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Organic–Inorganic Hybrid Composites

Self-Assembled Hybrid Oligo(*p*-phenylenevinylene)–Gold Nanoparticle Tapes**

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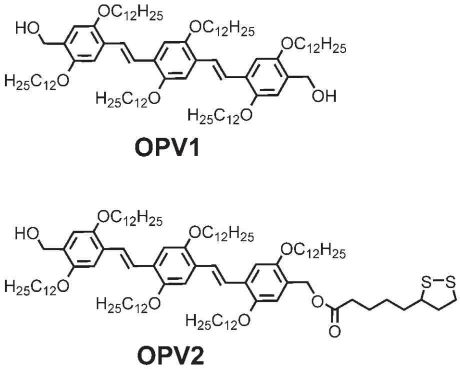
The internal organization of hybrid materials based on inorganic nanoparticles and π-conjugated polymers has a strong influence on their optoelectronic properties and affects the performance of devices with these materials as the active layer.[1] For example, photovoltaic action in hybrid organic–inorganic materials requires intimate mixing of the individual components and also continuous pathways through both phases for the transport of electrons and holes towards an electrode.[2] Furthermore, for the transport of electrons, holes, or excitations in hybrid materials, organization into domains with high aspect ratios (for example, rods, fibers, and tapes) is often preferred.[3] An attractive approach to control the internal organization of hybrid materials is to use noncovalent, supramolecular interactions.[4,5] The self-organization of organic molecules in solution into fiberlike structures, leading to gel formation, is well known.[6] Recently, one-dimensional arrangements of metal nanoparticles have been obtained using gel composites,[7] fibers,[8] and templates of organic molecules.[9] Noticeably, the combination of self-assembled, semiconducting π-conjugated organogelators and inorganic nanoparticles is unexplored and is of paramount importance from the viewpoint of hybrid optoelectronic materials. Herein, we report on a template approach[10] in which metal nanoparticles are bound in a supramolecular manner to self-assembled, π-conjugated oligo(*p*-phenylenevinylene) (OPV) tapes, thus resulting in linear hybrid superstructures. Spectroscopic measurements highlight the electronic communication between the OPV tapes and the inorganic particles.

The template chosen was an OPV derivative **OPV1** (Scheme 1), which is a gelator of toluene that forms tapelike structures as a result of π–π stacking, hydrogen-bonding, and van der Waals interactions.[11] Another OPV derivative **OPV2**, which contains a disulfide moiety at one end for binding to gold, was synthesized by the reaction of **OPV1** with thioctic acid.[12] **OPV2**–Au particles were synthesized by using the method developed by Brust et al., in which $HAuCl_4$ is reduced with $NaBH_4$ in the presence of **OPV2**.[12,13] The size of the gold core was approximately 2.4 nm, as determined by transmission electron microscopy (TEM).



Scheme 1. Chemical structures of **OPV1** and **OPV2**.

Hybrid **OPV1**/**OPV2**–Au supramolecular tapes were prepared by mixing **OPV1** and **OPV2**–Au in toluene followed by heating above the gelation temperature of **OPV1**. Subsequent cooling of the solution resulted in a clear gel. Gelation has been observed for molar ratios of **OPV1**/**OPV2**–Au of 750:1, 100:1, and 20:1. Interestingly, the critical gelator concentration (CGC) for the 100:1 and the 750:1 mixtures was lower than that of the gel of **OPV1** alone (Table 1). This observation indicates that **OPV2**–Au interacts with the **OPV1** tapes. In contrast, admixture of gold nanoparticles capped with an aliphatic disulfide derivative **C10**–Au with **OPV1** (1:100), left the CGC value unaffected (see the Supporting Information).

The **OPV1**/**OPV2**–Au hybrid tapes could be visualized with TEM. At low magnification, a network of micrometer-long fibers is visible for the 100:1 mixture (Figure 1a). At higher magnification, individual tapes can be distinguished and they typically have a width of approximately 30 nm. This width is comparable to those reported earlier for the **OPV1**

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Table 1: Critical gelator concentration (CGC)[a] and fluorescence intensity *I* (relative to **OPV1**) in toluene.

