**Supporting information**

# Identification of oligophenylene vinylene - naphthalene diimide heterocomplexes by scanning tunneling microscopy and spectroscopy at the liquid/solid interface

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## Synthesis of Naphthalene Diimides.

### 2,3,6,7-Tetrabromo-1,4,5,8-naphthalenetetracarboxylic acid diimide (2)

A mixture of tetrabromonaphthalene dianhydride **1** (500 mg, 0.857 mmol) and ammonium acetate (1.32 g, 17.1 mmol) in 20 mL of glacial acetic acid was heated to reflux for 2 h. At the beginning a yellow solution was formed and in the further reaction course a yellow solid was precipitated, which was separated from hot solution by filtration, washed with glacial acetic acid (3 mL), water (5 mL), saturated aqueous sodium bicarbonate (3 mL), and dried over phosphorous pentaoxide to afford 150 mg (30%) of **2**. MP: > 350 ºC. MS (EI): m/z 581.7 $[M]^+$ (calcd for $C_{14}H_2Br_4N_2O_4$ 581.7). This compound is not sufficiently soluble in common organic solvents, thus no NMR spectra could be recorded.

### 2,3,6,7-Tetra(*n*-hexylamino)-1,4,5,8-naphthalenetetracarboxylic acid diimide (NI6)

A mixture of tetrabromonaphthalene diimide **2** (138 mg, 0.237 mmol) and *n*-hexylamine (28 mL) was heated to reflux for 6.5 h. Afterwards, *n*-hexylamine was distilled off at the rotary evaporator. The residue was dissolved in dichloromethane (30 mL) and washed with 1 N HCl and water. The solvent was removed under reduced pressure at the rotary evaporator and the crude product was first purified by column chromatography (silica gel, $CH_2Cl_2$) and subsequently by HPLC on a reversed phase column (RP 18) using methanol/THF 63:37 as eluent to obtain 39.0 mg (25%) of **NI6** as a red violet solid. MP: 215-220 ºC. $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.17 (t, *J* = 5.7 Hz, 4 H), 8.35 (s, 2 H), 3.40 (m, 8 H), 1.47-1.25 (m, 32 H), 0.84 (t, *J* = 6.9 Hz, 12 H). HRMS (ESI): *m/z* 662.4517 (calcd for $C_{38}H_{58}N_6O_4$ 662.4519) $[M]^+$, 661.4470 (calcd for $C_{38}H_{57}N_6O_4$ 661.4441) $[M\text{-}H]^+$. UV-Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 636 (23000), 457 (8800).

### 2,3,6,7-Tetra(*n*-octylamino)-1,4,5,8-naphthalenetetracarboxylic acid diimide (NI8)

This diimide was prepared according to the procedure described above for diimide **NI6** using 201 mg (0.345 mmol) of tetrabromonaphthalene diimide **2** and 20 mL of *n*-octylamine in 49% (95 mg) yield:. MP: 193-195 ºC. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.16 (t, *J* = 6.1 Hz, 4 H), 8.31 (s, 2 H), 3.40 (m, 8 H), 1.50 (m, 8 H), 1.22 (m, 40 H), 0.85 (t, *J* = 6.9 Hz, 12 H). HRMS (ESI): *m*/*z* 775.5849 (calcd for $C_{46}H_{75}N_6O_4$ 775.5849) $[M+H]^+$. UV-Vis ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 640 (24000), 460 (8800).

### 2,3,6,7-Tetra(*n*-dodecylamino)-1,4,5,8-naphthalenetetracarboxylic acid diimide (NI12)

Diimide **NI12** was prepared according to the procedure described above for diimide **NI6** using 157 mg (0.270 mmol) of tetrabromonaphthalene diimide **2** and 20 mL of molten *n*-dodecylamine in 30% (80 mg) yield. MP: 162-164 ºC. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.1 (t, *J* = 6.2 Hz, 4 H), 8.30 (s, 2 H), 3.39 (m, 8 H), 1.50 (m, 8 H), 1.22 (m, 72 H), 0.87 (t, *J* = 6.9 Hz, 12 H). HRMS (ESI): *m*/*z* 999.8133 (calcd for $C_{62}H_{107}N_6O_4$ 999.8353) $[M+H]^+$. UV-Vis ($CHCl_3$): $\lambda_{max}$ = 640 nm, 461 nm.

