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Supporting Information

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

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General methods

Nuclear Magnetic Resonance spectroscopy (NMR). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25.0 °C on a Varian Mercury Vx (400 MHz) or on a Varian Gemini-2000 (300 MHz). Additionally ^{1}H-^{1}H COSY and HETCOR experiments were carried out to assign all peaks. Chemical shifts (δ) are given in ppm relative to tetramethylsilane, which was used as internal standard. Abbreviations used are s = singlet, t = triplet and m = multiplet.

Infrared spectroscopy (IR). Infrared spectra were run on a Perkin Elmer Spectrum One UATR FT-IR spectrophotometer.

Mass spectroscopy (MS). MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilising an α-cyano-4-hydroxycinnamic acid matrix; mode of operation: reflector; polarity: positive.

Optical spectroscopy. UV-vis measurements were performed on a Perkin Elmer Lambda 40 UV/Vis Spectrometer equipped with a Peltier Temperature Programmer model 1 (PTP-1) or a Perkin Elmer Lambda 900 UV/Vis/NIR Spectrometer. Fluorescence measurements were performed on a Edinburgh Instruments FS920 double-monochromator luminescence spectrometer using a Peltier-cooled red-sensitive photomultiplier. In order to prevent self-absorption in the fluorescence experiments, thin quartz cuvettes were used (1 mm path length) and the fluorescence was collected in a

front-face geometry. In steady-state fluorescence the excitation wavelength used was 380 nm. Time-correlated single photon counting fluorescence studies were performed using an Edinburgh Instruments LifeSpec-PS spectrometer. The LifeSpec-PS comprises a 400 nm picosecond laser (PicoQuant PDL 800B) operated at 2.5 MHz and a Peltier-cooled Hamamatsu micro-channel plate photomultiplier (R3809U-50). Lifetimes were determined from the data using the Edinburgh Instruments software package. To obtain the lifetime of a molecularly dissolved **OPV1** tetrahydrofuran (THF) was used as a solvent. Sub-picosecond pump-probe spectroscopy was performed using a Ti/sapphire laser system. The pump pulses (2.76 eV) were created via optical parametric amplification (OPA) and were focused to a spot size of about 1 mm^2 with an excitation flux of 5×10^2 μJcm^{-2} per pulse and applied with a repetition rate of 500 Hz. The probe pulse (1.77 or 0.86 eV) beam was generated using a separate OPA with a repetition rate of 1 kHz. The probe beam was linearly polarized at the magic angle of 54.7° with respect to the probe, to cancel out orientation effects in the measured dynamics. Pump and probe pulses are ~ 200 fs in width. The temporal evolution of the differential transmission was recorded using a Si or an InGaAs detector by a standard lock-in technique at 500 Hz.

Transmission Electron Microscopy (TEM). TEM grids, both 200 mesh carbon coated copper grids and R2/2 Quantifoil Jena grids were purchased from Aurion. For the conventional experiments TEM grids were prepared by applying a droplet of sample solution onto a 200 mesh carbon coated copper grid. Excess solution was blotted away using a filter paper. The samples were analyzed at room temperature on a FEI Tecnai 20, type Sphera TEM operating with a 200 kV LaB6 filament, equiped with a bottom mounted 1k x 1k Gatan CCD camera or alternatively on a JEOL JEM1010 at 60 kV. For the cryo-TEM experiments Quantifoil grids (R2/2 Quantifoil Jena) were surface plasma treated using a Cressington 208 carbon coater operating at 5 mA for 40 seconds prior to the vitrification procedure. The sample vitrification procedure was carried out using an

automated vitrification robot (FEI Vitrobot™ Mark III). 3 μL of a heated solution of the **OPV1**:**OPV2-Au** 100:1 mixture were applied to the Quantifoil grids within the environmental chamber of the Vitrobot™ instrument at room temperature. Excess liquid was blotted away with filter paper using an automatic blotting device within the environmental chamber of the Vitrobot™. The grid was subsequently shot through a shutter into melting ethane placed just outside the environmental chamber. The vitrified specimens were stored under liquid nitrogen and observed at ~ -170°C (Gatan cryo-holder) in a FEI Titan microscope equipped with a FEG operating at 300 kV, fitted with a Gatan GIF energy filter and a 2k x 2k CCD camera. Micrographs were taken in EFTEM mode using low dose conditions.

