

Subproject C3.8

**Self-Assembled Molecules as Pre-Organized Building Blocks
of Nanoscale Networks and Structures**

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Introduction and Summary

The CFN project C3.8 “Self-Assembled Molecules as Pre-Organized Building Blocks of Nanoscale Networks and Structures” profits from supramolecular interactions between molecular building blocks or between nanoscale objects and coating molecules. It is geared towards the assembly of 2d patterns, 3d architectures, surface functionalized nano-tubes and molecular junctions.

The first focus was set on **macrocycles comprising perfluorinated benzene subunits**. The concept was to profit from the stacking emerging from the opposed signs of the quadrupole moments of perfluorobenzene and benzene subunits. As these subunits are interlinked with diacetylenes as photopolymerizable subunits, the expected staples of macrocycles might become nano-tubes by intermolecular photopolymerization. A series of macrocycles consisting of diacetylene interlinked 3,5-hexylbenzene and *meta*-tetrafluorobenzene subunits were synthesized and fully characterized. The aggregation features of these macrocycles were subsequently investigated.[7][C3.8:4] As dimerization turned out to be the dominant self-assembly process in most cases, the dimensions of attainable nano-objects remained rather limited. However, the expected strength of the intermolecular interaction was corroborated as the dimerization constant measured for the self-complementary macrocycle **1** was more than one order of magnitude larger than the ones observed for macrocycles so far. [6][C3.8:2]

The large differences in electron density of benzene and perfluorobenzene induce a considerable dipole moment in molecular rods comprising these subunits. Furthermore, the fluorine substituents are able to provide lone-pairs for the formation of hydrogen bonds. Thus also the **lateral self-assembly of molecular rods and stars comprising perfluorinated benzene subunits** was of particular interest. Various oligophenylethynyl rods comprising perfluorinated phenyl subunits and in most cases a terminal dodecyl chain were synthesized and their self assembly at the solid/liquid interface was investigated by scanning tunneling microscopy (STM) experiments on a graphene substrate.[10,11][C3.8:11,C3.8:1] All molecular rods self-assemble to lateral patterns over large areas. In all cases a pairwise antiparallel arrangement of the molecular rods avoiding the formation of a net dipole moment was observed. As a similar lateral arrangement is also detected without perfluorinated phenyl subunits, the self-assembly is probably mainly driven by the optimization of the lateral packing of the building blocks. Large area porous and chiral networks were observed from *Mercedes*-star shaped rigid structures.[12][C3.8:3] The interplay between chiral guests and the obtained network is currently under investigation. Another present focus is the covalent interlinking of the molecular building blocks.

The interplay between delocalized π -systems and graphene surfaces is also of particular interest to cover single wall carbon nano-tubes (SWNTs). A particular focus was thus set on **tailor-made polymers to select SWNTs by dispersion**. A small library of polymers comprising 9,9-dialkylfluorene and/or N-alkyl-carbazole subunits was synthesized in order to investigate the correlation between polymer structure and dispersed SWNTs. These studies were made in a CFN internal cooperation with the team of Frank Hennrich and Manfred Kappes which was analyzing the dispersing features of our polymers. So far, a carbazole polymer which exclusively disperses semi-conducting SWNTs with a difference in chiral indices $n-m \geq 2$ [16][C3.8:9] and a fluorene anthracene copolymer which exclusively disperses SWNTs with a diameter larger than 0.95 nm were identified. We are currently expanding our polymer library with functional building blocks. In particular we are interested in strategies allowing to combine selectivity features.

The ability to coordinate molecules at the surfaces of SWNTs also enables the design of molecular rods for the functionalization of SWNT-junctions. In a CFN internal cooperation with the team of Ralph Krupke and Hilbert von Löhneysen the concept was developed to observe **single molecule electroluminescence from a CNT-molecule-CNT junction** as proof of the molecule's presence. While the team of experimental physicists optimized the required SWNT junction, we were developing a suitable molecular rod comprising an emitting chromophore.[17][C3.8:10] And indeed, the characteristic emission signature of the central chromophore was observed as electroluminescence signal of a CNT-molecule-CNT junction.[18][C3.8:8] We are currently investigating asymmetric rods and expanding collection of potentially emitting molecular rods.

In the timeframe 2006-2010, the subproject C3.8 has led to 11 accepted publications in peer reviewed journals. Among which are 1 article in *Nature Nanotechnology*, 2 in *J. Am. Chem. Soc* and 2 in *Chem. Comm*.

1. Macrocycles comprising perfluorinated benzene subunits

Shape persistent macrocycles (SPMs) consisting of in *meta*-position ethynyl or diethynyl interlinked benzene subunits display pronounced stacking properties in solution.[1] The initial idea of the project was to profit from the resulting supramolecular arrangement to organize molecular building blocks for the synthesis of nano-tubes. Thus, a macrocycle consisting of alternating benzene and 2,3,4,6-tetrafluoro benzene subunits was considered as potential molecular building block. The conceptual idea was to optimize the intermolecular stacking properties in order to obtain large staples of pre-organized macrocycles. In particular the opposite signs of their quadrupole moments of benzene and perfluorobenzene subunits[2,3] were expected to yield in the desired molecular stacking features. The proximity of the diethynyl units in the staple of macrocycles might allow the subsequent covalent interlinking of the supramolecular prearranged building blocks by photopolymerization. However, there exists a single paper reporting the successful interlinking of straight on top of each other stapled diethynyls resulting in *cis*-polybutadiyne.[4] Recently, *Frauenrath* and coworkers reported the partial photopolymerization in the solid state of diazetylenes organized by pentafluorophenyl/phenyl interactions yielding in a *trans*-polybutadiyne.[5]

As displayed in Figure 1 the macrocycle **1** was obtained by two different synthetic routes in rather low yields from the corresponding diethynyl precursors **7-9**.[6][C3.8:2] In spite of the parent design the three benzene corner units of **1** were functionalized with hexyl chains to provide the required solubility and process-ability of the target structure and its precursors.

