Macromolecules

Supramolecular Functionalization of Single-Walled Carbon Nanotubes (SWNTs) with a Photoisomerizable Conjugated Polymer

Patigul Imin, Mokhtar Imit, and Alex Adronov*

Department of Chemistry and Chemical Biology, The Brockhouse Institute for Materials Research, McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4M1, Canada

Supporting Information

ABSTRACT: A fluorene- and azobenzene-containing conjugated polymer, poly[2,7-(9,9-didodecylfluorene)-*alt*-4,4'-azobenzene] (F12AZO) has been successfully synthesized using Suzuki polycondensation. The introduction of two dodecyl chains on the flourene unit resulted in a highly soluble polymer. F12AZO possesses excellent thermal stability, with a decomposition temperature over 400 °C under Ar. The reversible photoisomerization of the azobenzene units was achieved upon alternating photoirradiation with light of wavelength less than



450 nm (*cis*-form), and light in the range of 450–600 nm (*trans*-form). The supramolecular complex formation of *trans*-F12AZO, and *cis*-F12AZO with single-walled carbon nanotubes (SWNTs) has been studied, and it was found that this polymer can form very strong supramolecular polymer-nanotube assemblies. Furthermore, the *trans* and *cis* isomers of F12AZO enable the selective dispersal of individual SWNTs in toluene or THF, and the selectivity of the SWNTs is strongly dependent on the solvent, as well as the type of isomer used. UV–vis–NIR, and photoluminescence–excitation spectroscopy (PLE) were used for the characterization and identification of the nanotube species that are solubilized and exfoliated by this polymer.

INTRODUCTION

Since their discovery,¹ single-walled carbon nanotubes (SWNTs) have attracted significant attention due to their remarkable mechanical, thermal, optical, and electronic properties.^{2–9} Various potential applications of SWNTs, including their incorporation within chemical sensors,¹⁰⁻¹² field-effect transistors,¹³⁻¹⁶ nanoscale integrated radio receivers,^{17,18} photovoltaics,¹⁹⁻²¹ field-emission displays,^{22,23} and many other devices^{24,25} have been extensively explored over the past 2 decades. However, the inherent insolubility of carbon nanotubes in most organic and aqueous solvents and coexistence of various tube types in as-produced SWNT samples have severely limited the widespread application of these novel nanostructures. To improve their solubility and processability, various carbon nanotube surface modification techniques have been developed, including covalent and noncovalent functionalization.^{26–28} Noncovalent functionalization of SWNTs with aromatic macromolecules or conjugated polymers is of particular interest because this approach does not introduce any defects in the nanotube sidewall, thus leaving the extended nanotube π -network, along with all of its consequent properties, unperturbed.29-32

Recently, supramolecular functionalization of SWNTs with fluorene-containing conjugated polymers has generated significant interest due to the excellent solubility and solution stability of the resulting polymer-SWNT nanocomposites.^{31–35} Interest in this class of conjugated polymers has increased as reports of selective solubilization of certain SWNT species have begun to be published.^{33,36–38} It has also been shown that

noncovalent functionalization of SWNTs with stimuli-responsive polymers that are modulated by light, pH, and temperature enables reversible modification of electronic properties within the resulting CNT-based nanostructures.^{39–41} In particular, structural components that can control the strength of polymer binding to the nanotube surface in response to external stimuli are of significant interest.

Azobenzene (AZO) is a well-known photoisomerizable molecule exhibiting a reversible trans to cis isomerization that can easily be achieved upon photoirradiation, even when incorporated within polymeric structures.^{39,42,43} The conformational change of the AZO unit upon photoirradiation can significantly affect the molecular shape of AZO-containing polymers, resulting in reversible coiling/uncoiling processes.^{44,45} Recently, several conjugated polymers incorporating the AZO unit have been reported, and have even been shown to undergo supramolecular functionalization of SWNTs.^{39,40,43} For example, Imahori and co-workers found that alternating copolymers of AZO with phenylene or vinylene units enable the dissolution of SWNTs, where the degree of dissolution depended on the *cis/trans* ratio of the AZO units in the starting polymer.⁴³ Interestingly, it was not possible to isomerize the AZO units after nanotube complexation in solution because of the strong supramolecular interaction between the AZO units in the polymer backbone and the nanotube sidewall, a result

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Scheme 1. Synthetic Route to the F12AZO Polymer



that has also been found in other studies.^{39,40,43} Furthermore, the polymers reported in these studies were not found to be selective toward specific nanotube types within a mixture.