## Experimental details on STM and STS measurements

**STM** experiments were performed using a Molecular Imaging PicoSPM (Agilent). Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.2 mm). Prior to imaging, all compounds under investigation were dissolved in 1-phenyloctane (Aldrich 99%), and a drop of the solution was applied onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, OH). Then, the STM tip was immersed in the solution and images were recorded at the liquid/solid interface. The STM images were acquired in the constant-current (variable height) mode. For analysis purposes, recording of a monolayer image was followed by imaging the graphite substrate underneath. Before image analysis, the images were corrected for drift, via scanning probe image processor (SPIP) software (Image Metrology ApS), using the recorded graphite images for calibration purposes. The imaging parameters are indicated in the figure captions: tunneling current ($I_{set}$), and sample bias ($V_{set}$). The bright spots in the images correspond to high tunneling efficiencies ('high' areas), while the darker parts correspond to low tunneling efficiencies ('low' areas).

**STS.** Tunneling spectroscopy (*IV*-curve measurements) was performed in the single point spectroscopy mode, i.e., the tip is positioned at a coordinate of choice with the feedback loop closed, thereby adjusting the tip-sample distance. A voltage ramp between +1.5 and -1.5 V (step size 15 mV per ~1 ms) is applied with the feedback loop open. A single curve is the average of 5 loops (both ramping directions). Note that only those spectra were used which pass through the set-point current under feedback conditions (set point ± 8 pA). The pronounced differences in the shape of the curves (rectification behavior) permitted to divide the curves into different categories by a visual inspection procedure. About 15% of the curves were discarded because of noise.

## Solution composition for the STM and STS experiments

STM-experiments for pure **$(OPV4)_2M$** were carried out in 1,2,4-trichlorobenzene, tetradecane and 1-phenyloctane. 1-Phenyloctane gave the best results and was chosen as the solvent for further experiments.

1) [**$(OPV4)_2M$**] = 1.5 mM
2) 1:1 mixture → [**$(OPV4)_2M$**] = [**NI6**] = 1.5 mM → no rosette formation
3) 1:50 mixture → [**$(OPV4)_2M$**] = 1.5 mM ; [**NI6**] = 75 mM → rosette formation, but unclear
4) 1:1 mixture → [**$(OPV4)_2M$**] = [**NI12**] = 1.5 mM → no rosette formation
5) 1:5 mixture → [**$(OPV4)_2M$**] = 1.5 mM; [**NI12**] = 7.5 mM → no rosette formation
6) 1:50 mixture → [**$(OPV4)_2M$**] = 1.5 mM; [**NI12**] = 75 mM → rosette formation, disordered, but clear

## Extra STM-images and models

### Pure $(OPV4)_2M$ at the 1-phenyloctane/graphite interface

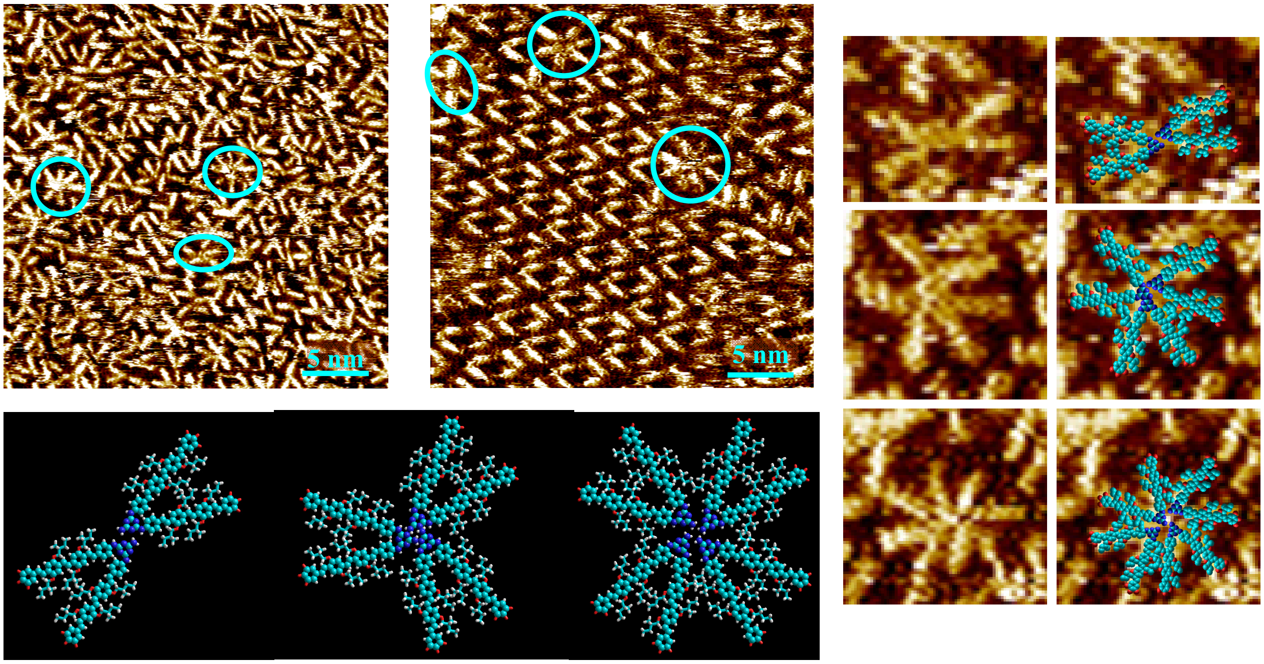
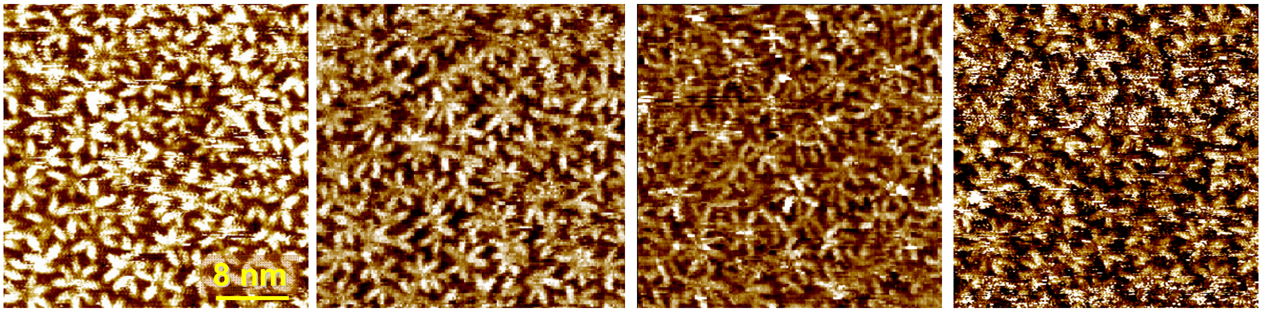


