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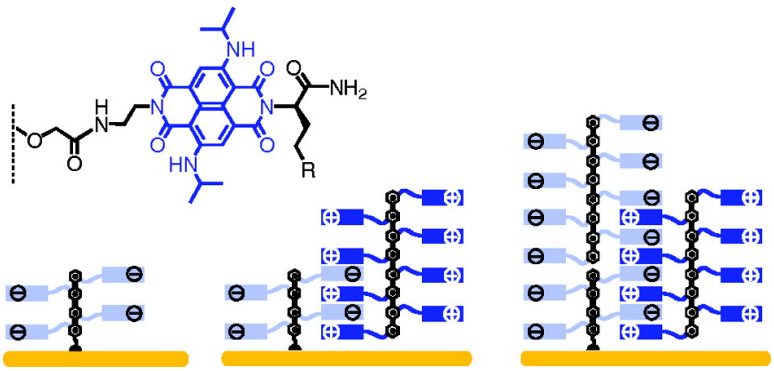

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Zipper Assembly of Photoactive Rigid-Rod Naphthalenediimide π-Stack Architectures on Gold Nanoparticles and Gold Electrodes

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In this report, we introduce zipper assembly as a simple and general approach to complex functional architectures on conducting surfaces (Figure 1). In domains such as organic optoelectronics, reliable access to sophisticated synthetic architectures is often essential to create significant function.[1−3] Zipper assembly was conceived on the basis of early findings[4] related to the Vernier assembly,[5] where mismatches of rod length led to higher-order assembly of mixed rigid-rod molecules. This characteristic implied that rigid-rod molecules with "sticky-ends" could serve as powerful modules to create complex architectures on conducting surfaces.

Rigid-rod π-stack architectures composed of *p*-oligophenyl rods and naphthalenediimide (NDI)[6,7] stacks[3] were selected to explore zipper assembly. The design was as follows. To initiate zipper assembly, short *p*-quaterphenyls **1** with four anionic NDIs are deposited on gold (Figure 1, Supporting Information Figure S1). For propagation, double-length *p*-octiphenyls **2** with eight cationic NDIs are added. Directed by flanking hydrogen-bonded chains (Figure S2)[3] and interstack ion pairing (Figure S3), one-half of these NDIs was expected to form π-stacks with initiator **1**. The free half of the cationic propagator **2** remains available as unbendable sticky-ends on the surface to zip up with the anionic propagator **3** added next. The resulting anionic sticky-ends can zip up with cationic propagator **2** and so on. This zipping up of *n*-semiconducting NDI stacks along *p*-semiconducting[8] *p*-oligoanisol rods could produce supramolecular *n*/*p*-heterojunctions.[1] Importantly, the photo- and electrochemical variability of NDIs without global structural changes[9] promised access to multicomponent zippers where the direction of electron flow is controlled and light is absorbed at various wavelength.

For zipper assembly, the *p*-quaterphenyl initiator **1** with anionic NDIs and a disulfide anchor was synthesized (Scheme S1).[10] Moreover, the already available *p*-octiphenyl **2** with cationic NDIs[3] was complemented with the anionic propagator **3** (Scheme S2). The blue, red-fluorescent *p*-octiphenyl **2** has been shown to exhibit ultrafast (<2 ps), quantitative (>97%), and reasonably long-lived (61 ps) photoinduced charge separation ($E_{HOMO} = -5.4$ eV, $E_{LUMO} = -3.5$ eV, Table S1).[3,10]

Zipper assembly was initially evaluated on gold nanoparticles (Figures 1, 2).[11] Freshly prepared, citrate-stabilized gold nanoparticles ($d \approx 13$ nm) were coated with initiator **1**, and then repeatedly exposed to cationic and anionic propagators **2** and **3**. Zipper growth was evidenced in absorption spectra of the resulting coated nanoparticles not only by the expected increase in NDI absorption around 630 nm but also by the bathochromic shift of the surface plasmon resonance (SPR) band near 520 nm, providing an accurate measure for the increase in layer thickness during zipper assembly (Figures 2A and S4).[10] Moreover, the appearance of a hypsochromic maximum around 600 nm indicated significant face-to-face π-stacking of the NDIs in the zipper.[3]