These observations inspired us to investigate the incorporation of the AZO unit within conjugated polymer backbones that have been previously found to be selective for specific nanotube chiralities, such as poly(9,9-di-*n*-alkylfluorene)-based polymers,^{46,47} and to determine if AZO photoisomerization can influence this selectivity. Here, we report the supramolecular functionalization of SWNTs using a photoresponsive conjugated polymer, poly[2,7-(9,9-didodecylfluorene)-*alt*-4,4'-azobenzene] (F12AZO), and describe the detailed optoelectronic and photo physical characterization of the resulting F12AZO-SWNT complexes. The effect of changing solvent, and changing the polymer conformation upon photoirradiation on the interaction between the polymer and nanotubes is also described.

RESULTS AND DISCUSSION

4,4'-Diiodoazobenzene (1) was synthesized according to literature procedures starting from 4-iodoaniline.⁴⁸ Poly[2,7-(9,9-didodecylfluorene)-*alt*-4,4'-azobenzene] (F12AZO) was prepared using a Suzuki polycondensation from 9,9-didodecylfluorene-2,7-bis(trimethyleneboronate) and 4,4'-diiodoazobenzene as depicted in Scheme 1. F12AZO was obtained as an orange solid in 76% yield, and the resulting polymer exhibited excellent solubility in common organic solvents, including THF, toluene, and chloroform. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) relative to polystyrene standards, and indicated a number-average molecular weight (M_n) of 6.6 kg/mol with a polydispersity index (PDI) of 2.0.

The chemical structure of F12AZO was confirmed by ¹H NMR spectroscopy (Figure 1). The multiplet centered at 7.85 ppm corresponds to the aromatic protons from flourene, and the peaks centered at 8.06 and 7.71 ppm correspond to the aromatic protons of AZO. On the basis of the relative areas of these peaks, the molar ratio of fluorene and azobenzene was determined to be 1:1, which is consistent with the alternating



Figure 1. ¹H NMR spectrum of the polymer in CDCl₃.

copolymer structure expected from the Suzuki polycondensation. Phenyl groups were also successfully introduced at both ends of the polymer as end-caps, and the two sets of small multiplets centered at 7.57 and 7.51 ppm, and the doublet at 7.97 ppm (Figure 1) were assigned as the end group phenyl protons.⁴⁹ On the basis of the integration ratio of the fluorene proton signals in the polymer repeat units to the end-group proton signals, the average degree of polymerization (DP) and M_n were estimated to be approximately 9 and 6.3 kg/mol, respectively. The estimated M_n value by NMR is in surprisingly good agreement with the molecular weight measurements from GPC.

The thermal stability of F12AZO was characterized by thermogravimetric analysis (TGA), carried out under an Ar atmosphere (Figure S1, Supporting Information). This data indicates that the major mass loss occurs at 400 °C for F12AZO, amounting to 50%. This mass loss corresponds well with the loss of side chains within this polymer. Above this temperature, the mass decreases slowly, and levels off at ca. 45% when heated to 800 °C, at which point it is likely converted to char.

Optical properties of the F12AZO were characterized by UV–vis absorption spectroscopy. F12AZO exhibits an absorption maximum (λ_{max}) at 417 nm in THF (Figure S2, Supporting Information), which is in good agreement with

previously reported values for similar polymers of nearly equal molecular weight.⁴² It has been reported that all azobenzene units in the polymer backbone are most stable in the *trans* form when the polymer is kept in solution.⁴²⁻⁴⁵ To achieve *trans*-tocis isomerization, a THF solution of F12AZO (0.017 g/L) in a quartz cuvette was irradiated with light of wavelength <450 nm for 20 min. This resulted in a decrease in the absorption band centered at 417 nm (Figure S2, Supporting Information, A). The reverse isomerization (cis-to-trans) was achieved by irradiating with light in the range of 450-600 nm. In both cases the absorption spectra recorded at different irradiation times indicated that the full extent of isomerization was complete within 15 min of irradiation (Figure S2, Supporting Information). The changes of the polymer absorption in THF upon alternating photoirradiation in the two wavelength ranges (<450 nm, and 450-600 nm) at room temperature for 15 min were also measured to confirm that F12AZO can undergo reversible *trans-cis* photoisomerization (Figure S3, Supporting Information).

