

D22.1

## **2-WP2: Chemical Synthesis (P7-HU Berlin WP Manager)**

Within this work package synthetic chemistry is developed to prepare various molecular building blocks and molecule logic gate according to the design rules described in 2-WP1 above. The monomers are subsequently used to bottom-up construct molecular wires and soon circuits in Unit 3. The stand-alone molecule logic gates are directly used in Unit 3 with single metal atoms as logical inputs.

In the second AtMol year, this work package has been devoted towards accomplishing the following tasks: synthesis of monomers suitable for the on-surface synthesis of molecular wires (Task 2-T2.1), synthesis of various nodes for defined interconnection with the molecular wires to achieve semi-classical intramolecular circuits (Task 2-T2.2), preparation of a long latch molecule (Task 2-T2.3) as well as the synthesis of large and complex stand-alone molecule gates (Task 2-T2.4).

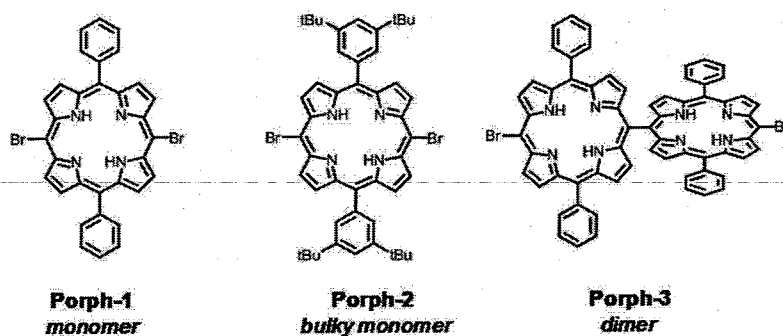
### **2-T2.1: Monomer Synthesis for on-surface polymerization of very low gap molecular wires**

**(Man month, real/foreseen: P1: 3/6.5 and P7: 12/12)**

Molecular wires consisting of elongated  $\pi$ -systems with low band gaps below 1 eV require an extended  $\pi$ -system. Bond length alternation due to Peierl's distortion should be minimized by use of a lateral rigidified, ladder-type architecture. The conduction mechanism through those molecular wires can be pseudo ballistic when reaching the molecular electronic states of the polymer by increasing the bias voltage or tunneling in a low bias voltage regime. In this last case, alternating donor and acceptor moieties must be introduced to further lower the band gap and optimize the  $m^*$  effective mass of the tunnel electrons passing through the molecular wire (see Task 2-T1.1 above).

#### **a) Porphyrin tapes synthesis (P7-HUBerlin)**

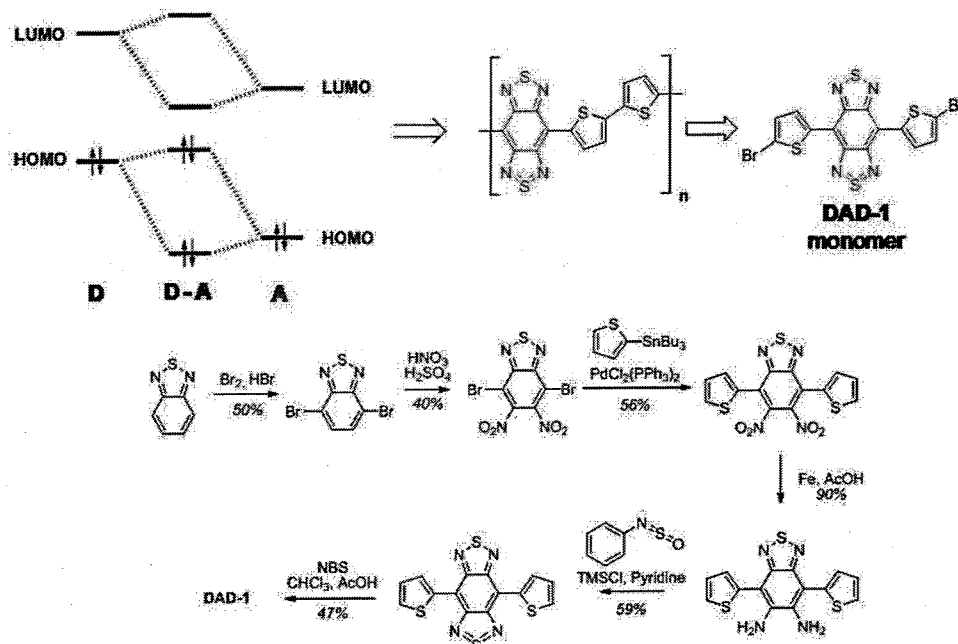
The first building blocks synthesized by P7-Berlin were porphyrin derivatives functionalized with bromo atoms, designed to form very low gap porphyrin tapes while polymerized on the surface. Three different precursors (**Porph-1**, **-2**, and **-3**, see Fig. 1 (2-T2.1)) have been prepared and delivered to P6-FHBerlin during the AtMol first year. After a year of unsuccessful attempts to polymerize these dibrominated compounds (most likely because of steric congestion during the course of the coupling reaction), it was decided to follow two alternative approaches, one based on alternating donor-acceptor polymers (see 2-T2.1, b), and another one based on graphene nanoribbons with zigzag edge structures (see 2-T2.1, c).