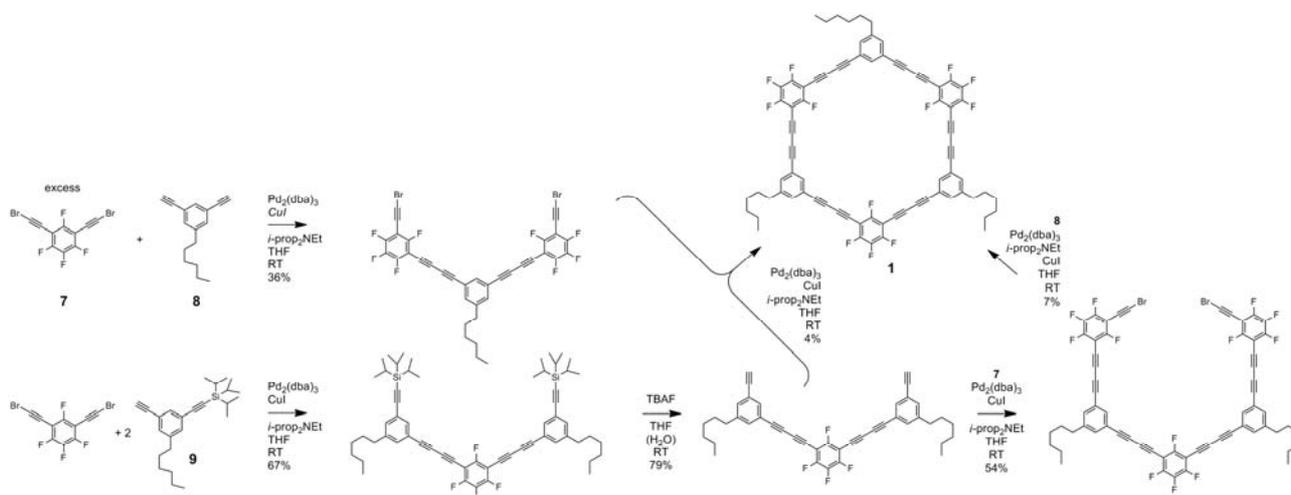


Fig.1: Two synthetic pathways yielding in the size persistent macrocycle **1** comprising tetrafluoro-benzene subunits.

NMR-titration experiments revealed strong intermolecular stacking of **1** as expected for a macrocycle consisting of building blocks with alternating quadrupole moments. The dimensions of the staples formed by intermolecular stacking were investigated by vapor pressure osmometry (VPO). Unfortunately only dimers of the SPM **1** were observed as displayed in Figure 2. Probably the hexyl chains at the benzene corner units are already bulky enough to prevent the formation of extended staples. Interestingly, the measured dimerization constant K_{Dim} is with $1875 \pm 605 \text{ M}^{-1}$ in chloroform at room temperature almost one order of magnitude larger than the dimerization constants reported for SPMs so far. [6][C3.8:2]

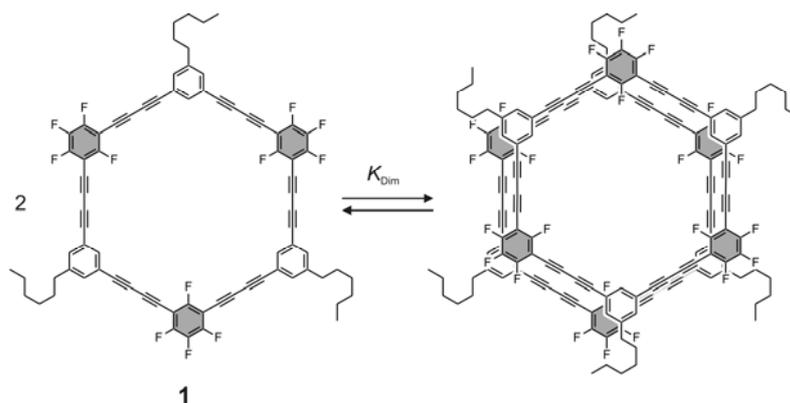


Fig.2: Stacking behavior of the macrocycle **1**. Instead of elongated staples exclusively dimers of **1** were observed in various solvents by $^1\text{H-NMR}$ titration and VPO experiments.

The developed modular synthesis and the availability of the corresponding precursors **7-9** allowed the assembly of the entire series of macrocycles **1-6** with various numbers and spatial arrangement of perfluorinated corner units displayed in figure 3.[7][C3.8:4] The aggregation behavior of each member of the series was investigated in chloroform by concentration dependent NMR-experiments and by VPO studies. For the macrocycles comprising perfluorinated corner units (**1** and **3-6**) considerable stacking in solution was observed by NMR-titration. With the exception of the macrocycle **3**, the molecular weights observed by VPO of these aggregates were consistent with dimer formation as the dominant aggregation process. Only the macrocycle **3** with a single perfluorinated corner unit displayed aggregation beyond dimer formation. With dimerization as the dominant aggregation process[8] of SPMs **1, 4-6** and an isodesmic association model[9] for SPM **3**, least square curve fitting provided the dimerization constants (K_{Dim}) for **4-6** and association constants (K_{Ass}) for **2** at 25°C displayed in figure 3. The variation of the investigation temperature gave access to thermodynamic data of these aggregation processes by *van't Hoff* analysis. The aggregation of SPMs **1, 3-6** comprising fluorinated corner units is enthalpically driven. The largest enthalpy contribution together with the largest entropic loss has been observed for SPM **4** having two fluorinated corner units facing each other.