The supramolecular interaction of F12AZO with SWNTs was studied using our previously reported methods.³² In a typical experiment, a SWNT sample (2.5 mg) was added to a solution of polymer in THF or toluene (7.5 mg/10 mL), and the mixture was ultrasonicated in a bath sonicator for 1 h. The resulting solution was centrifuged for 45 min at 8,300 g, allowed to stand overnight, and then the supernatant was carefully transferred by pipet to another vial. A dark colored, relatively concentrated polymer–nanotube complex solution was observed in THF, while significant nanotube precipitation was observed in toluene, leaving a clear, orange solution (Figure S4, Supporting Information).

The supramolecular complexes of trans-F12AZO with SWNTs in THF were further investigated to determine if polymer can be released from the carbon nanotube surface upon photoirradiation. In a typical experiment, the isolated supernatant in THF was further diluted with 50 mL of THF, sonicated for 5 min, filtered through a 200 nm pore diameter Teflon membrane, and repeatedly washed with THF until the filtrate was colorless, ensuring removal of excess free polymer. A 10 mL aliquot of THF was added to the recovered SWNT residue and the vial was further sonicated for 5 min. The resulting dark suspension was centrifuged at 8300g for 45 min and allowed to stand overnight undisturbed. The UV-vis absorption properties of trans-F12AZO and their corresponding SWNT complexes in THF were measured (Figure S5, Supporting Information). It was found that the absorption maximum of the polymer exhibited a characteristic bathochromic shift and slight broadening once bound to the nanotube surface (Figure S5A, Supporting Information).

A diluted THF solution of *trans*-F12AZO-SWNT (after removal of excess polymer) in a glass cuvette was irradiated to cause *trans*-to-*cis* isomerization, and the changes in the absorption spectra were recorded. Although the polymer absorption band intensity slightly decreased when irradiated below 450 nm, the change in SWNT absorption was negligible. There was no noticeable SWNT aggregation or precipitation observed after irradiation for 4 h (Figure S5B, Supporting Information). It is possible that either the polymer conformation is "locked" by its interaction with the nanotube surface, or there is a rapid energy transfer that occurs from the excited state of the polymer to the SWNT, both of which would inhibit the photoisomerization. To rule out the latter possibility, we measured the emission spectrum of the F12AZO-SWNT

complex when excited at the absorption maximum of the polymer ($\lambda_{ex} = 417$ nm), in both THF and toluene. This resulted in no observable sensitized nanotube emission (Figure S6, Supporting Information), indicating that energy transfer from the excited-state polymer to the nanotube does not occur. This result is in agreement with previous studies, which found that it was not possible to photoisomerize the AZO units once they are bound to the nanotube surface.^{39,40,43}

In order to confirm how the interactions between the F12AZO and the SWNTs can be affected by the conformational changes (*trans* vs *cis*) of the F12AZO, the supramolecular complexes of F12AZO-SWNT were prepared using the above protocol with both *trans* and *cis* isomers of F12AZO (see Supporting Information), and THF or toluene as the dispersing solvents. The UV–vis-NIR absorption spectra of both *trans*-F12AZO-SWNT and *cis*-F12AZO complexes in THF and toluene are depicted in Figure 2. For reference, the absorption spectrum of just the nanotubes dispersed in D₂O using sodium dodecylbenzenesulfonate (SDBS) surfactant is also shown in Figure 2 (curve a).