Atomic Force Microscopy (AFM). Atomic force microscopy (AFM) measurements were carried out at room temperature with an AFM (Digital Instruments) equipped with a Nanoscope IIIa controller (Digital Instruments) in the Tapping Mode. MICA substrates were freshly cleaved before use.

Synthesis

5-[1,2]Dithiolan-3-ylpentanoic Acid (*E*,*E*)-4-{4-(4-hydroxymethylstyryl)-2,5-bis[(*S*)-2-methylbutoxy]-styryl}-2,5-bis[(*S*)-2-methylbutoxy]benzyl Ester (OPV2)

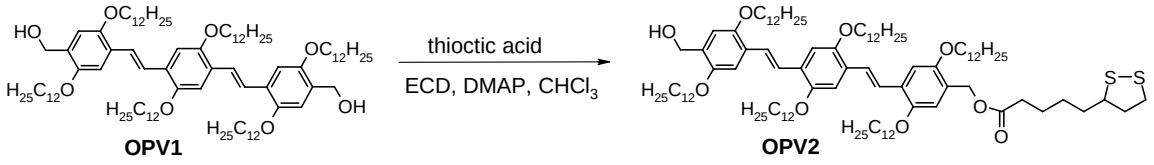

Figure S1. Synthesis of **OPV2**.

300 mg (0.21 mmol) of bisalcohol (**OPV1**) and thioctic acid (43 mg, 0.21 mmol) were dissolved in 30 mL chloroform. The mixture was stirred for 15 minutes at 0 °C under an argon atmosphere. Then a solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide

(ECD) (60 mg, 0.31 mmol) and 4-(dimethylamino)-pyridine (DMAP) (8 mg, 0.06 mmol) in 5 mL dicloromethane was added and stirring was continued at 0 °C for another 15 minutes. Stirring for an additional 24 hours at room temperature gave a mixture of **OPV1**, **OPV2** and the bisfunctionalized product. Then the reaction mixture was washed three times with water, dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. Purification by column chromatography on silica gel (methanol/chloroform 2/98), preparitive size-exclusion chromatography (Bio-Beads S-X3) with tetrahydrofuran as eluent and finally precipitation from methanol yielded pure **OPV2** (60 mg, 18%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 0.87 (t, 18 H, *19*, *39* and *59*), 1.25 - 1.83 (m, 121 H, *9* - *18*, *29* - *38*, *49* - *58* and *67*), 2.38 (t, *J* = 7.3 Hz, 2 H, *62*), 2.44 (m, 1 H, *67*), 3.15 (m, 2 H, *68*), 3.55 (m, 1 H, *66*), 3.98 - 4.05 (m, 12 H, *8*, *28* and *48*), 4.68 (s, 2 H, *1*), 5.16 (s, 2 H, *60*), 6.87 (s, 1 H, *3*), 6.89 (s, 1 H, *46*), 7.12 (s, 2 H, *6* and *43*), 7.14 (s, 2 H, *23* and *26*), 7.45 (s, 4 H, *20*, *21*, *40* and *41*).