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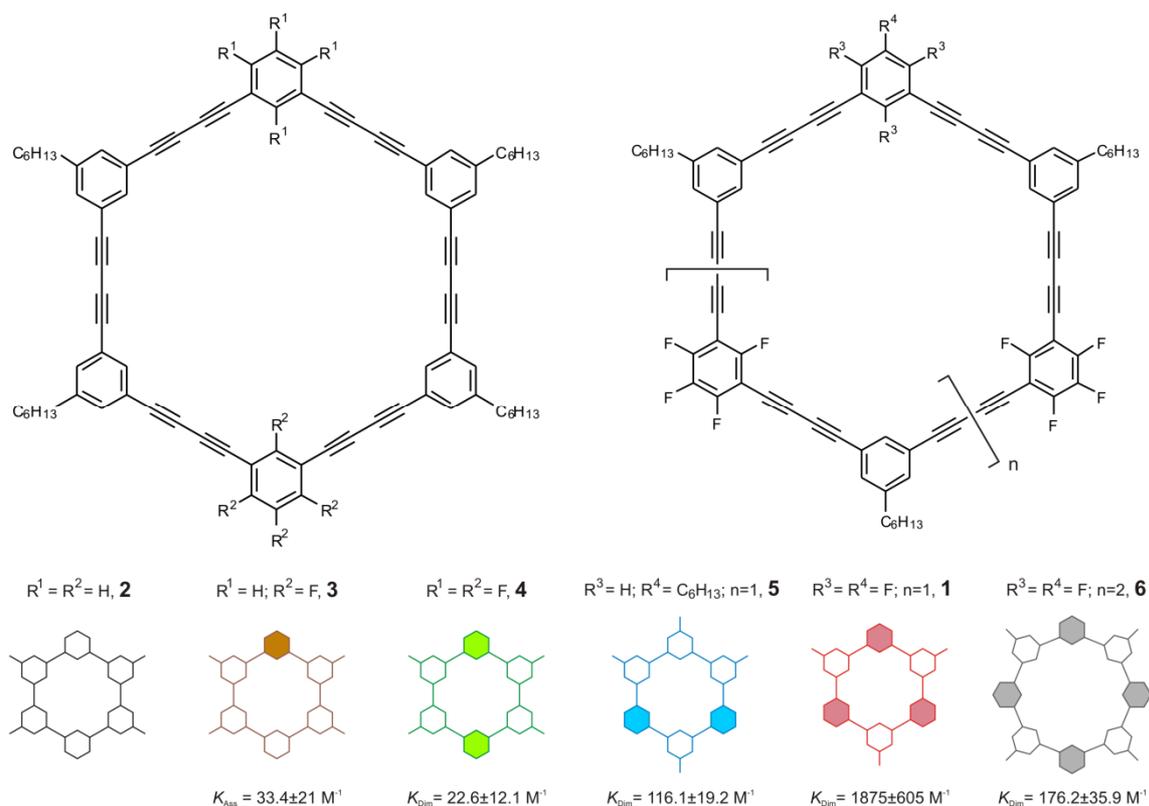


Fig.3: Series of SPMs **1-6** with various numbers and positions of tetrafluorobenzene corner units (colored hexagon in the schematic representation). The association constant and the dimerization constants at 25°C were determined by least square fitting of NMR-titration data.

Interestingly, the SPM **4** precipitates at 50°C in toluene providing hexagonal crystallites with an aspect ratio of 1/10 and diameters in the order of several micrometers. Analysis of the material of these rods displayed the formation of dimeric and trimeric structures, probably arising from a heat triggered coupling between stacked SPMs.[7][3.8:4] Even more remarkable are the observed healing features of these crystallites exposed to the electron beam of the scanning electron microscope (Fig.4).

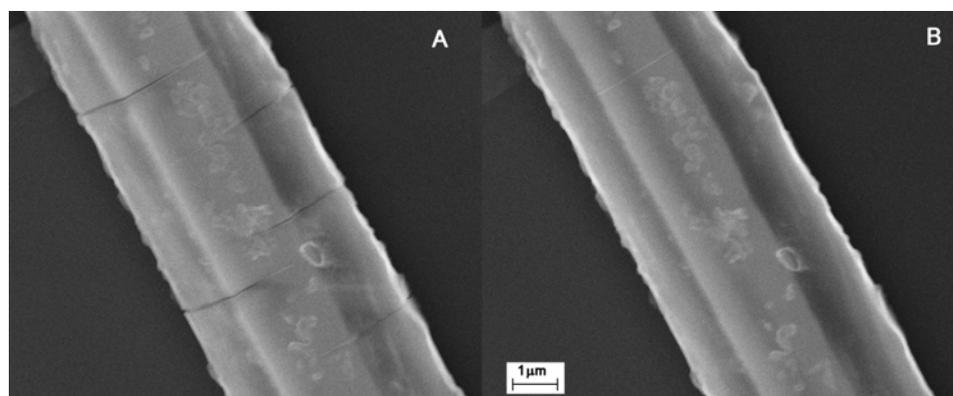


Fig.4: SEM images of a hexagonal rod-like crystallite formed in a 50°C hot solution of SPM **4** in toluene. As-prepared sample (A), after irradiation for 5 minutes (B).

In conclusion, a series of SPMs **1-6** has been synthesized and fully characterized. The number and the relative position of perfluorinated corner units have been varied systematically to investigate the strength of intermolecular interactions arising from benzene/tetrafluorobenzene quadrupole interactions. Self-assembly investigations of these SPMs pointed at dimerization as the dominant aggregation process, reducing their attractivity as precursors of nano-tubes considerably. An intermolecular oligomerization has been observed for the SPM **4** upon heating in toluene. The obtained mixture of compounds precipitates as hexagonal crystallites with surprising healing features during SEM investigations.

2. Lateral self-assembly of molecular rods and stars comprising perfluorinated benzene subunits

Self-assembly of rigid and size persistent molecules comprising perfluorinated benzene subunits is also interesting at the solid/liquid interface. In molecular rods an electron poor terminal pentafluorobenzene subunit provides a dipole moment along the rod axis which is assumed to be reflected in the molecules packing on a substrate. Furthermore, hydrogen bonds between the benzene hydrogens and the lone pairs of the fluorine substituents may influence the molecular arrangement on a flat surface. Based on the chemistry developed for the assembly of the SPMs discussed above, the molecular rods **10-14** displayed in figure 5 were synthesized.[10][C3.8:11] The variations in the numbers of perfluorinated subunits and in the presence of a terminal alkyl chain within the series of molecular rods should enable to identify the interactions dictating the molecular self-assembly at the solid/liquid interface.