Figure 2. NIR absorption spectra of SDBS/SWNT (a), trans-F12AZO + SWNT in THF (b), cis-F12AZO + SWNT in THF (c), trans-F12AZO + SWNT in toluene (d), and cis-F12AZO + SWNT in toluene (e). Dotted lines are meant to guide the eye in comparing absorption bands from identical nanotubes.

The spectra show that the dispersing ability is affected by both the conformational state of the F12AZO polymer (trans vs cis isomers) and the solvent. In comparison to aqueous dispersions of SWNTs using the surfactant SDBS (Figure 2, curve a), the absorption peaks of the F12AZO-SWNT complexes in both toluene and THF (Figure 2, curves b, c, d, and e) are more intense, indicating efficient exfoliation into individual tubes, and exhibit relatively strong absorptions at wavelengths corresponding to semiconducting SWNTs (600-800 and 900-1500 nm). All of the transitions of F12AZO-SWNT complexes were found to be red-shifted 8-25 nm relative to the aqueous solution, which is consistent with what has been reported previously with comparable systems.^{33,37,38} Upon closer examination of the each individual absorption spectrum, small shifts and changes in intensity of several signals can be observed, indicating that the trans- and cis-F12AZO show a slightly different preference for certain SWNT tube types in both THF and toluene solution. The total absorbance of several species is reduced in toluene solution when compared to THF, due to the substantial reduction in the number of different nanotube species present in F12AZO/



Figure 3. PL contour maps of HiPco SWNTs dispersed with *trans*-F12AZO in THF (A), *trans*-F12AZO in toluene (B), *cis*-F12AZO in THF (C), *cis*-F12AZO in toluene (D), and SDBS in D_2O (E).



Figure 4. Normalized PLE signal intensities of the major SWNT species observed in solution, in order of increasing diameter (left to right): (a) *trans*-F12AZO+SWNT in THF, (b) *cis*-F12AZO+SWNT in THF, (c) *trans*-F12AZO+SWNT in toluene, and (d) *cis*-F12AZO+SWNT in toluene.

toluene solutions. Several major absorption peak positions in the 900–1500 nm region were correlated to the corresponding chiral indices (n, m), where the assignments are based on previously reported results.^{50,51} It has been shown that the absorbance intensity of SWNTs is proportional to the amount of solubilized SWNTs present, independent of whether the tubes are isolated or bundled.^{51,52} Therefore, it is difficult to attribute the changes in absorption peak intensities to individual, exfoliated tube types.

Photoluminescence spectroscopy has been used as a powerful tool to identify the solubilized species due to its sensitivity to the degree of SWNT exfoliation.^{37,51} Thus,