^{13}C-NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 14.11 (6 C, *19, 39* and *59*), 22.68 (6 C, *18, 38* and *58*), 24.76 (1 C, 63), {26.18, 26.24, 26.30} (6 C, *10, 30* and *50*), 28.76 (1 C, *64*), {28.76, 29.39, 29.47, 29.50, 29.55, 29.63, 29.70, 29.72} (42 C, *9*, *29*, *49*, *11*, *16*, *31* - *36*, *51* - *56*), 31.92 (6 C, *17*, *37* and *57*), 34.51 (1 C, *62*), 34.61 (1 C, *65*), 38.47 (1 C, *68*), 40.17 (1 C, *67*), 56.31 (1 C, *66*), 61.71 (1 C, *60*), 62.32 (1 C, *1*), {68.54, 68.91, 69.49, 69.01, 69.68} (6 C, *8*, *28* and *48*), {109.04, 109.59, 110.67, 113.97, 115.07} (6 C, *3*, *6*, *23*, *26*, *43* and *46*), {123.22, 123.37, 123.89, 124.41, 127.17, 127.23, 127.44, 128.17, 129.32} (10 C, *2*, *5*, *20*, *21*, *22*, *25*, *40*, *41*, *42* and *45*), {150.47, 150.63, 151.03, 151.07, 151.35} (6 C, *4*, *7*, *24*, *27*, *44* and *47*), 173.39 (1 C, *61*).

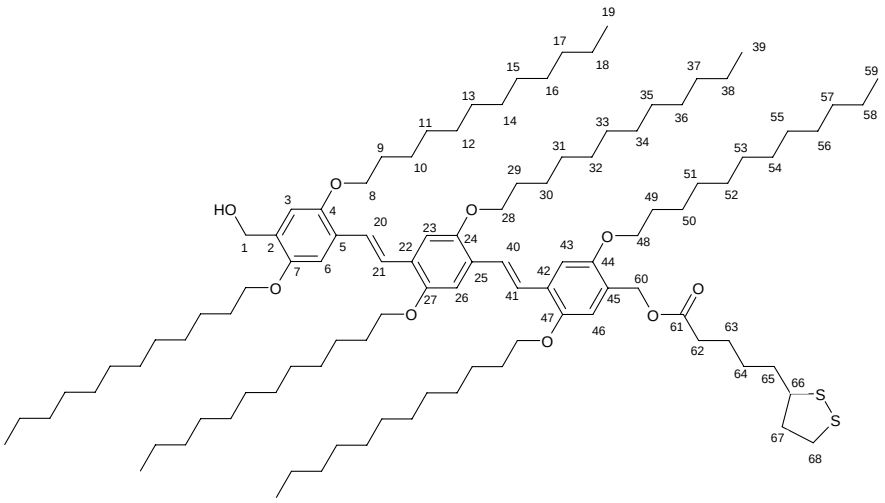

Figure S2. Numbering of the protons and carbon atoms of **OPV2**.

IR (UATR): ν (cm^{-1}): 2920, 2848 (C-H stretch); 1732 (C=O stretch); 1578, 1510, 1466, 1422, 1388, 1345, 1255, 1208, 1073, 1045, 1000, 964, 851, 722. MALDI-TOF-MS (MW = 1636.29): m/z: 1636.30 $[M]^+$

Synthesis of OPV2-Au particles. Solutions of 19 mg of $HAuCl_4 \cdot 3H_2O$ in 10 mL of deionized water and 67 mg of tetra-*n*-octylammonium bromide in 15 mL of toluene were shaken in a separatory funnel. The yellow water layer became clear and the transparent toluene layer became red as the $AuCl_4^-$ was phase-transferred. The water layer was removed and 10 mg of **OPV2** was dissolved. The resulting solution was stirred vigorously in a round-bottom flask and a freshly prepared solution of 18 mg of $NaBH_4$ in 2 mL of deionized water was added all at once after which the solution darkened. After three hours of stirring the water was removed by extraction and subsequently the toluene was evaporated *in vacuo*. The black residue was redissolved in dichloromethane and unbound ligands were removed by preparative size-exclusion chromatography (Bio-Beads S-X1) with dichloromethane as eluent. The size of the gold core of these particles

was 2.4 ± 0.6 nm as determined by transmission electron microscopy (TEM) after measurement of 124 gold particles.

5-[1,2]Dithiolan-3-ylpentanoic Acid Decyl Ester (C10)

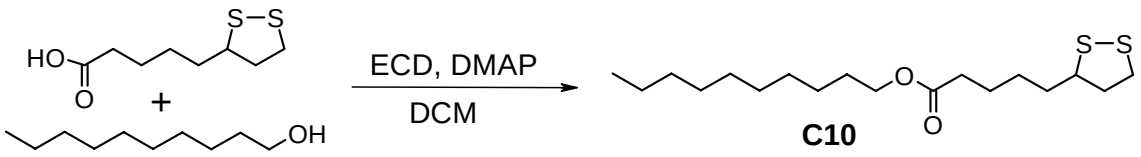

Figure S3. Synthesis of **C10**.