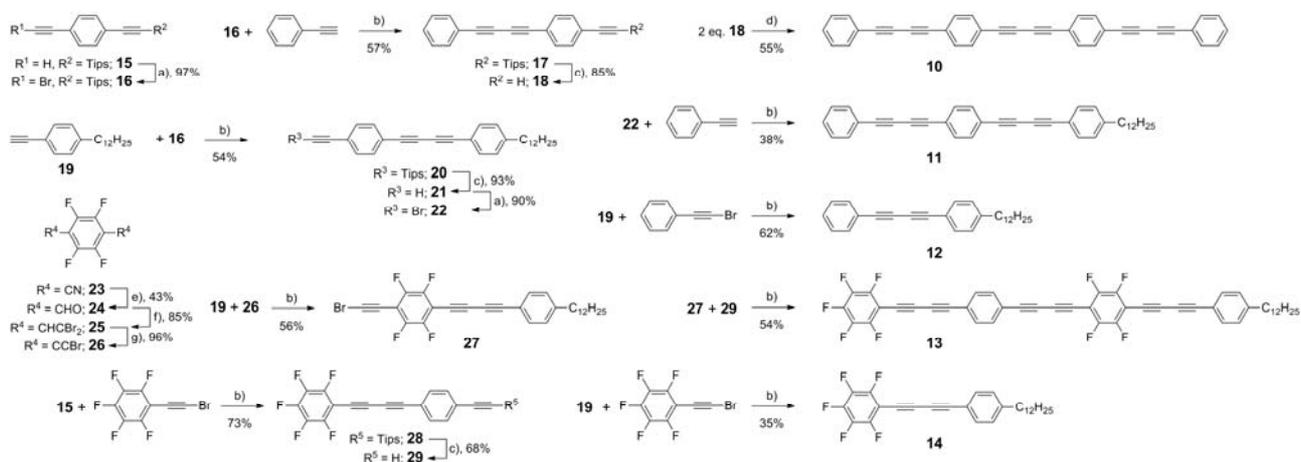


Fig.5: Synthesis of the molecular rods **10-14**. Reagents and conditions: a) NBS, AgNO₃, CH₃COCH₃, r.t.; b) Pd₂(dba)₃·CHCl₃, CuI, C₆H₅CH₃, EtN(*i*-prop.)₂, r.t.; c) TBAF, wet THF, r.t.; d) PdCl₂(PPh₃)₂, CuI, THF, EtN(*i*-prop.)₂, r.t.; e) DIBAL-H, C₆H₅CH₃, r.t.; f) CBr₄, Zn, PPh₃, CH₂Cl₂, r.t.; g) aq. KOH, BTEAC, THF, r.t.

The self-assembly of the molecular rods **10-14** was investigated at the solid/liquid interface with scanning tunneling microscope (STM) experiments performed by the team of Lifeng Chi at the University of Münster (Germany). Saturated solutions of the molecular rod under investigation in phenyloctane were deposited on highly oriented pyrolytic graphite (HOPG) substrates and the interface between HOPG and phenyloctane was investigated at ambient temperature with a *Nanoscope III* STM equipped with mechanically cut Pt/Ir (90:10) tip.

Preliminary studies with the simplest rod **14** already comprising a terminal pentafluorophenyl subunit and a dodecanyl chain at the opposed end displayed large area formation of parallel stripes (Fig.6 A).[11][C3.8:1] Closer inspection of the dimensionality of these stripes revealed the rod **14** lying flat on the surface as the parent building block of the surface pattern. In figure 6B the molecules are overlaid to illustrate their position in the pattern. As expected the dipole moment of the rod results in a pairwise anti-parallel arrangement of two molecules **14**. The subsequent intercalation of the dodecyl chains yields in a zipper like arrangement of molecules in parallel ribbons.

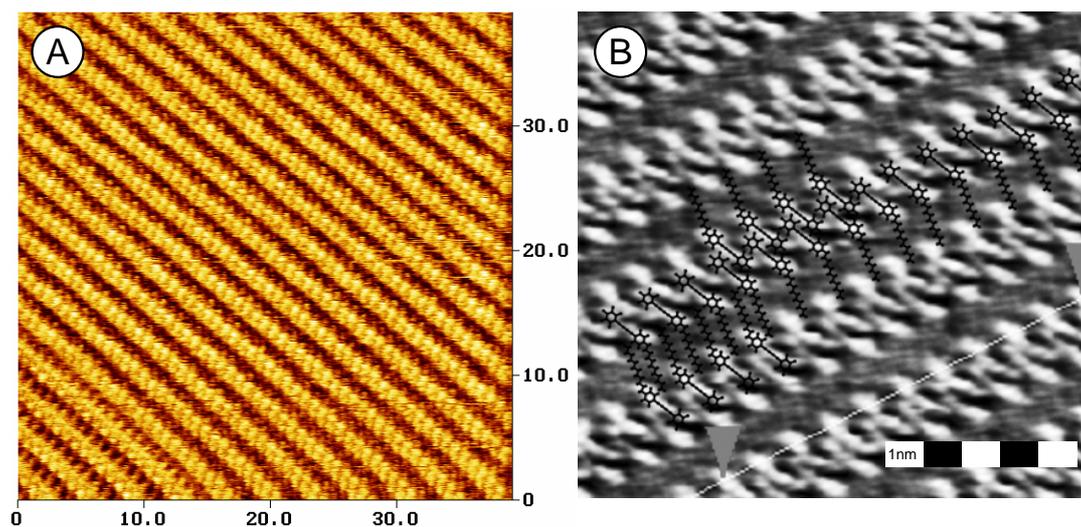


Fig.6: A) Large area pattern of parallel stripes on a HOPG surface covered with **14**. B) High resolution STM image of the self-assembled ribbons. A model of the molecular structure of **14** is overlaid to illustrate the lateral packing.[11][C3.8:1]

Our first hypothesis was that the lateral packing might be supported by an attraction between the electronegative fluorine substituents and the electron rich diacetylene of the neighboring molecule. Subsequent studies with the molecular rod **12** with comparable dimensions as **14** but lacking the fluorine substituents displayed almost identical surface packing.[10][C3.8:11] The surface pattern seems thus to emerge mainly from the tight packing of the molecules at the solid/liquid interface which is the same for both rods. Such self-assembly patterns, characterized by the maximization of the surface area covered by each molecule, are entropically driven by the large amount of released solvent molecules at the interface.