Compound	CGC [mM]	*I*
OPV1	0.77 ± 0.03	1
750:1 **OPV1**/**OPV2**–Au	0.53 ± 0.03	0.5
100:1 **OPV1**/**OPV2**–Au	0.49 ± 0.03	0.03
20:1 **OPV1**/**OPV2**–Au[b]	1.24 ± 0.06	0.02
100:1 **OPV1**/**C10**–Au	0.81 ± 0.04	0.4

[a] CGC is the minimum concentration required for the formation of a stable gel at room temperature. [b] Metastable gel with precipitation within a few minutes.

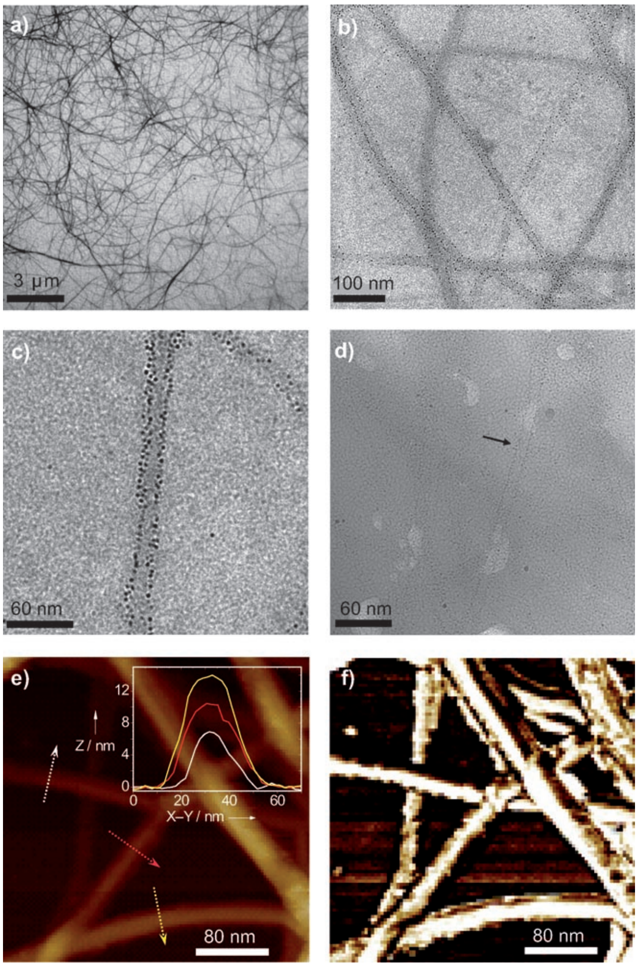

Figure 1. a–c) TEM images at different magnifications of the **OPV1**/**OPV2**–Au (100:1) tapes deposited from toluene. d) Cryo-TEM image of the same 100:1 mixture in vitrified toluene. White patches are the result of radiation damage in the vitrified toluene matrix induced by the electron beam. e–f) AFM height and phase images of the 100:1 mixed tapes, drop cast from toluene on mica. Inset: height profile of three different tapes (white, red, and yellow curves) with the direction of the cross sections indicated by the arrows in the main figure.

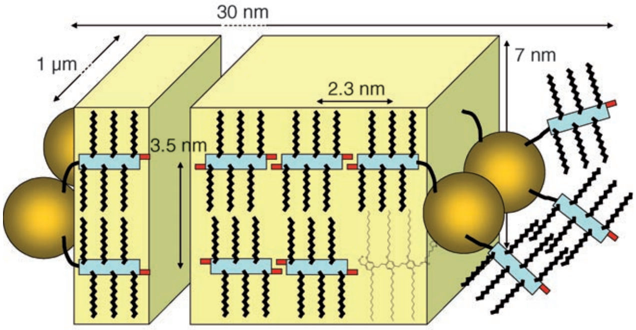

Figure 2. Schematic representation of a possible structure of the **OPV1**/**OPV2**–Au hybrid tapes.[12,14]

tapes.[12,14] Interestingly, arrays of **OPV2**–Au particles with diameters of 2.4 ± 0.6 nm are observed on both sides of the tape (Figure 1 b and c). The lateral distance between the gold particles at the edges of the tape can get as small as 2.6 nm, which implies intercalation of the **OPV2** ligands of the neighboring **OPV2**–Au particles.