1 g (6.3 mmol) of decanol and thioctic acid (1.56 g, 7.6 mmol) were dissolved in 75 mL freshly distilled dichloromethane (DCM). The mixture was stirred for 15 minutes at 0 °C under an argon atmosphere. Then a solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (ECD) (1.82 mg, 9.5 mmol) and 4-(dimethylamino)-pyridine (DMAP) (0.23 mg, 1.9 mmol) in 15 mL dicloromethane was added and stirring was continued at 0 °C for another 15 minutes. After stirring an additional 24 hours at room temperature the reaction was completed. The reaction mixture was washed with NH_4Cl (sat), $NaHCO_3$ (sat) and NaCl (sat), dried over $MgSO_4$ and evaporated *in vacuo*. Purification by column chromatography on silica gel (DCM) gave pure **C10** (1.96 g, 90%).

^{1}H-NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ 0.88 (t, *J* = 6.7 Hz, 3 H, *1*), 1.2 - 1.4 (m, 14 H, *2 – 8*), 1.48 (m, 2 H, *14*), 1.55 - 1.75 (m, 6 H, *9*, *13*, *15*), 1.92 (m, 1 H, *17*), 2.31 (t, *J* = 7.4 Hz, 2 H, *12*), 2.45 (m, 1 H, *17*), 3.05 - 3.25 (m, 2 H, *18*), 3.57 (m, 1 H, *16*), 4.06 (t, *J* = 6.7 Hz, 2 H, *10*).

^{13}C-NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ 14.06 (1 C, *1*), 22.62 (1C, *2*), 24.67 (1C, *13*), 25.89 (1C, *7*), {28.59, 28.72, 29.19, 29.25, 29.47} (6 C, *3* - *6*, *8*, *14*), 31.83 (1C, *3*), 34.07 (1C, *12*), 34.56 (1C, *15*), 38.42 (1C, *18*), 40.15 (1C, *17*), 56.29 (1C, *16*), 64.47 (1C, *10*), 173.52 (1C, *11*).

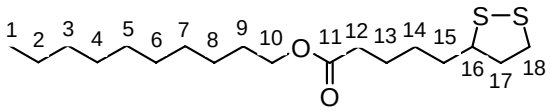

Figure S4. Numbering of the protons and carbon atoms of **C10**.

IR (UATR): ν (cm^{-1}): 2923, 2853 (C-H stretch); 1733 (C=O stretch); 1458, 1418, 1390, 1357, 1303, 1257, 1240, 1172, 1068, 983, 932, 749, 722.
MALDI-TOF-MS (MW = 346.60): m/z: 346.12 $[M]^+$

Synthesis of 5-[1,2]dithiolan-3-ylpentanoic acid decyl ester capped gold particles (C10-Au). Solutions of 50 mg of $HAuCl_4 \cdot 3H_2O$ in 15 mL of deionized water and 174 mg of tetra-*n*-octylammonium bromide in 20 mL of toluene were shaken in a separatory funnel. The yellow water layer became clear and the transparent toluene layer became red as the $AuCl_4^-$ was phase-transferred. The water layer was removed and 88 mg of **C10** was dissolved. The resulting solution was stirred vigorously in a round-bottom flask and a freshly prepared solution of 34 mg of $NaBH_4$ in 5 mL of deionized water was added all at once after which the solution darkened. After four hours of stirring the water was removed by extraction and subsequently the toluene was evaporated *in vacuo*. The black residue was suspended in ethanol and washed extensively over a glass frit with ethanol and acetone until the filtrate remained colourless. The **C10**-functionalized gold nanoparticles (**C10-Au np**) on the frit were redissolved by washing with toluene. Finally, unbound ligands were removed by preparitive size-exclusion chromatography (Bio-Beads S-X1) with toluene as eluent.