To further study the underlying rules resulting in these surface patterns the molecular rods **11** and **13** were investigated under comparable conditions. Figure 7A displays the pattern which was observed over large areas for **13**. In all cases stripes consisting of staggered oligophenylenethynyl (OPE) cores were observed which were separated from each other by stripes consisting of intercalating alkyl chains. With increasing length of the molecular rod the thickness of the stripes formed by the staggered OPE cores increased. The presence of fluorine substituted subunits in **13** does not seem to influence the resulting packing pattern considerably. The additional dipole moments of the molecular rods **13** and **14** were expected to result in an anti-parallel arrangement of the molecular building blocks. However, as already with the molecular rods **10-12** without fluorine-substituted subunits an anti-parallel arrangement of the molecular building blocks was observed, the experiments were not suited to quantify the extend of potential additional stabilization by the fluorine substitution pattern.[10][C3.8:11]

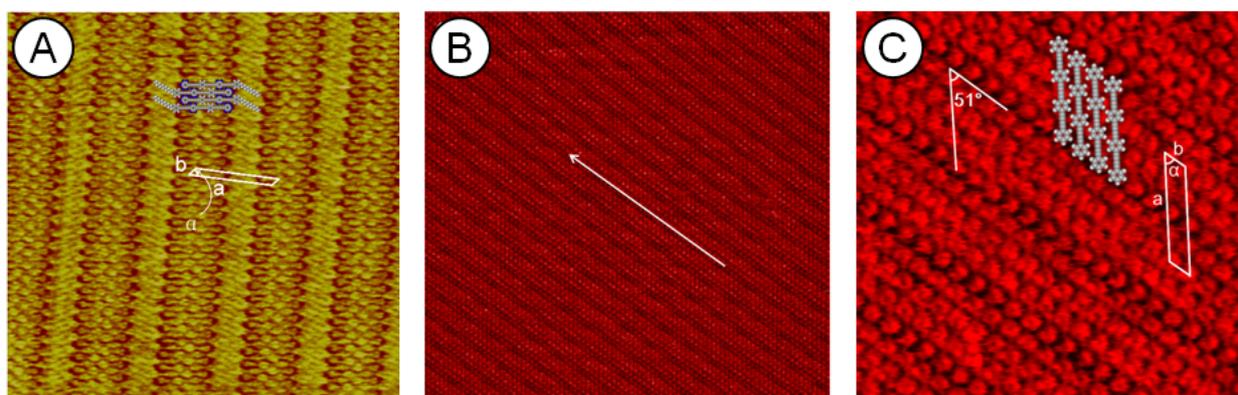


Fig.7: A) Large area pattern of parallel stripes on a HOPG surface covered with **13**. A model of the molecular structure and the unit cell of the lateral packing are overlaid. B) Large area pattern of parallel stripes formed by self-assembly of **10**. C) High resolution picture of the pattern with a model of the molecular structure and the unit cell of the lateral packing overlaid.[11][C3.8:1]

Finally we wondered if the dodecyl chain of the rods **11-14** is a crucial requirement for the stripe formation. Thus the molecular rod **10** lacking any alkyl chain was synthesized and investigated under comparable conditions. As displayed in Figure 7B, a large area lateral pattern consisting of parallel stripes was also observed for **10**. Again the stripe formation emerges from the staggered arrangement of the OPE core. The direction of the stripes is tilted by 51° from the main axis of the molecular rods and by about $9 \pm 2^\circ$ from one of the three main axes of graphite (Fig.7C).

As alternative approach to steer the lateral pattern of rigid molecular structures comprising per-fluorinated benzene subunits Ar-H \cdots F-Ar hydrogen bonds were considered. Thus the *Mercedes* star type structure **30** displayed in figure 8 was designed and synthesized. The rays of the star are functionalized with pentafluorobenzene units and its central 1,3-di(phenylethynyl)benzene subunit (blue in figure 8) has three hydrogen atoms ideally arranged to provide a complementary pocket for hydrogen bonding. The *Mercedes* star provides three pentafluorobenzene units as well as three central pockets. The expected intermolecular hydrogen bonding pattern is schematized in one of the three pockets of **30** in figure 7 with an additional pentafluorobenzene unit in red.

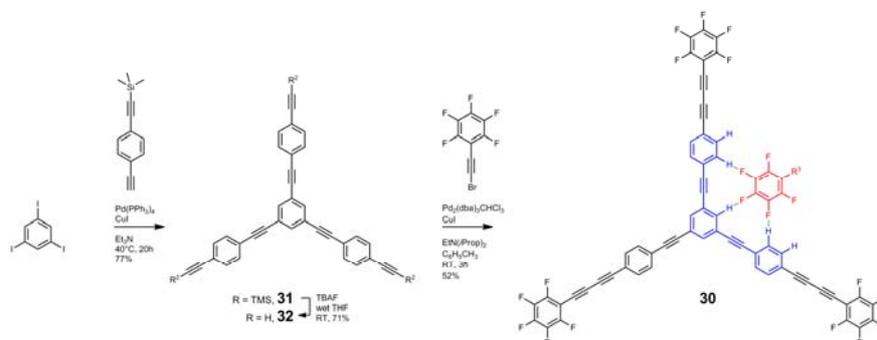


Fig.8: Synthesis of the *Mercedes* star structure **30**. The complementary hydrogen bonding substructures are displayed with an additional pentafluorobenzene subunit in red.[12][C3.8:3]

Comparable techniques and conditions as described above for molecular rods were used to investigate the self-assembly of **30** at the solid/liquid interface. Large area patterns of perfectly ordered *Mercedes* stars were observed as displayed in figure 9. Six star-type molecules are arranged in a circular fashion optimizing both, the number of Ar-H \cdots F-Ar hydrogen bonds and the surface coverage by the molecules. Interestingly, the six molecules are arranged either clockwise or anti-clockwise defining a chiral pore. Entire domains as chiral porous network were observed. Naturally, equal amounts of domains of both chiralities were detected.

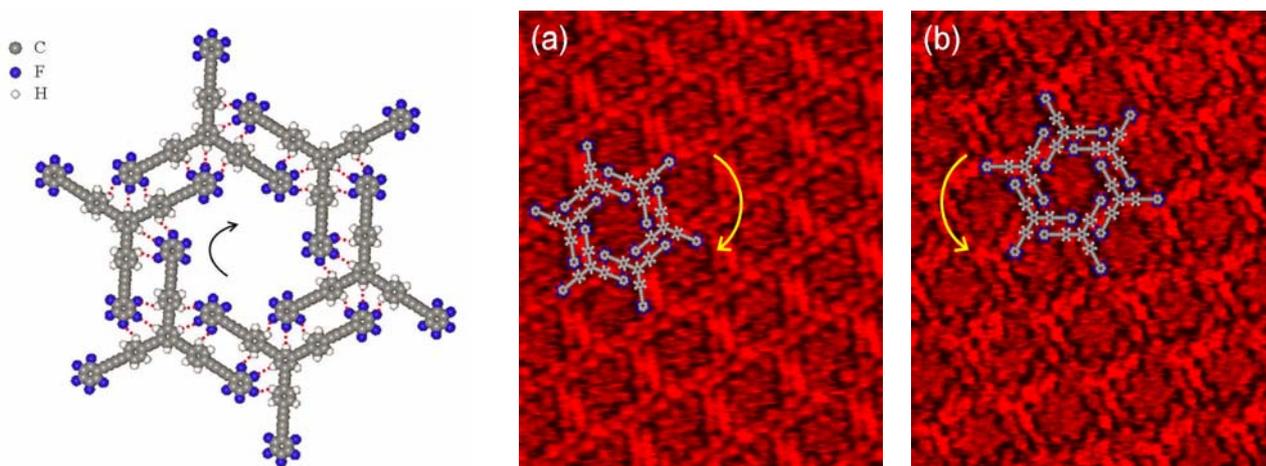


Fig.9: Large area pattern of porous chiral networks on a HOPG surface covered with **30**. The picture a) and b) display opposite chirality. On the left side the hexagonal pore defined by the Aryl-F \cdots H-Aryl hydrogen bonds (red dotted lines) of 6 molecules **30** is displayed.[12][C3.8:3]

