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Debundling, selection and release of SWNTs using fluorene-based photocleavable polymers[†]

Fabien Lemasson,^a Jana Tittmann,^a Frank Hennrich,^a Ninette Stürzl,^a Sharali Malik,^a Manfred M. Kappes^{*abc} and Marcel Mayor^{*acd}

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Photocleavable polymers based on 9,9-dialkylfluorene backbone and o-nitrobenzylether were designed and synthesized to obtain stable (n,m) enriched suspensions of semiconducting SWNTs in toluene. Photoirradiation of the suspensions triggered the precipitation of the SWNTs and TEM images indicate close packing of SWNTs pointing at partial removal of the coating polymer.

Single-walled carbon nanotubes (SWNTs) exhibit unique physical and electronic properties which make them excellent candidates for micro- and optoelectronics¹ as well as for nanocomposites.² Nevertheless, limitations in their use arise from their non-selective synthesis providing a mixture of semiconducting and metallic tubes with many different (n,m)chiral indices. Thus, several methods for SWNTs sorting were developed.³ In particular those which make use of non-covalent interactions are of interest due to the preservation of the SWNT intrinsic physical properties.^{4–7} Among these methods, polymer wrapping has already demonstrated promising results and is of great potential due to almost unlimited structural variation.⁷ While several polymers displaying various selectivities for particular SWNTs were reported, their subsequent removal from the SWNTs' surface remains a major challenge.8 Recently, Imahori and coworkers addressed this issue with an azobenzene based polymer which solubilizes and releases SWNTs bundles upon photoisomerization.9 Moore, Zang and coworkers reported the reversible solubilization and release of SWNTs using a foldamer.¹⁰ However, both approaches were not selective for particular (n,m) SWNT species. Here we report the first example of debundling, sorting and release of individual SWNT using fluorene-based photocleavable polymers.

Poly(9,9-dialkyl)fluorenes are known to suspend efficiently only a few (n,m) SWNTs in organic media.^{7a} The subsequent

removal of the polymer is troublesome, probably due to the wrapping of the polymer arround the SWNT being supported by extensive van der Waals and/or π - π stacking interactions.⁷ Embedding a photocleavable moiety in the polymer main-chain would allow us to shorten the polymer length by irradiation and thus, to render its displacement. Photocleavable subunits in polymer main-chains have so far been used as linkers in diblock copolymers¹¹ and star polymers.¹² To the best of our knowledge, this is the first example of an alternating copolymer displaying a photocleavable moiety in the polymer main-chain.

The investigated polymers **6a–e**, depicted in Scheme 1, are composed of fluorene subunits as recognition sites to interact exclusively with specific (n,m) SWNTs and of an *o*-nitrobenzylether as a photocleavable linker. The photocleavable dibromide 3^{13} was synthesized in 2 steps from aldehyde 1 by sodium borohydride reduction followed by a Mitsunobu reaction



Scheme 1 Synthesis of the polymers **6a–e** and their building blocks. *Reagents and conditions*: (a) NaBH₄, THF, 0 °C, 80%; (b) 4-bromophenol, PPh₃, DIAD, THF, 0 °C to rt, 68%; (c) PdCl₂(dppf), (Bpin)₂, KOAc, dioxane, 80 °C; (d) Pd(PPh₃)₄, toluene/1 M Na₂CO₃, 80 °C; pin: pinacol, DIAD: diisopropyl azodicarboxylate, dppf: 1,1'-bis(diphenylphosphino)ferrocene.

^a Karlsruhe Institute of Technology (KIT), Institute for

Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany ^b Institut für Physikalische Chemie, Karlsruher Institut für

Technologie, D-76128 Karlsruhe, Germany.

E-mail: manfred.kappes@kit.edu

^c DFG Center for Functional Nanostructures, 76028 Karlsruhe, Germany

^d University of Basel, Department of Chemistry, St. Johanns-Ring 19, CH-4056 Basel, Switzerland. E-mail: marcel.mayor@unibas.ch

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with 4-bromophenol. Its reaction with diboronic esters $5a^{14}$ and 5b in a Suzuki coupling led to polymers 6b and 6c, respectively. Polymers 6d and 6e were synthesized using a similar coupling protocol but by complementing the dibromide content with 2,7-dibromofluorene 4a in order to reach a final stoichiometry fluorene/photocleavable group of 3/1 and 7/1 for polymers 6d and 6e, respectively. Thus, the *o*-nitrobenzene moiety was randomly installed in the polymer chain of 6d and 6e. Also, all of the polymers 6b-e lack regioselectivity with respect to the orientation of the photocleavable subunit. Polyfluorene 6a was synthesized by *Suzuki* coupling of dibromide 4a and diboronic ester 5a. Polymers 6a-e were characterized by NMR spectroscopy and sized exclusion chromatography (ESI†).