Optical Spectroscopy

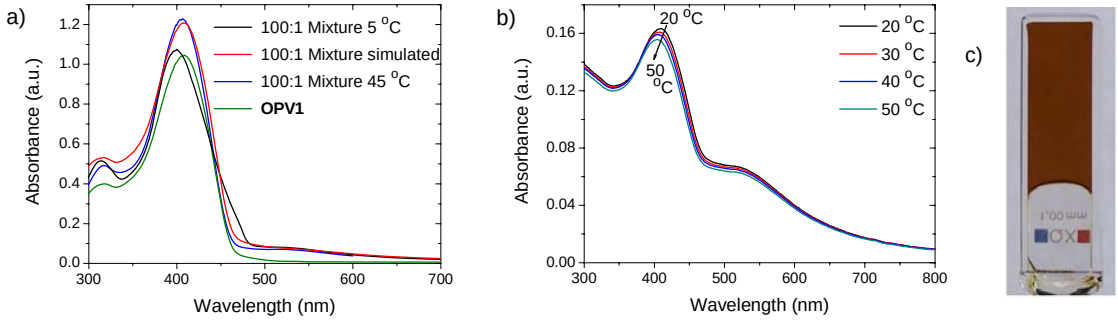

Figure S5. a) UV-vis absorption of **OPV1**, a 100:1 mixture of **OPV1** and **OPV2-Au** and the summation of the separate spectra of **OPV1** and **OPV2-Au**, all in toluene at a concentration of 2.5×10^{-4} M (**OPV1**) and 2.5×10^{-6} M (**OPV2-Au**). The electronic absorption spectrum of the 100:1 mixture of **OPV1** and **OPV2-Au** in toluene provides the usual spectroscopic features indicative of aggregated OPV chromophores: a slight blue shift of the absorption maximum combined with a red shift of the onset of absorption. b) Temperature dependent UV-vis absorption of **OPV2-Au** particles in toluene (2.5×10^{-6} M). At elevated temperatures, a transition from stacked to molecularly dissolved species occurs. The surface plasmon band of the gold particles can be discerned in the 530 nm wavelength region. The shape and position of the surface plasmon band in UV-vis absorption corresponds according to the known relations with the size and shape of the gold nanoparticles. c) Photograph of a gelated **OPV1** (10^{-3} M), **OPV2**-Au 100:1 mixture.

TEM pictures

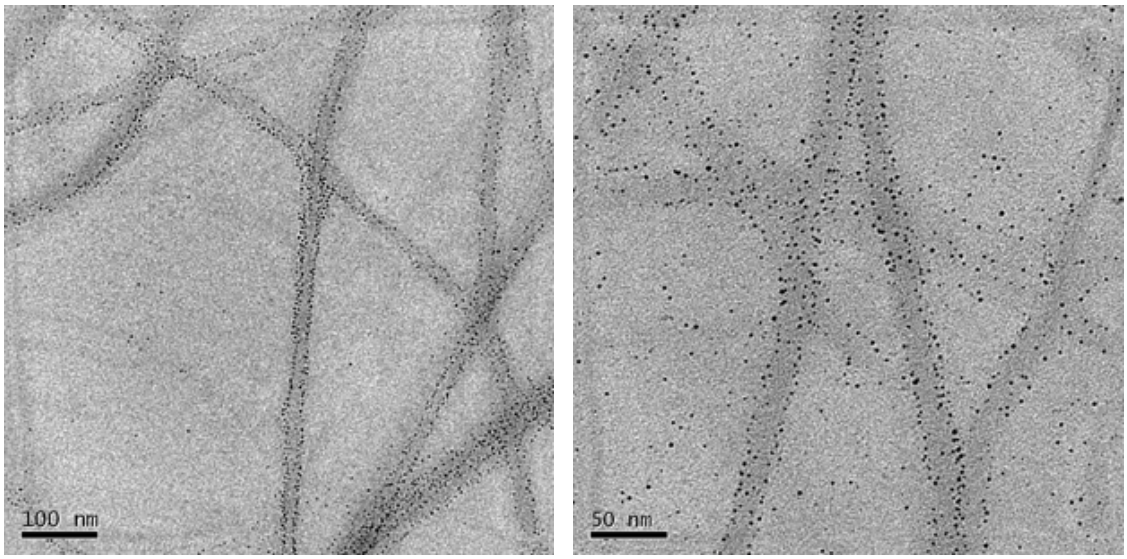

Figure S6. TEM images of a 100:1 mixture of **OPV1** and **OPV2-Au** co-assembled from toluene.