In conclusion, rigid molecular structures comprising suitable functional groups to steer their self-assembly into well defined surface patterns have been synthesized and their assembly on HOPG has been investigated by STM. In particular, large area porous and chiral networks with considerable stability have been formed. Currently, we are investigating the interdependence between chiral guests and the chirality of the observed network. We are further investigating intermolecular as well as molecule-surface linking chemistry in order to stabilize the self assembled molecular pattern.

3. Tailor-made polymers to select SWNTs by dispersion

Surface decoration by delocalized π -systems is not only interesting on planar graphite substrates but also on bent surfaces of single-walled (carbon) nano-tubes (SWNTs). Inspired by the pioneering studies with SWNTs in the group of Frank Hennrich and Manfred Kappes, we became interested in the interplay between the polymer and the dispersed SWNT. In particular polymers comprising 9,9-dialkyl-2,7-fluorene subunits in their backbones displayed surprising selectivities by dispersing exclusively semiconducting SWNTs with differences in their chiral indices $n-m = 1$ or 2.[13-15]

As the polymer/SWNT interactions responsible for the dispersion selectivities are not fully understood, we decided to assemble a polymer library in order to study systematically the polymer structure/nano-tube chirality correlation. Inspired by the selecting power of the 9,9-dialkyl-fluorene building block, we became interested in N-alkyl carbazoles as structural proxy of the fluorene with a single alkyl chain. First members **33-44** of the polymer library were assembled by classical C-C coupling reactions and are displayed in figure 10.

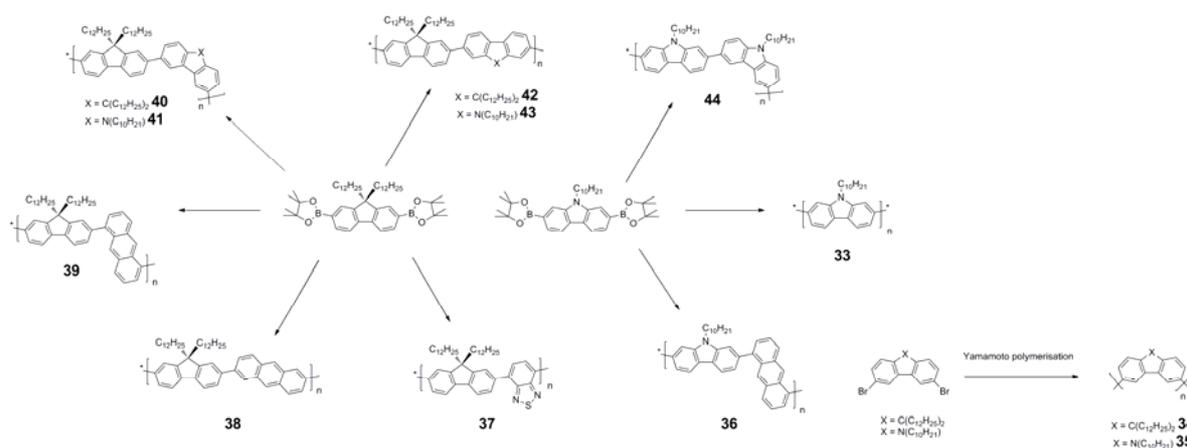


Fig.10: First members **33-44** of the polymer library comprising a 9,9-didodecyl-fluorene and/or a N-decyl-carbazole subunit.

The dispersion properties of these polymers were investigated by Jana Tittmann and Frank Hennrich at the INT@KIT in the group of Manfred Kappes. Therefore ~ 1 mg of as-prepared HiPco SWNTs together with ~ 50 mg of the polymer under investigation in ~ 15 ml of toluene were treated with a titanium sonotrode for 2 hours. Larger agglomerates were removed by gel filtration and density gradient centrifugation (DGC) was applied as purification method able to collect the entirety of polymer stabilized dispersions. The composition of the dispersions was subsequently analyzed by UV/Vis absorption, raman and photoluminescence excitation (PLE) spectroscopy.

Already the small library displayed in figure 10 contained several surprises. The polymer **33** disperses exclusively semiconducting SWNTs with differences in their chiral indices $n-m \geq 2$. In spite of the structural similarity with the fluorene polymer **42**, the two polymers disperse nano-tubes with complement chiral angles θ . These findings are nicely displayed with the chiral angles (θ) vs. nano-tube diameter (\varnothing) map displayed in figure 11B. The figure 11A shows the PLE map recorded for the SWNT dispersion stabilized by **33** which allows to assign the chiral indices of the dispersed SWNTs.[16][C3.8:9]