**Figure 1 (2-T2.1):** Precursors for the on-surface synthesis of very low band gap porphyrin tapes (delivered to P6-Berlin between July and December 2011).

### b) Alternating donor-acceptor polymers (P7-HUBerlin)

Low band gap polymers are common synthetic targets in the context of organic photovoltaics. They can be used as active layers in such organic photovoltaic devices with the advantage of absorbing light in the near infra-red region of the solar spectrum. The typical design relies on alternating donor and acceptor groups within the backbone of a linear polyaromatic chain. A good and regular electronic interaction between the D and A fragments along the chain leads to a very small gap as recall in Fig. 2 (2-T2.1). Many different combinations have been described in the literature. In terms of band gap engineering, one of the best low gap polymer makes use of alternating benzobis(thiadiazole) acceptor units (Fig. 2 (2-T2.1) shown in red) and thiophene donor units (Fig. 2 (2-T2.1) shown in blue).



**Figure 2 (2-T2.1):** Schematic energetic diagram of a D-A monomer and synthesis of monomer building-block **DAD-1** (delivered to P6-FUBerlin in October 2012).

Calculations performed by P1-Toulouse (2-WP1) have confirmed the rather low HOMO-LUMO gaps (0.5–1.5 eV) leading to low  $\beta(E_f)$  values (0.1–0.3  $\text{\AA}^{-1}$ ) and to reduced effective mass  $m^*/m_0$  (0.1–0.3) for a tunnel transport through such molecular wires. Exceptionally low values are reached for compounds in which the thiophenes are functionalized with nitro

groups (see AtMol Annual Report Year 1, page 62). Considering thermal stability of the monomer during vacuum deposition for on surface synthesis of the molecular wires, the DAD-1 compound presenting the bromines as the only labile substituent, was chosen as the first target monomer. It was synthesized in a linear sequence of six steps starting from the commercial benzothiadiazole compound (see Fig. 2 (2-T2.1)) by adapting the protocols described in the literature by Yamashita in 1996 and Krebs in 2006. Those compounds were delivered to P6-FUBerlin in October 2012 (see 3-T1.1).

### c) Graphene nanoribbons with zigzag edge structure (Z-GNRs) (P7-HUBerlin)

Graphene nano-ribbons (GNR) have lately attracted much attention as wire-like graphene in which a gap can be opened to access carbon-based semi-conductivity stripes. Since GNRs are finite linear structures, the shape of their edges plays a critical role (in particular below a critical thickness evaluated to be around 3.5 nm). Calculations performed by P1-Toulouse (2-WP1) and others indicate that GNRs with zigzag edges have superior properties (lower HOMO-LUMO gaps and  $\beta(E_f)$  values) when compared to their isomeric structures with armchair edges. However, from a chemical point of view it is much more challenging to synthesize GNRs with zigzag edges. Indeed, synthesis of polyaromatic compounds usually relies on the direct connection of preformed phenyl rings, an approach, which inevitably results in structures with armchair edges. As a consequence, the chemical synthesis of Z-GNRs, in solution or directly on an atomically planar surface, has thus far not been reported. In the second year of the AtMol project, P7-HUBerlin had developed innovative chemical approaches for the synthesis of Z-GNRs in solution, which could be adapted to on-surface synthesis in a second phase. The elementary steps of our synthesis are outlined in Fig. 3 (2-T2.1) below. The first steps have been successfully performed, but some synthetic difficulties arise in the last two steps, which so far have prevented us to conclude the synthesis of this unprecedented class of molecular wires. Once successful we plan to adapt this synthesis for longer oligomeric wires.