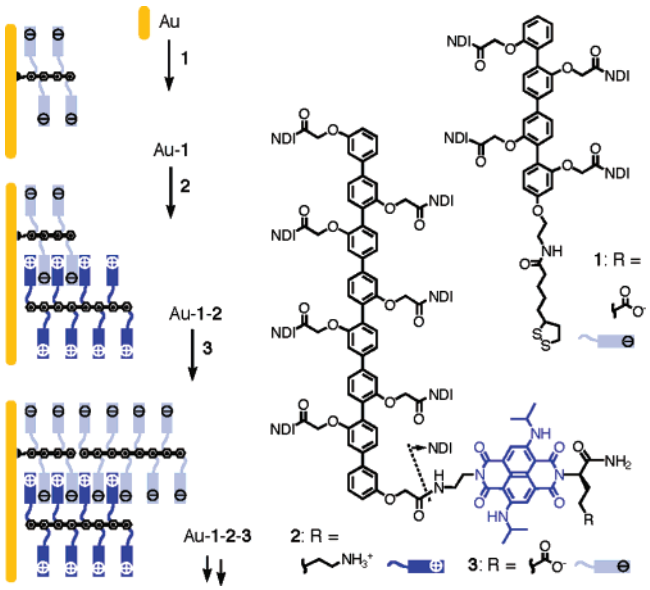

Figure 1. The concept of zipper assembly on gold. All shown suprastructures are simplified, in part speculative representations that are, however, consistent with experimental data on function (below) and molecular models.[3]

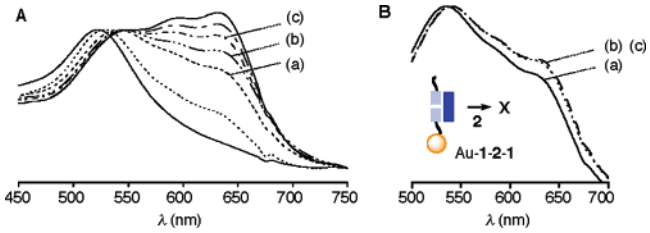

Figure 2. Zipper assembly on gold nanoparticles. (A) Change in absorption during assembly of a zipper (sequence Au-**1**-**2**-**3**-**2**-**3**-**2**) with increasing absorption at 630 nm on gold nanoparticles (solid, (a) Au-**1**-**2**; (b) Au-**1**-**2**-**3**; (c) Au-**1**-**2**-**3**-**2**). (B) Same for the sequence (a) Au-**1**-**2**, (b) Au-**1**-**2**-**1** and (c) Au-**1**-**2**-**1** + **2** (c, all in 50% aqueous TFE).[10]

Zipper assembly with cationic ends (Au-**1**-**2**) could be effectively terminated using anionic *p*-quaterphenyls **1**. The addition of terminator **1** to an Au-**1**-**2** zipper caused the expected 50% increase in NDI absorption of Au-**1**-**2**-**1** compared to Au-**1**-**2**-**3** (Figure 2, curves b). Addition of propagator **2** to the terminated Au-**1**-**2**-**1** did not cause any increase in absorption, whereas addition to Au-**1**-**2**-**3** resulted in further increase of absorption, proving the formation of Au-**1**-**2**-**3**-**2** (Figure 2, curves c). This complete inhibition of zipper assembly with terminator **1** demonstrated the existence of sticky-ends in zipper assembly. Moreover, the found rod-length

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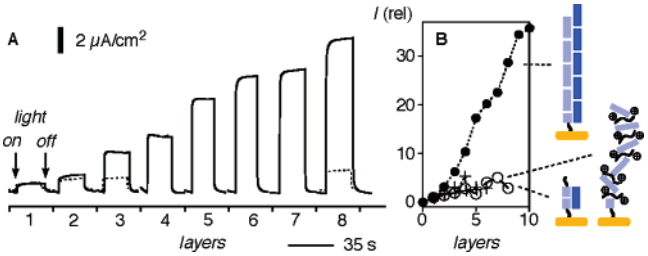