**Figure S1:** STM-images of $\mathbf{(OPV4)_2M}$ at the 1-phenyloctane/graphite interface. $I_{set}$=39 pA, $V_{set}$=-860 mV. A dimer, trimer and tetramer are encircled in blue and tentative models corresponding to these supramolecular motifs are shown.

### Bias depending imaging of $(OPV4)_2M$ (1.5 mM in 1-phenyloctane)



$V_{set}$= -1.2 V $V_{set}$= -0.7 V $V_{set}$= +0.9 V $V_{set}$= +1.2 V

**Figure S2:** Bias dependent imaging of pure $\mathbf{(OPV4)_2M}$ at the 1-phenyloctane/graphite interface: $I_{set}$ = 38 pA. The bias voltage ($V_{set}$) is indicated underneath the images.

## Correlation

A linear correlation between the area of a bright spot and the number of OPV-units involved in the supramolecular structure was found (1:50 mixture of $(OPV4)_2M$ and NI12). The threshold brightness was chosen by decreasing the brightness until the OPV-units were clearly visible. The average and standard deviation of the size of the 'bright spots' were calculated, leaving 11 data points, which are shown in the graph.

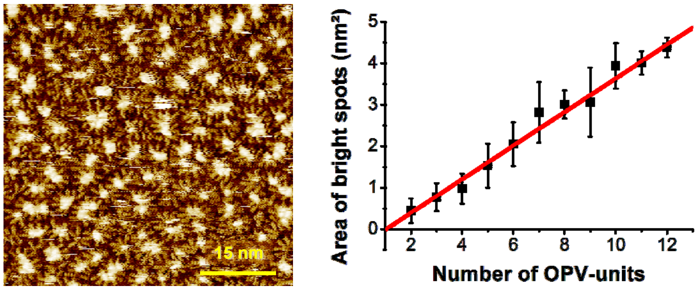


**Figure S3:** Bias Left: STM-image at the 1-phenyloctane/HOPG interface. $I_{set}$=28 pA, $V_{set}$=+1.3V, right: Linear correlation between the area of bright spots (attributed to **NI12**) and the number of OPV-units within a supramolecular motif (combined analysis of 110 structures).

## Extra information on STS experiments

Same settings and concentrations were used for STM and STS experiments. Concentration of pure $\mathbf{(OPV4)_2M}$ is 1.5 mM in 1-phenyloctane. For the mixture, a 1:50 ratio was used with $\mathbf{[(OPV4)_2M]}$ = 1.5 mM and **[NI12]** = 75 mM.

Many curves (± 150 for pure $\mathbf{(OPV4)_2M}$ and ±150 for the 1:50 mixture) were recorded at different places on different samples and at different days. The curves with a lot of noise were discarded (± 15%). The remaining curves clearly showed distinctive properties and could be divided into 4 categories. The average was taken per category and for every data point the standard deviation was calculated and represented in the curves.