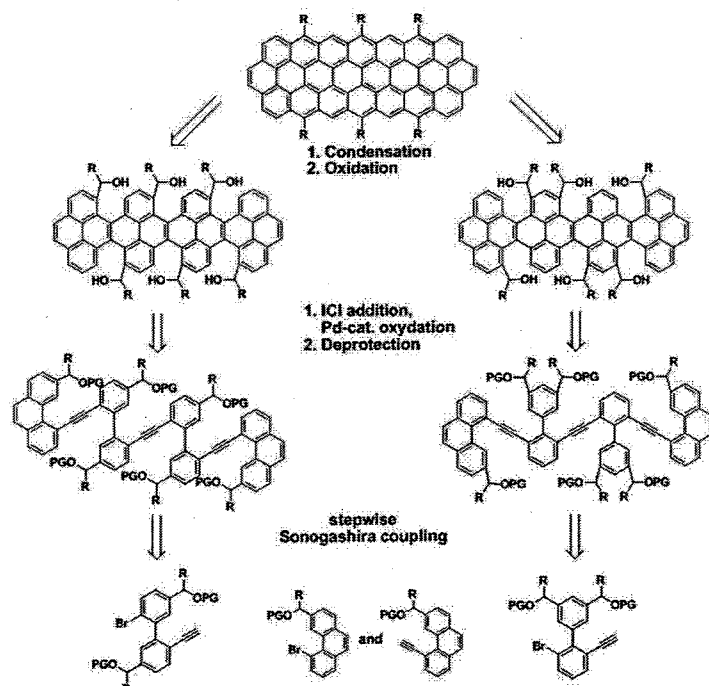
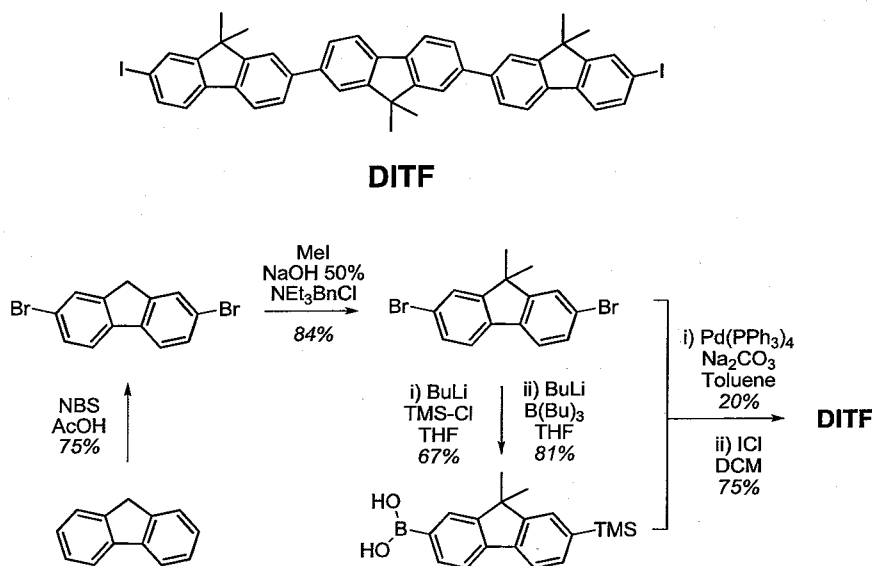


Figure 3 (2-T2.1): the Retrosynthetic approach to Z-GNRs in solution (PG = protecting groups, R = solubilizing groups).

#### d) Diiodoterfluorene for polymerization on semi-conducting surfaces (P7-HUBerlin)

In AtMol, the construction of a molecular chip where the molecular wires or the molecule logic gates are interconnected to DB atomic scale surface wires or directly to metallic nanopads requires a passivated semi-conducting surface such as Si(100)H or Ge(001)H (see 3-WP2). Therefore, it is important in AtMol to learn how to directly synthesize or transfer such molecular wires on a Si(100)H or Ge(001)H surface. In AtMol, the two approaches are followed. In the first one (see Task 3-T1.5) the molecular wires are on-surface synthesized on a metallic surface such as Au(111) and subsequently stamped onto semi-conducting passivated surface. Alternatively, those molecular wires are synthesized directly on hydrogen-passivated Si(100) or Ge(100) surfaces (see the first case in Task 3-T1.3). On-surface polymerization processes had so far mainly been performed on a metallic surface. But P7-HUBerlin had started the synthesis of a tailor-made building-block for the polymerization on a semi-conducting surface following the first successful attempts on a TiO<sub>2</sub> surface by P10-Krakow (see Task 3-T1.3).