Figure 3. Zipper assembly on gold electrodes. (A) Change in photocurrent during assembly of a blue zipper (sequence Au-**1**-**2**-**3**-**2**-**3**-**2**-**3**-**2**, solid) and a capped control zipper (Au-**1**-**2**-**1** + **2** + **3** + **2** + **3** + **2**, dotted) on gold electrodes (Conditions: **2**, **3** (~10 μM) in TFE/H_2O (0.5 mM $Na_nH_{3-n}PO_4$, 0.5 M NaCl, pH 7) 1:1, room temp, 14 h; rinsed with H_2O and EtOH). (B) Dependence of photocurrent on number of oligo-NDI layers of the blue zipper (●) compared to blue LBLs (Au-**1**-pK-**3**-pK-**3**-pK-**3**-pK-**3**-pK-**3**, pK = polylysine, +) and the capped Au-**1**-**2**-**1** + **2** + **3** + **2** + **3** + **2** (○).[10]

dependence in propagation and termination steps confirmed that indeed zipper assembly as depicted in Figure 1 is operational and not the conventional layer-by-layer (LBL) assembly.[2]

Zipper assembly on gold electrodes was explored next. Deposition of initiator **1** on the electrode surface caused complete inhibition of electrochemical ferricyanide reduction (Figure S5). This result indicated the absence of large uncoated areas that would allow the approach of ferricyanide to the gold electrode despite charge repulsion from **1**. Zipper assembly from Au-**1** by repeated dipping into first cationic and then anionic propagators **2** and **3**, respectively, gave rise to increasing photocurrents as expected from the increased absorption of light (Figure 3A, solid, B, ●). With triethanolamine (TEOA) as sacrificial electron donor, the gold electrode served as electron acceptor and the Pt electrode as cathode.

As on gold nanoparticles, terminator **1** could effectively stop the growth of zipper assembly on gold electrodes. After capping of Au-**1**-**2** electrodes with terminator **1**, repeated addition of propagators **2** and **3** did not cause any significant increase in photocurrent (Figure 3A, dotted, B, ○). The consistent results obtained using different surfaces and methods corroborated the existence of operational sticky ends.[12]

As a second control experiment, conventional, purely electrostatic LBL assemblies were prepared by replacing the cationic NDI *p*-octiphenyls **2** by poly-L-lysine (pK). Nearly negligible photocurrents were obtained (Figure 3B+). This result suggested that electron transfer through less ordered LBL layers is inefficient and thus supported the functional importance of the refined architectures in zipper assembly (Figure 3B, ● vs +).