photoluminescence excitation (PLE) maps of the *trans-* and *cis*-F12AZO-SWNT in toluene and THF were measured over a large range of excitation (500–900 nm) and emission (900– 1450 nm) wavelengths. Figure 3 depicts the PLE maps of SWNTs dispersed in toluene and THF using both *trans-*F12AZO (maps A and B) and *cis*-F12AZO (maps C and D), which can be compared to the PLE map of a dispersion in D₂O using the nonselective SDBS surfactant (map E). In these maps, areas of high intensity are depicted in red and areas of low intensity are depicted in blue. The chiral indices (*n*, *m*) for the identified species are labeled on the maps, where the assignments are based on previously reported results.^{51,53} The PLE map of the pristine SWNT sample dispersed in D₂O using SDBS shows the presence of 17 different semiconducting nanotubes, a distribution that is similar to what has previously been reported.33,53 When the same material was mixed with trans-F12AZO and cis-F12AZO in toluene or THF, entirely different results were obtained. Parts A and B of Figure 3 depict the PLE maps of the SWNT complexes with trans-F12AZO in THF and toluene, and parts C and D of Figure 3 show the PLE maps of cis-F12AZO complexes in THF and toluene, respectively. The observed strong nanotube emission indicates that individual SWNTs are solubilized and isolated by the polymer. It was found that both excitation and emission wavelengths of the trans-F12AZO + SWNT complex was redshifted relative to the aqueous solution by 10-30 nm, which is consistent with previously reported comparable systems (Table S1, Supporting Information).^{21,33,37,38} It is obvious from the PLE maps (Figure 3, A and B) that the distribution of SWNT species depends on the solvent used, and the relative emission intensity of each solubilized species is considerably different with each solvent. When trans-F12AZO was used, eight major carbon nanotube species were identified in THF, including (6, 5), (8, 4), (7, 5), (7, 6), (9, 4), (9, 5), (8, 6), and (8, 7), and the dominant species were found to be (6, 5) and (7, 5) (Figure 3A). Figure 4 depicts the normalized PLE signal intensities of 8 major SWNT species, where the most intense signal from each solution was set to a value of 1 (for numerical data, see Table S2, Supporting Information). The nanotube species depicted in Figure 4 are organized by diameter, which ranges from 0.757 nm for the (6, 5) tube to 1.032 nm for the (8, 7) tube (for a complete list of diameters, see Table S2, Supporting Information). It is interesting to note that the nanotube diameter seems to dictate both the relative solubility in the two solvents and the selectivity of cis- or trans-F12AZO polymers for specific nanotube types. The polymer-nanotube complexes with SWNTs having diameters below 0.90 nm (consisting of the (6, 5), (7, 5), (8, 4), and (7, 6) species) all exhibit higher emission intensities in THF relative to toluene, while those with diameters above 0.92 nm (the (8, 6), (9, 5), and (8, 7) species) exhibit higher intensities in toluene than in THF. Furthermore, as can be seen from Figure 4, the largest differences in emission intensities as a function of cis/trans polymer conformation were observed for the low diameter tubes (most notably for (6, 5), (7, 5), and (7, 6) species), whereas cis/trans selectivity was weakest for the highest diameter tubes (specifically the (8, 6), (9, 5), and (8, 7) species, especially in toluene). It is not clear why the cis-F12AZO polymer seems to show greater preference for solubilizing the (7, 6) tube, while trans-F12AZO shows greater preference for the (6, 5) and (7, 5) species in THF. All of these results warrant further investigation. It should be noted that the above discussion implies a correlation between nanotube emission intensity and solution concentration, which assumes that SWNT fluorescence quantum yield is not affected by the polymer conformation or the surrounding solvent. This assumption will need to be tested in future studies.

CONCLUSIONS

The photoresponsive azobenezene containing polymer, poly-[2,7-(9,9-didodecylfluorene)-*alt*-4,4'-azobenzene] (F12AZO) has been synthesized using Suzuki polycondensation, and the resulting polymer exhibited good solubility in a number of organic solvents, including THF, toluene, and chloroform. Thermogravimetric analysis indicated that F12AZO exhibits excellent thermal stability under Ar. The changes to the polymer absorption in THF upon alternating photoirradiation below 450 nm and between 450 and 600 nm, respectively, at room temperature confirmed that F12AZO can undergo reversible trans-cis photoisomerization. The trans-F12AZO and cis-F12AZO were utilized for the preparation of supramolecular polymer-SWNT composites, and excellent nanotube solubility and solution stability was achieved in THF. UVvis absorption measurements revealed a bathochromic shift and broadening in the polymer absorption spectrum as a result of complex formation with nanotubes. Photoirradiation of trans-F12AZO-SWNT complexes below 450 nm does not cause polymer isomerization on the nanotube surface, and no noticeable SWNT aggregation or precipitation was observed. Photoluminescence excitation maps showed that efficient and selective dispersal of SWNTs is possible by using trans-F12AZO or cis-F12AZO and that both solvent and polymer conformation played a role in the selectivity. It was found that low diameter nanotubes are more strongly differentiated by the cis- and trans-F12AZO polymer conformers, and nanotube diameter also determines whether the polymer-nanotube complexes will be more soluble in THF or toluene.

ASSOCIATED CONTENT

S Supporting Information

Full experimental procedures as well as TGA, UV–vis, and fluorescence data and a photograph of F12AZO in THF, the F12AZO + SWNT complex in THF, and the F12AZO + SWNT complex in toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Telephone: (905) 525-9140 x 23514. Fax: (905) 521-2773. Email: adronov@mcmaster.ca.

Notes

The authors declare no competing financial interest.

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