We performed cryo-TEM on the vitrified solution to ensure that the structures observed on the TEM grid were not caused by drying effects as a result of the TEM preparation method (Figure 1 d).[15] In the cryo-TEM images, pairs of parallel rows of metal particles are visible, which resemble those observed for the dried samples. This observation indicates that the tapelike structures with gold particles on the sides are already formed in solution. As a result of the sensitivity of the vitrified toluene matrix to the electron beam, the clusters could not be studied at a higher resolution.

Atomic force microscopy (AFM) showed tapes and bundles of tapes similar to those observed by TEM analysis (Figure 1 e and f). Single tapes were found to be around 40 nm wide and the minimum-detected tape height was 7 nm (Figure 1 e). Remarkably, although gold particles are not discernable in the height image, they can be distinguished in the phase image (Figure 1 f). Apparently, the core of the tapes was high enough (7 nm) to mask the gold particles (with a diameter of 2.4 nm) at its side. Starting with solutions that contained only **OPV1** and by using the same conditions for sample preparation, AFM analysis showed tapes that were around 50 nm wide and at least 7 nm high,[12] which indicates that the presence of bound **OPV2**–Au does not disrupt the inner structure of the **OPV1** tapes.

On the basis of the microscopy data and the existing knowledge on **OPV1** tapes,[14] we propose the following structural model for the hybrid tapes (Figure 2). The **OPV1** molecules would hydrogen bond to each other and thus form short chains that would pack together into supramolecular tapes. These tapes would be held together by lamellar π–π interactions along the long axis of the tape. Assuming that the tapes lie flat on the supporting surface, the minimum-observed tape height in this structure corresponds to two molecular layers of **OPV1** molecules (7 nm). In addition, tapes with a thickness of three (10.5 nm) and four (14 nm) layers were also observed by AFM analysis (Figure 1 e). In the case of the hybrid tapes, the **OPV2** ligands on the gold particles would bind to the tape through noncovalent interactions, similar to those that hold the **OPV1** tapes together. The orientation of the **OPV1** molecules in the tape would be such that the **OPV2**–Au could only bind at the sides of the tape without disrupting the internal hydrogen-bonding network of the tapes.

