the viologen component of the cross-linker **1** in different layer arrays: (a) to (e) correspond to one up to five layers of Au-particles. Recorded under argon in 0.1 M phosphate buffer solution, pH = 7.2, scan rate 100 mV·s⁻¹

Au-particles were generated. Formation of the cross-linked Zn(II)-protoporphyrin IX–bis-bipyridinium dyad and Au-particle superstructure was confirmed and characterized by several methods. Figure 1A shows the absorbance spectra of the array upon the stepwise assembly of the layers. The typical plasmon absorbance associated with the Au-nanoparticles, $\lambda = 519$ nm, increases in intensity upon growth of the layers. The growth of the number of layers results in the appearance of an additional absorbance band at ca. $\lambda = 650$ nm, which shifts to longer wavelengths with increased layer growth. The latter spectral changes are attributed to excitons originating from interparticle plasmon coupling that are facilitated upon formation of the superstructure. In fact, similar spectral changes are observed upon addition of a bipyridinium salt to a Au-colloid suspension resulting in the time-dependent aggregation of the Au-particles and their ultimate precipitation.¹³ The absorbance of the Zn(II)-porphyrin–bis-bipyridinium “molecular glue” components is not clearly observed upon the build-up of the superstructure. This is due to the low surface coverage of **1** in the superstructure and to the fact that the absorbance region of **1** is perturbed by the changing absorbances of the gold colloid. The growing absorbance shoulder at ca. $\lambda = 420$ nm is attributed to the Zn(II)-porphyrin chromophore of **1**. Figure 1A, inset, shows the spectrum resulting upon the subtraction of the spectrum of the primary Au-colloid layer from the spectrum obtained upon the assembly of **1** on the Au-layer, Figure 1, curve a. A spectrum characteristic of **1** ($\lambda = 420, 548, \text{ and } 586$ nm) is obtained, implying that the dyad **1** is, indeed, associated with the Au-particles. Figure 1B shows the cyclic voltammograms of the assembled layers of the Au-particles that show the surface oxidation of the Au-particles, and the concomitant reduction of the surface oxide layer. The roughness of the assembly, or the total surface area of the Au-particles, increases upon the growth of the number of layers. Knowing the total surface area of the Au-particles per layer, and the diameter of the particles, 15 ± 1 nm, and assuming that the entire particle surface is exposed to the electrochemical reactions, we estimate the lower limit of the Au-particle density to be on average 0.5×10^{11} particles·cm⁻² per layer for the first 5 layers. This value is in reasonable agreement with the surface coverage of a densely packed 13-nm Au-colloid monolayer determined by AFM, 1.0×10^{11} particles·cm⁻². In addition, evidence of the presence of the Zn(II)-porphyrin units is observed in the cyclic voltammograms. Peaks for the oxidation of the porphyrin ring first to the radical cation, then to the dication, are seen at ca. 0.7 and 1.05 V, respectively.¹⁴

Further support that the Zn(II)-porphyrin–bis-bipyridinium dyad (**1**) acts as molecular cross-linker of the Au-nanoparticles is obtained by following the electrochemical response of the bipyridinium units. Figure 1C shows the cyclic voltammograms of the dyad **1**, molecular glue component, upon the growth of the Au-particle superstructure. The electrochemical response of the bipyridinium units of **1**, $E^\circ = -0.48$ V vs SCE, increases with the number of layers, indicating that tetracationic dyad cross-links the negatively charged citrate-modified Au-particles. Coulometric analysis of the electrochemical responses of **1** indicates that the surface coverage of the dyad increases almost linearly with the build-up of the layers, and we estimate that approximately 250 molecules of **1** are associated with each particle. The fact that the electrochemical response of **1** increases upon the growth of the superstructure implies that the array exhibits three-dimensional conductivity.

Photoexcitation of the dyad **1** in an aqueous solution results in intramolecular electron transfer and the rapid recombination of the redox-photoproducts. Indeed, preliminary studies indicate that photoirradiation of the Zn(II)-porphyrin–bis-bipyridinium dyad–Au-nanoparticle superstructure in the presence of Na₂EDTA as sacrificial electron donor results in a photocurrent originating from charge injection into the ITO electrode through the Au-nanoparticle array. The observed current density increases with the number of layers, and for a five-layer array it corresponds to ca. $3.0 \mu\text{A}\cdot\text{cm}^{-2}$. Thus, the three-dimensional conductivity and roughened surface of the Au-nanoparticle array probably facilitates the electron–hole separation and the effective electron transport to the bulk ITO-electrode.

In conclusion, we have developed a novel method for the organization of a photosensitizer-electron acceptor/Au-nanoparticle superstructure exhibiting three-dimensional conductivity. The high surface area of the layered particle allows the controllable immobilization of the photoactive dyad on the porous Au-support. This, together with the conductivity of the array, suggests that these superstructure-modified electrodes could be used as new materials for photocells.

Acknowledgment. This research is supported by the Volkswagen Stiftung, Germany. A.N.S. and T.G. acknowledge postdoctoral fellowships from the Royal Society (UK) and MINERVA Foundation (Germany), respectively.

(13) Lahav, M.; Shipway, A. N.; Willner, I., unpublished results.

(14) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982.