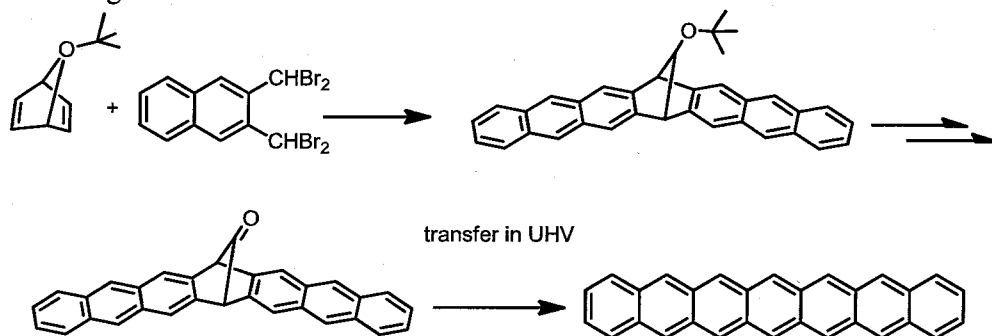
**Figure 4 (2-T2.1):** Iodo-functionalized terfluorene (**DITF**) for polymerization on semi-conducting surfaces (delivered to P10-Krakow in November 2012).

Dibromoterfluorene monomers can polymerize very efficiently on the Au(111) surface when the substrate is heated to 520 K as demonstrated by P6-FHBerlin. However, this process is not suitable for hydrogen-passivated surfaces which would decompose at such elevated temperatures. Therefore, P7-HUBerlin had prepared another monomer, the diiodoterfluorene compound (**DITF**, see Fig. 4 (2-T2.1)), since the C-I bonds are cleaved at much lower temperature than the C-Br bonds. **DITF** was synthesized as sketched in Fig. 4 (2-T2.1) for Br and delivered to P10-Krakow in November 2012 for testing on semi-conducting TiO<sub>2</sub> and the passivated Ge (001)H surfaces (see Task 3-T1.3).

#### e) The Oligoacenes precursors (P1-Toulouse)

Polyacenes are a class of polyaromatic hydrocarbons composed of linearly fused benzene rings. One of their attractive properties is their narrow HOMO-LUMO gap which decreases

rapidly with the number of fused rings which must lead to a pseudo ballistic regime of transport (see 2-WP1). However, their preparation is limited by both their low solubility and their low stability in solution. One of the P1-Toulouse objectives is to prepare long acenes (from hexacene and upwards) by transferring on a metal surface and in the UHV non-conjugated (less reactive) and non-planar (more soluble) precursors that will be transformed in oligoacenes by a on-surface reactions like an intramolecular aryl-aryl coupling, a retro-Diels-Alder or a photo-induced expulsion of CO from mono and diketone precursors. Hexacene has recently been prepared by Watanabe in 2012 following this strategy and P1-Toulouse had started to investigate this reaction first with the heptacene molecule according to the following scheme:



**Figure 5 (2-T2.1):** the synthesis of an heptacene carbonyl precursor for an on-surface synthesis.

Work in progress involve double annulation by reaction of 2,3-bis(dibromomethyl)naphthalene with 7-tert-butoxynorbornadiene in presence of sodium iodide, hydrolysis of the tertbutoxy group, which is then oxidized to give the dihydromethanoheptacene-one compound which will be transferred in UHV to a metal surface for an on-surface reaction.

## 2-T2.2: Monomer Synthesis for surface chemistry of semi-classical molecular circuits

(Man month, real/foreseen: P4: 12/12 and P7: 12/12)

In order to assemble a semi-classical intramolecular circuit, the molecular wire constructs have to be covalently bonded to different functional nodes. This task involves the synthesis of various central molecule-node building blocks. They are supposed to allow an efficient electronic interaction between the molecular wire and the node branching location. For this purpose, a variation of substitution patterns will allow for the control of  $\pi$ -conjugation pathways through the molecule-node, while the coupling chemistry has to be optimized to facilitate such a heterostructure formation on a metallic surface following the on-surface synthesis technique.

### a) The Hexabenzocoronene (HBC) nodes (P7-HUBerlin):

In the first year of the AtMol project, di-functional HBC molecules, i.e. building blocks functionalized with either two bromo or two iodo substituents, were synthesized by P7-HUBerlin and delivered to P6-FHBerlin in order to test the possibility to on-surface bond polyfluorene wires to these HBC molecular nodes (see Fig. 1 (2-T2.2) a).