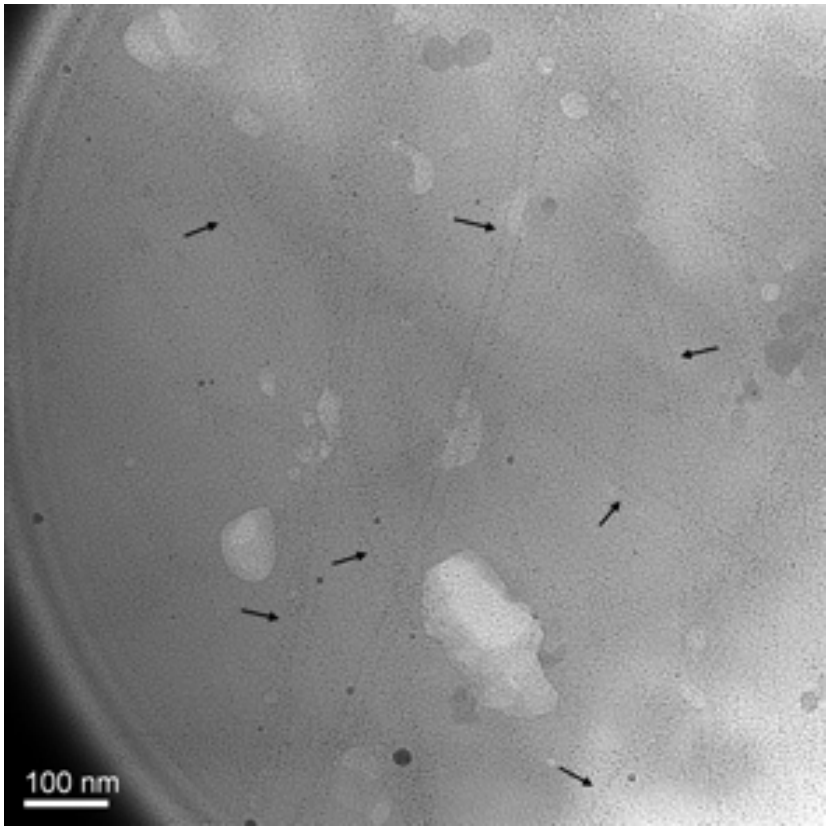

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Figure S7. cryo-TEM image of a 100:1 mixture of **OPV1** and **OPV2-Au** co-assembled in toluene. Arrows point to the nanoparticle arrays.