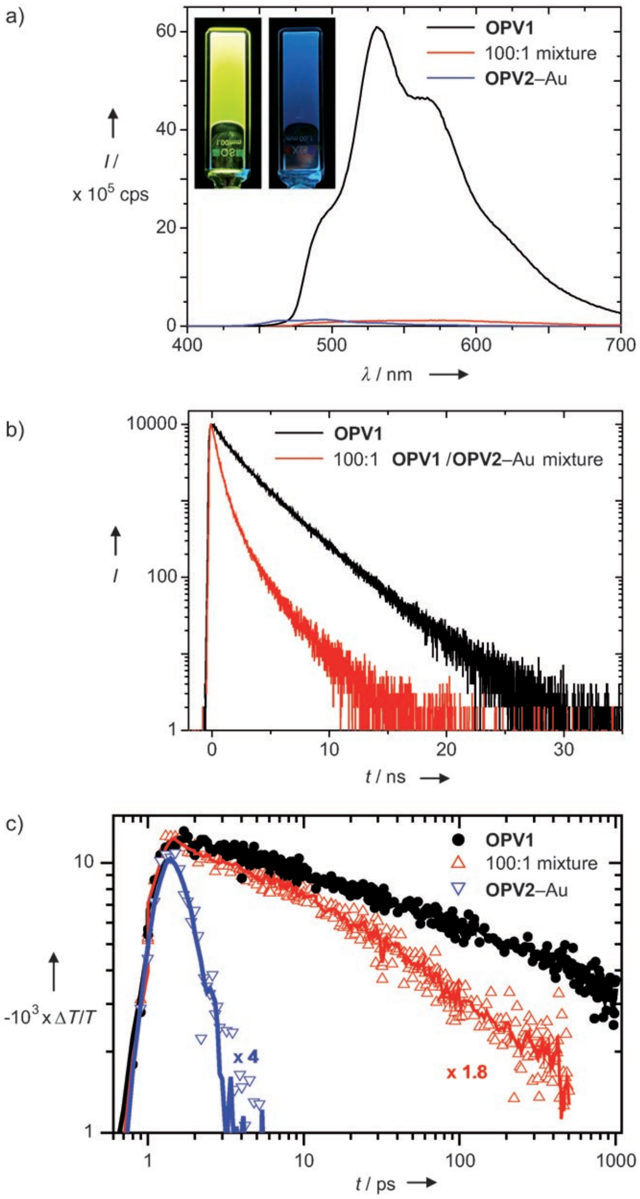

Figure 3. a) Fluorescence spectrum of a 100:1 mixed gel of **OPV1** and **OPV2**–Au and of the separate compounds in toluene at concentrations of 7.7×10^{-4} M (**OPV1**) and 7.7×10^{-6} M (**OPV2**–Au). Inset: photographs of the luminescent **OPV1** gel (left) and of the 100:1 **OPV1**/**OPV2**–Au mixed gel (right). The latter displays a faint-blue emission that can be ascribed to molecularly dissolved **OPV1**. b) Time-resolved photoluminescence for the **OPV1** gel and for 100:1 **OPV1**/**OPV2**–Au gel detected at $\lambda = 600$ nm. c) Photoinduced absorption spectra ($-\Delta T/T$) of a 100:1 mixed gel of **OPV1** and **OPV2**–Au, and of the separate compounds in toluene, in which the absorption for the S_1-S_n transition of the OPV chromophore was probed ($\lambda_{pump} = 460$ nm and $\lambda_{probe} = 740$ nm).

Although the **OPV1** gels are fluorescent, incorporation of **OPV2**–Au into the tapes caused considerable quenching of the luminescence in solution (Figure 3a). In the case of the 100:1 mixture, the intensity was reduced by a factor of 33, whereas admixture of gold particles capped with an aliphatic ligand (**C10**–Au, 100:1)[12] reduced the intensity by only a factor of 2 (Table 1). Time-resolved photoluminescence, monitored at 600 nm, revealed that the luminescence from the **OPV1** gels has a lifetime exceeding that of the molecularly dissolved **OPV1** (1.8 ns). This finding is in agreement with H-type aggregation of the OPV unit, which leads to a lower probability for radiative decay from the lowest exciton state. Incorporation of **OPV2**–Au resulted in a shortening of the lifetime (Figure 3b). This observation indicates that at least part of the quenching is attributable to a dynamic process that takes place on the nanosecond timescale and involves diffusion of the electronic excitations through the tape towards the docked gold particles. This supposition was confirmed using photoinduced absorption (PIA) spectroscopy to probe the absorption for the S_1–S_n transition of the OPV chromophore ($\lambda_{pump} = 460$ nm and $\lambda_{probe} = 740$ nm).[16] The population of the excited state in the **OPV1**/**OPV2**–Au hybrid gel 1 ps after excitation was only a factor of 2 lower than that in the **OPV1** gel. The PIA spectrum in Figure 3c shows a clear difference in the population of the excited state for the organic and hybrid gels for times exceeding 0.1 ns, which indicates that the quenching mainly takes place on the nanosecond timescale. The PIA signal of **OPV2**–Au particles exhibited a very short lifetime because of rapid transfer of energy from the **OPV2** to the gold core (Figure 3c).[17] The spectroscopic data show that the **OPV1** tapes and the bound **OPV2**–Au particles interact electronically, and reveal that these π-conjugated tapes are excellent probes with which to study hybrid materials.

In conclusion, an organic–inorganic hybrid material which consists of π-conjugated OPV tapes and gold nanoparticles has been constructed. The key feature of the self-assembly of the hybrid was the functionalization of the nanoparticles with ligands which can interact with the **OPV1** tapes through noncovalent interactions similar to those that hold the tape together. The proximity of the metal particles to the π-conjugated tapes facilitates electronic communication. The hybrid tapes have a high aspect ratio which makes them attractive for the transport of electrical charges.

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