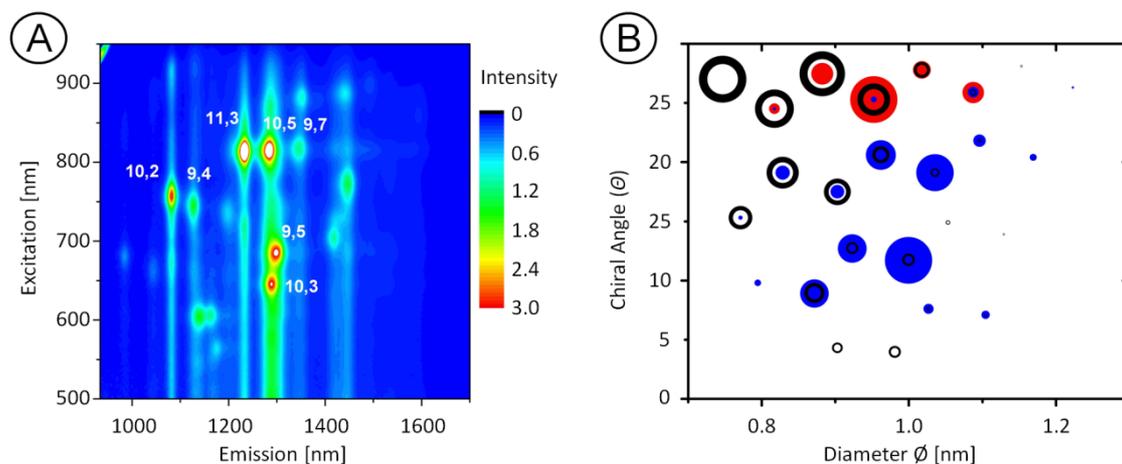


Fig.11: A) PLE map (color-coded emission intensity in arbitrary units vs. excitation and emission wavelengths) of Tol/33 dispersion after DGC, B) θ/\varnothing map from extracted PLE intensities transformed into normalized area of cycles (D₂O/Na-cholate in black, Tol/33 in blue and Tol/42 in red).

Another polymer displaying unexpected selectivity features is the copolymer consisting of alternating 9,9-didodecyl-2,7-fluorene and 1,5-anthracene subunits **39**. The PLE map and the obtained chiral angles (Θ) vs. nano-tube diameter (\emptyset) map of the SWNT dispersion of **39** are displayed in figure 12. As indicated by a light red colored band, the polymer **39** seems to be selective for semiconducting SWNTs with diameters close to 1 nm. While there is a clear exclusion of SWNTs with diameters < 0.95 nm, the upper border at about 1.1 nm is the given by the HiPco SWNT population which hardly contains tubes with larger diameters. Dispersion experiments with **39** and nano-tubes obtained by pulsed laser vaporization (PLV) which have larger diameters clearly showed that **39** is only defining a threshold value for tubes with diameters smaller than 0.95 nm.

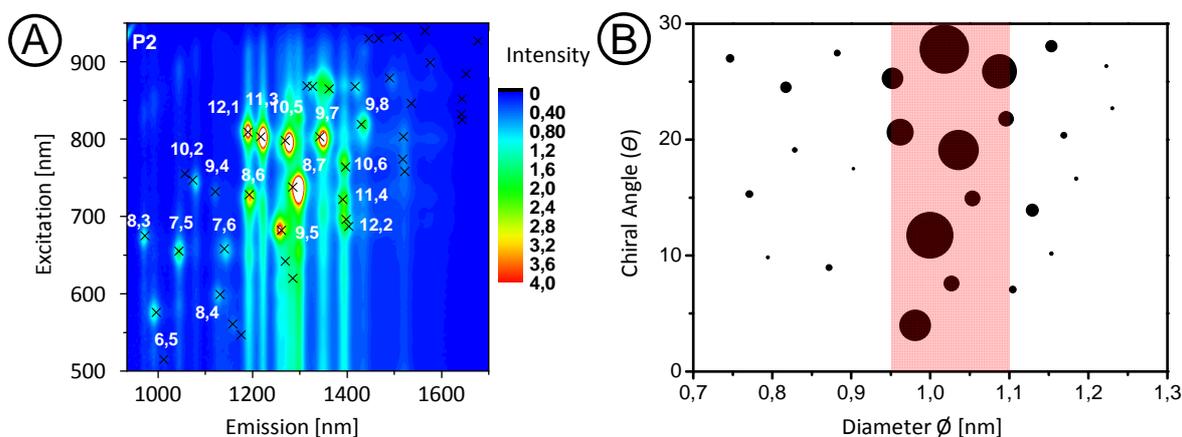


Fig.12: A) PLE map (color-coded emission intensity in arbitrary units vs. excitation and emission wavelengths) of Tol/**39** dispersion after DGC, B) Θ/\emptyset map from extracted PLE intensities transformed into normalized area of cycles.

In conclusion we are currently expanding and exploring a library of various polymers in order to obtain the data required to develop models for the interactions between polymers and carbon nano-tubes. While the complexation mechanism is a topic of current debates several members of the polymer library display surprising selectivities. While the crbazole polymer **33** mainly disperses semiconducting SWNTs with chiral angles (Θ) smaller than 23° , the fluorene-anthracene copolymer **39** exclusively disperses semiconducting SWNTs with diameters larger than 0.95 nm. In addition to the comprehension of SWNTs dispersion mechanisms we try currently to combine the selectivity features of particular polymer building blocks either by their combination in a copolymer or by their subsequent application as dispersion agent. Furthermore, we are introducing additional functional units in the polymer backbone. In a recent experiment photo-cleavable subunits allowed to release the disperses SWNT after irradiation of the dispersion.

4. Single Molecule Electroluminescence from a CNT-molecule-CNT junction

Molecular electronics – understood as the integration of individual molecules as smallest functional unit – has become a fast growing research field in the last decade. Numerous reports dealing with single molecule junctions provided a considerable comprehension of the structure vs. electrical property correlation on a single molecule level. However, the proof of the identity of the integrated molecule is usually solely based on the electrical features of the junction. In order to complement

the electrical signal an optical identification of the integrated molecule would be most welcome. Unfortunately, the proximity of metal electrodes which quench excited states of molecules make such experiments in most common molecular junctions very unlikely.

Within the framework of the CFN however, the groups providing the expertise enabling such an experiment are gathered together. In close cooperation with the group of Ralph Krupke and Hilbert von Löhneysen a joint strategy towards electroluminescent single molecule CNT junctions was developed.

Conducting single-walled carbon nano-tubes *c*-SWNTs would be ideal electrodes for a single molecule electroluminescence experiment. They are very good conductors with a rather low number of itinerant (delocalized) electrons reducing their quenching efficiency for an excited molecule. Ralph Krupke and coworkers are not only able to integrate a single *c*-SWNT, they also developed the technique required to burn a small gap (~ 5 nm) in the *c*-SWNT providing a pair of electrodes.