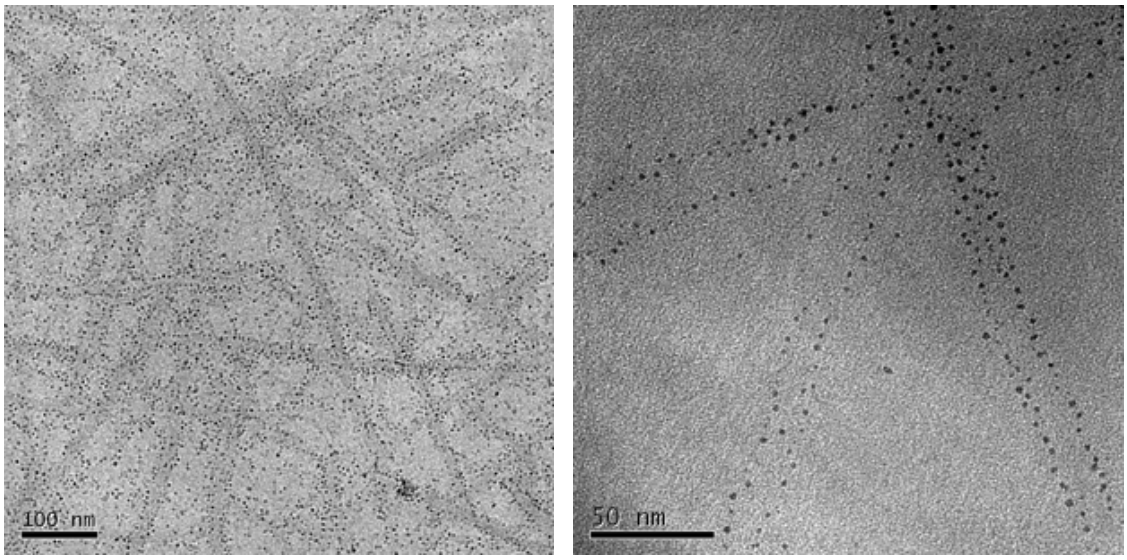

Figure S8. TEM images of a 20:1 mixture of **OPV1** and **OPV2-Au** co-assembled from toluene. Some gold nanoparticles not bound to the gel fiber may be discerned.

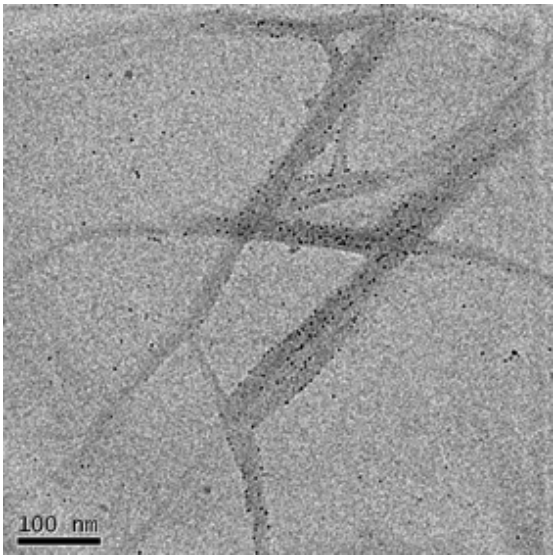

Figure S9. TEM images of a 750:1 mixture of **OPV1** and **OPV2-Au** co-assembled from toluene.

For **OPV1**:**OPV2-Au** 750:1 mixtures, the tapes are only sparingly decorated with gold particles.