In conclusion, we have presented evidence for the existence and functional significance of zipper assembly. Steady zipper growth with mismatched rods and the absence of zipper growth with matched rods were both demonstrated on gold nanoparticles and gold electrodes by three independent methods (i.e., photocurrent generation, NDI absorption, and shift of the SPR band).[12] The shown feasibility to terminate the zipper assembly and the much weaker photocurrent observed with conventional LBL controls are in support of the ordered structure in zipper assembly. Although various surface characterization studies are ongoing to gain additional insights on structure, the here reported studies provide the ultimately relevant functional evidence and promise attractive perspectives. Preliminary results on increasing zipper complexity with differently colored NDIs to address more challenging functions are very promising.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines*, Wiley-VCH: Weinheim, Germany, **2003**. (b) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066−1096. (c) Yamamoto, Y.; Fukushima, T.; Suna, Y.; Ishii, N.; Saeki, A.; Seki, S.; Tagawa, S.; Taniguchi, M.; Kawai, T.; Aida, T. *Science* **2006**, *314*, 1761−1764. (d) Würthner, F.; Chen, Z.; Hoeben, F. J. M.; Osswald, P.; You, C.-C.; Jonkheijm, P.; Herrikhuyzen, J.; Schenning, A. P. H. J.; van der Schoot, P. P. A. M.; Meijer, E. W.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2004**, *126*, 10611−10618. (e) Kang, S.; Umeyama, T.; Ueda, M.; Matano, Y.; Hotta, H.; Yoshida, K.; Isoda, S.; Shiro, M.; Imahori, H. *Adv. Mater.* **2006**, *18*, 2549−2552. (f) Fukuzumi, S. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 177−195. (g) Jones, B. A.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Chem. Mater.* **2007**, *19*, 2703−2705. (h) Morisue, M.; Yamatsu, S.; Haruta, N.; Kobuke, Y. *Chem. Eur. J.* **2005**, *11*, 5563−5574. (i) Chaignon, F.; Falkenstrom, M.; Karlsson, S.; Blart, E.; Odobel, F.; Hammarstrom, L. *Chem. Commun.* **2007**, *42*, 64−66.
(2) (a) Decher, G. *Science* **1997**, *277*, 1232−1237. (b) Mwaura, J. K.; Pinto, M. R.; Witker, D.; Ananthakrishnan, N.; Schanze, K. S.; Reynolds, J. R. *Langmuir* **2005**, *21*, 10119−10126. (c) Fushimi, T.; Oda, A.; Ohkita, H.; Ito, S. *Langmuir* **2005**, *21*, 1584−1589. (d) Lahav, M.; Heleg-Shabtai, V.; Wasserman, J.; Katz, E.; Willner, I.; Dürr, H.; Hu, Y.-Z.; Bossmann, S. H. *J. Am. Chem. Soc.* **2000**, *122*, 11480−11487. (e) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855−4856. (f) Abdelrazzaq, F. B.; Kwong, R. C.; Thompson, M. E. *J. Am. Chem. Soc.* **2002**, *124*, 4796−4803.
(3) Bhosale, S.; Sisson, A. L.; Talukdar, P.; Fürstenberg, A.; Banerji, N.; Vauthey, E.; Bollot, G.; Mareda, J.; Röger, C.; Würthner, F.; Sakai, N.; Matile, S. *Science* **2006**, *313*, 84−86.
(4) Das, G.; Matile, S. *Chirality* **2001**, *13*, 170−176.
(5) Hunter, C. A.; Tomas, S. *J. Am. Chem. Soc.* **2006**, *128*, 8975−8979.
(6) (a) Lokey, R. S.; Iverson, B. L. *Nature* **1995**, *375*, 303−305. (b) Gorteau, V.; Bollot, G.; Mareda, J.; Perez-Velasco, A.; Matile, S. *J. Am. Chem. Soc.* **2006**, *128*, 14788−14789.
(7) (a) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423. (b) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478−481. (c) Langford, S. J.; Latter, M. J.; Woodward, C. J. *Photochem. Photobiol.* **2006**, *82*, 1530−1540. (d) Pantos, G. D.; Wietor, J. L.; Sanders, J. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 2238−2240.
(8) Khanna, R. K.; Jiang, Y. M.; Creed, D. *J. Am. Chem. Soc.* **1991**, *113*, 5451−5453.
(9) (a) Thalacker, C.; Röger, C.; Würthner, F. *J. Org. Chem.* **2006**, *71*, 8098−8105. (b) Blaszczyk, A.; Fischer, M.; von Hänisch, C.; Mayor, M. *Helv. Chim. Acta* **2006**, *89*, 1986−2005.
(10) See Supporting Information.
(11) (a) Liu, G. L.; Yin, Y.; Kunchakarra, S.; Mukherjee, B.; Gerion, D.; Jett, S. D.; Bear, D. G.; Gray, J. W.; Alvisatos, A. P.; Lee, L. P.; Chen, F. F. *Nat. Nanotechnol.* **2006**, *1*, 47−52. (b) Haes, A. J.; Zou, S.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2004**, *108*, 109−116.
(12) Preliminary results with quartz crystal microbalance reproduced the steady zipper growth found by photocurrent generation, NDI absorption, and shift of the SPR band.

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