One of these *IV*-curves (curve 1d) matches a linear combination (sum) of curve 1a, attributed to the signature of **(NI12),** and curve 1b, attributed to the signature of $\mathbf{(OPV4)_2M}$. Most likely, it originates due to drift while recording the STS curves, so partially recording on top of **NI12** and $\mathbf{(OPV4)_2M}$ units.

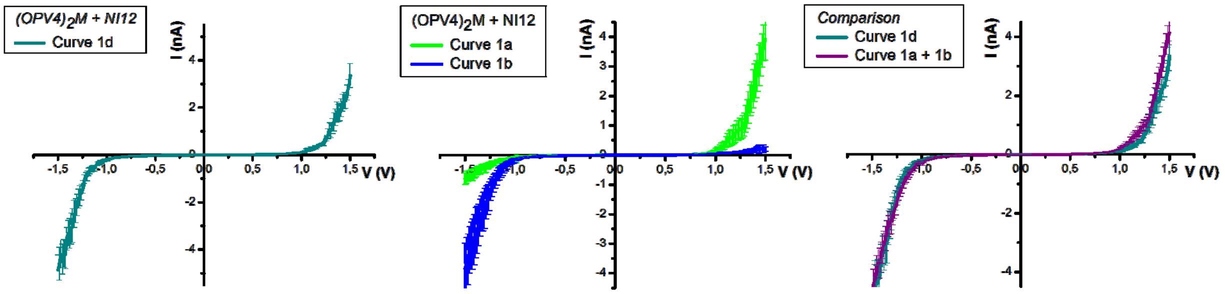


**Figure S4:** Typical averaged *IV*-curve recorded for **NI12** / **(OPV)$_2$M** mixtures at the 1-phenyloctane/graphite interface. Curve 1d is almost identical to the sum of curve 1a and curve 1b.

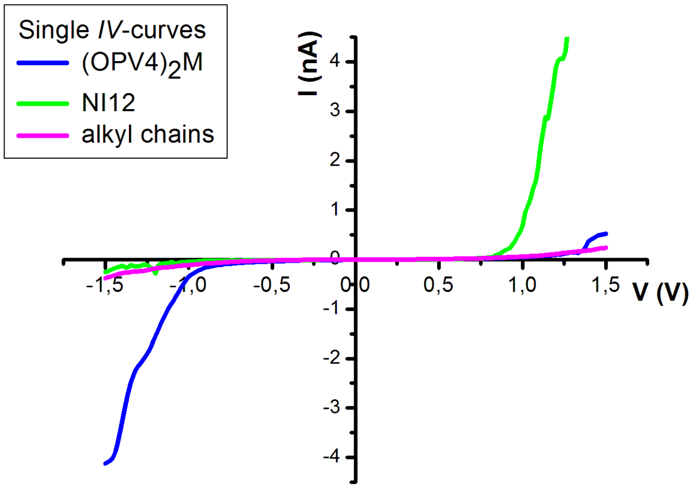


**Figure S5:** Selected non-averaged *IV*-curves.

## Absorption spectra in solution

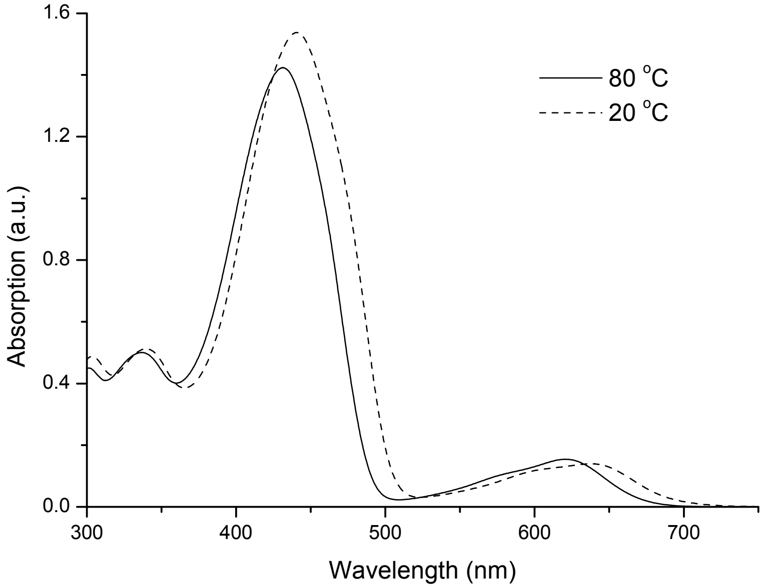


**Figure S6:** Absorption spectra of a **(OPV4)$_2$M** and **NI** mixture in 1-phenyloctane ([**(OPV4)$_2$M**] = [**NI**] = **0.1 mM**).