Our job in project is to provide an ideal molecule for the single molecule electroluminescence experiment. The molecule has to fulfill several boundary conditions. 1) It must be a rod like structure longer than ~ 5 nm in order to bridge both *c*-SWNT electrodes. 2) It must consist of a polarizable backbone structure in order to be trapped between both *c*-SWNTs electrostatically. 3) It should comprise a central chromophore in order to emit light upon electrical excitation. 4) The chromophore has to be linked to a molecular wire on both sides enabling its feeding with electrons and holes respectively. 5) The ends of the molecular wires must be flat in order to optimize the interaction with the *c*-SWNTs by π - π stacking while the chromophore should be rather bulky in order to reduce its tendency to deposit on the SWNT electrode. 6) And finally, from a chemist point of view the most important requirement, the structure must be synthesizable. Based on these considerations we suggested the molecular rods **45-47** displayed in figure 13.

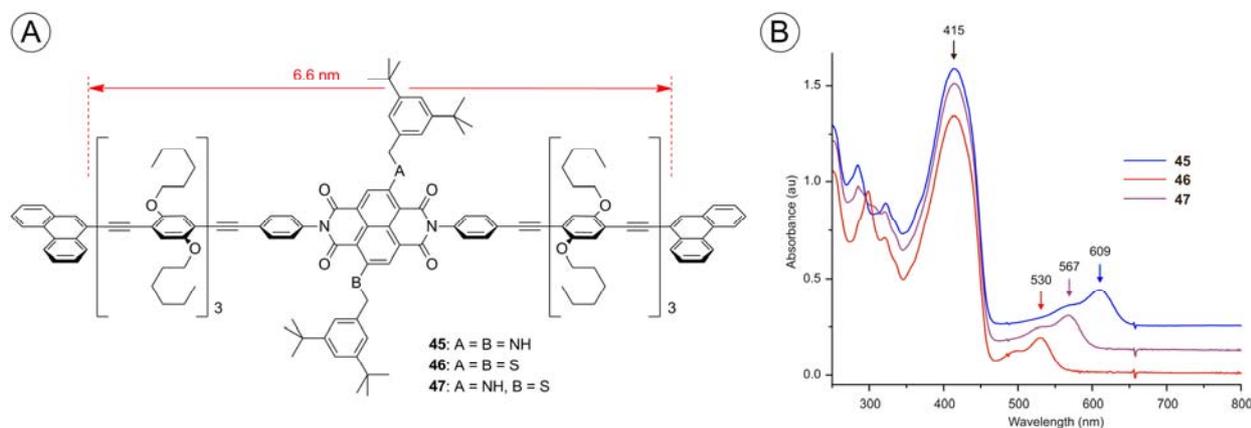


Fig.13: A) Over 5 nm long molecular rod structure comprising a central, by its core substituents tuneable, NDI-chromophore. B) Absorption spectra of the molecular rods **45-47** illustrating the dependence between the longest wavelength absorption and the NDI-core substituents.[17][C3.8:10]

Due to the limited synthetic manpower available within the CFN, the synthesis of the molecular rods **45-47** was mainly achieved with coworkers financed by other resources (University of Basel, INT@KIT and NCCR nanoscale sciences of the Swiss National Science Foundation). The rods **45-47** were synthesized and fully characterized.[17][C3.8:10] An efficient energy transfer from the peripheral molecular wires to the central chromophore were observed spectroscopically for the rod **47** comprising a central bezylamino core substituted NDI chromophore.

With this molecule in hand, our attempts to assemble a *c*-SWNT-**47**-*c*-SWNT junction were successful.[18][C3.8:8] Details concerning the assembly and characterization of the junctions can be found in the report of Ralph Krupke. The experiment with the immobilized molecular rod inside the *c*-SWNT junction is sketched in figure 14A. As the observed electrical characteristics of the junction indicated the presence of the molecule **47** inside the junction, the electroluminescence properties of the junction were of particular interest. And indeed, upon applying a voltage of about 5 V, light emission from the junction was detected. Spectral resolution of the emitted light (red circles in Fig.14B) and its comparison with photoluminescence signal of a molecular layer of **47** on graphite (black line in Fig.14B) corroborated the immobilized molecular rod as the emitting light source of the junction.

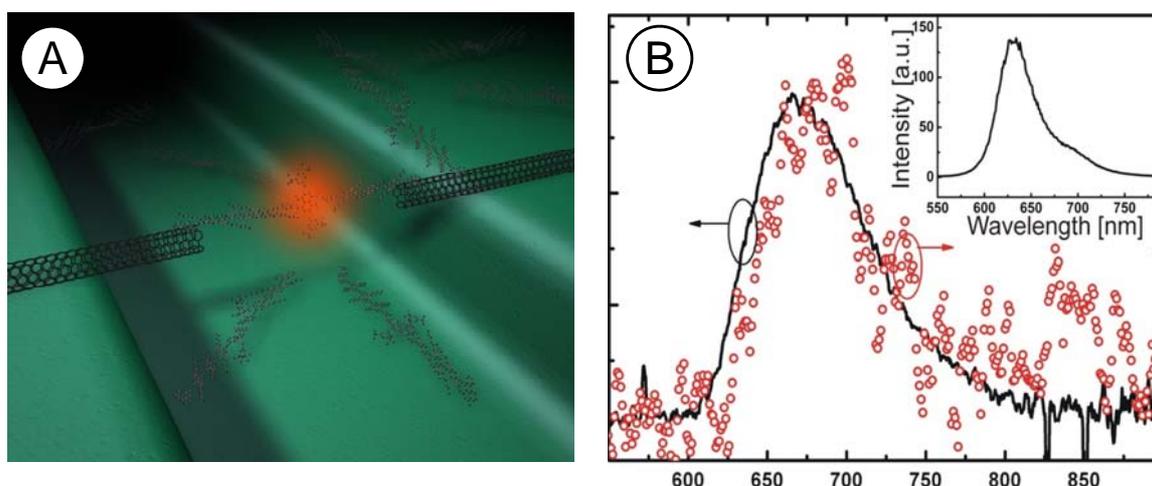


Fig.14: A) Artistic representation of the experimental set-up displaying the *c*-SWNT junction above a trench with the molecular rod **47** bridging the gap. B) \circ : Electroluminescence of the single molecule junction observed at r.t. in UHV; -: Photoluminescence of a molecular layer of **47** on graphene recorded at r.t. in UHV. The inlay displays the fluorescence signal of the molecular rod **47** dissolved in mesitylene.

In conclusion the presence of a molecule in the molecular junction has been corroborated by the electroluminescent features of the junction. We are currently exploring alternative dye structures in order to tune the emission properties of the junction.

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