The SWNTs suspensions 7a-e, obtained with polymers **6a–e**, respectively, were prepared by ultrasonicating $\sim 1 \text{ mg}$ of as prepared HiPco SWNTs and ~ 50 mg of the desired polymer in 15 mL toluene with a titanium sonotrode.[†] The suspension was filtered to remove large agglomerates and further purified using density gradient centrifugation (DGC). It is noteworthy that only DGC provides a complete picture of the SWNT/polymer suspension as SWNT/polymer complexes with densities above those of the solvent get lost during "classical" centrifugation. Furthermore, the excess polymer is removed during DGC.[†] Stable suspensions 7b-e were obtained. Obviously, the photocleavable moiety installed in the polyfluorene backbone does not impair the debundling and solubilisation processes. Suspensions 7a-e were analyzed by photoluminescence excitation (PLE) spectroscopy (Fig. 1). Despite a hypsochromic shift of the signals, the assignment of each semiconducting (n,m) species is possible.¹⁵ The PLE map of suspension 7b indicates the presence of numerous different (n,m) SWNTs, reflecting roughly the composition observed with sodium cholate stabilized HiPco SWNTs in

 D_2O .¹⁶ In contrary, suspension 7c, prepared from polymer 6c in which three consecutive fluorene units are present, displayed a drastic increase in the selectivity, reaching almost that of polymer 6a. Suspensions 7d and 7e also showed impressive selectivities despite the randomly installed *o*-nitrobenzylether moiety. Based on these results we concluded that subunits of several adjacent fluorene moieties are required in order to observe selectivity for particular (*n*,*m*) species.

The absorption spectra of suspensions **7b** and **7c** were recorded (ESI: Fig. S4).† Intense absorption features of semiconducting SWNTs ($\lambda > 600$ nm) were observed for both suspensions. While minor traces of metallic HiPco SWNTs (300 nm > $\lambda > 600$ nm) were observed for **7b**, **7c** disperses exclusively semiconducting SWNTs according to its UV spectrum (Fig. S4, ESI†).

Photoirradiation of suspension 7b for approximately 2 min with a xenon lamp caused precipitation of SWNTs (ESI[†]). Simple heating of the sample did not cause precipitation of SWNTs corroborating the light induced cleaving of the polymer backbone as the SWNT releasing mechanism. The SWNTs were collected by centrifugation and analyzed by Raman spectroscopy.† The low ratio between the defect induced D band and the tangential G band (D/G band ratio, Fig. S3, ESI⁺) indicates that neither defect formation nor sidewall functionalization of the SWNT occurs during the photocleavage of the o-nitro-benzylether moiety, despite the radical nature of the process.¹⁷ Also the SWNTs with particular (n,m)indices selected by dispersing with 6c precipitate upon irradiating 7c for 2 minutes (Fig. 2). While increasing the fluorene amount in the polymers increased its selectivity for particular (n,m)species, it slowed down the rate of precipitation upon irradiation. Suspension 7d started to precipitate only 12 hours after irradiation, and no precipitation at all was observed for suspension 7e. According to these results, we assume that over a critical length, the oligofluorenes stemming from the



Fig. 1 PLE maps in toluene of (a) suspension 7a; (b) suspension 7b; (c) suspension 7c; (d) suspension 7d; (e) suspension 7e; (f) HiPco SWNTs suspended with sodium cholate in D₂O.



Fig. 2 Suspension **7c** (a) before and (b) after 2 min irradiation showing the precipitation of the enriched (n,m) SWNTs.

polymer photodegradation are still able to stabilize the SWNTs. In a hypothetical full cleavage of all *o*-nitrobenzylether subunits, the polymer **6c** would release trimers, which are not long enough to stabilize SWNTs. The polymer **6d** on the other hand releases longer oligomers also, which presumably are able to stabilize SWNTs. It is worth noting that all these suspensions were stable for at least 2 months in the dark.

The precipitated (n,m) enriched SWNTs from suspensions **7c** and **7d** were collected by centrifugation. TEM images of SWNTs from suspension **7d** displayed residual polymer coating wrapped arround the tube (Fig. S8, ESI†). The SWNTs from suspension **7c** were washed several times with toluene using a mild sonication bath. The TEM images in Fig. 3 show bundles of SWNTs due to their strong π - π stacking interactions. The close contact between the tubes points at least to partial removal of the polymer at their surfaces.

In conclusion, polymers composed of 9,9-dialkylfluorenes as a SWNT selecting template and *o*-nitrobenzylether as a photocleavable linker were designed, synthesized and their SWNT dispersing features were analyzed. Copolymers of both subunits with HiPco SWNT selecting properties comparable with poly(9,9-dialkyl)fluorenes were obtained as soon as at least three



Fig. 3 TEM picture with enhancements of precipitated (n,m) enriched semiconducting SWNTs from suspension 7c which formed bundles.

consecutive fluorene subunits were present in the backbone. The release of SWNTs after photoirradiation can be varied from seconds to hours depending on the place and amount of photocleavable moiety in the polymer backbone. To the best of our knowledge, this is the first study involving controlled precipitation of solubilized (n,m) enriched semiconducting SWNTs.

We are currently investigating the role of the polymer length for its dispersing features and we are screening potential recognition templates for SWNTs.

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