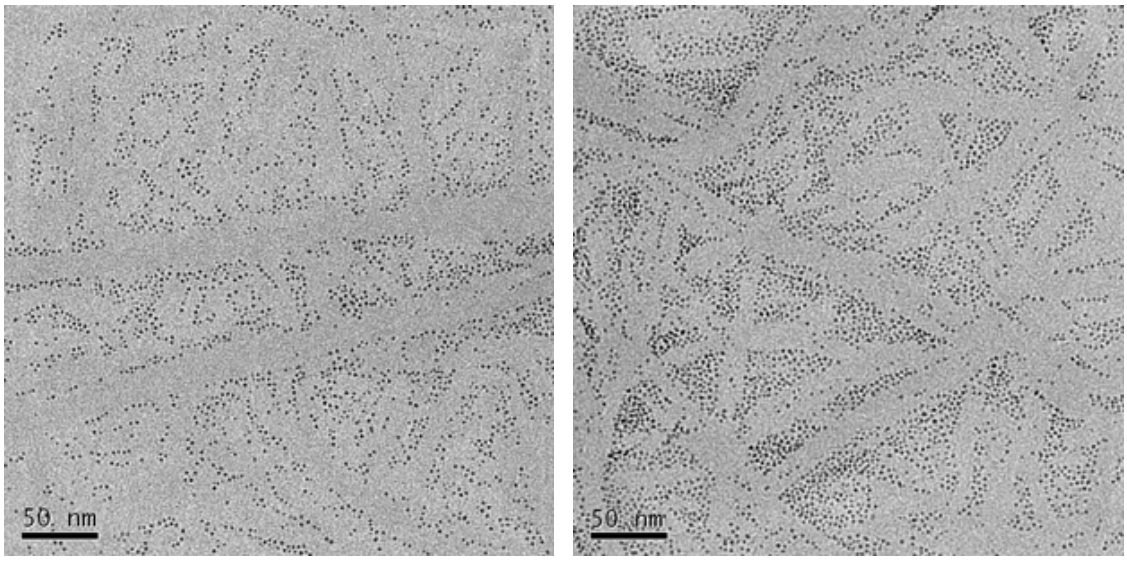

Figure S10. TEM images of a 100:1 mixture of **OPV1** and **C10-Au** co-assembled from toluene.

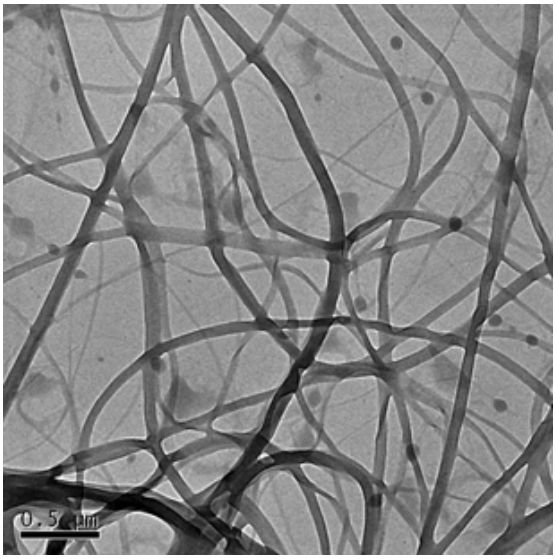

Figure S11. TEM images of an **OPV1** gel, deposited from toluene.

AFM pictures

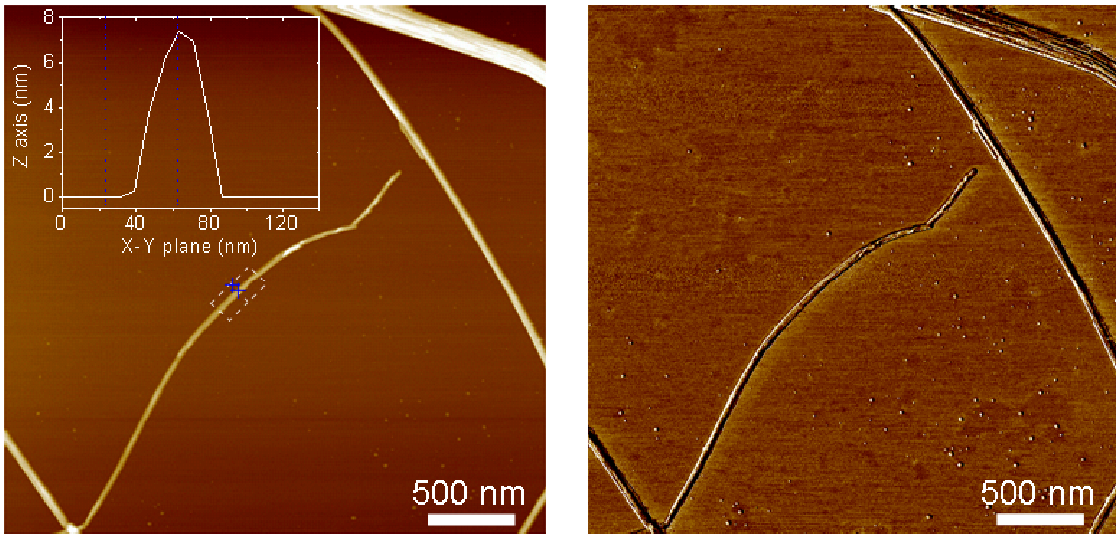

Figure S12. AFM height (left) and phase (right) images of **OPV1**, drop-cast from toluene on MICA. Inset (left): height profile of a single tape averaged over the size of the white box.