DOI: 10.1002/ejoc.200700506

Unexpected Outcome in the Reaction of Triazolinedione with Carbon Nanotubes

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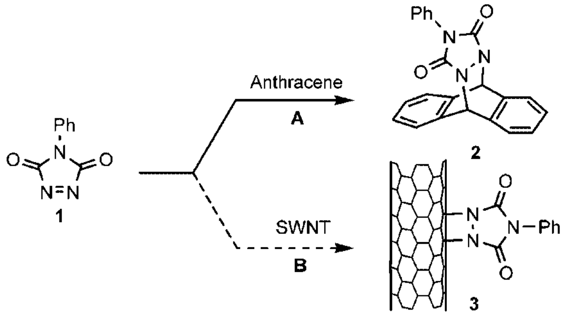
Dedicated to the memory of Charles Mioskowski [‡]

Keywords: Carbon nanotubes / ESR / Triazolinedione / Electron donors / Dimerization

The reactivity of triazolinedione (TAD) was investigated in the Diels–Alder reaction with carbon nanotubes. However, an unexpected conversion of TAD into its deaza dimer was observed. ESR spectroscopy suggested that the process was initiated by electron transfer from the nanotubes.

Introduction

Since their discovery by Iijima in 1991,[1] carbon nanotubes have emerged as one of the most promising nanomaterials because of their unique mechanical,[2] electronic[3] and optical[4] properties. However, their potential in nanotechnology has been impeded by low solubility and processability. One route to overcome these difficulties is the chemical functionalisation of their surface. Among the various methods developed for this purpose,[5] cycloaddition reactions are particularly attractive processes. For example, Diels–Alder[6] and 1,3-dipolar cycloadditions[7] are efficient reactions for the covalent functionalisation of the graphene sidewalls of nanotubes. As part of our ongoing program on the development of novel methods of functionalisation, we report here our findings on the reactivity of triazolinediones (TADs) in the presence of carbon nanotubes. TADs are strong electron acceptors and known to be powerful dienophiles/enophiles[8] that readily undergo [2+2] cycloadditions with C_{60} fullerenes[9] and [4+2] Diels–Alder reactions with anthracene derivatives[10] (Scheme 1, Path A). Because these processes are usually fast and occur under mild conditions, we conceived that TADs could also be reactive towards carbon nanotubes. Therefore, the initial objective of this study was to investigate the cycloaddition reaction of TADs with nanotubes (Scheme 1, Path B).



Scheme 1. Expected reaction of PTAD with carbon nanotubes.

Results and Discussion

In a typical experiment, 3 mg of single-walled carbon nanotubes (SWNTs from MER Corp.) were dispersed in dichloromethane by using an ultrasonic bath (see Supporting Information for details). To the resulting suspension was added 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, **1**) in excess, and the mixture was heated to reflux for 15 h. The nanotubes were then filtered, washed thoroughly with dichloromethane and dried under vacuum. The overall sequence was repeated four times before the sample was analysed by spectroscopic techniques, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). Naked-eye observation of the reacted nanotubes (r-

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SWNTs) indicated that their overall appearance had changed. Indeed, whereas pristine nanotubes (p-SWNTs) are typically thin-black particles, r-SWNTs were isolated as a grey compact powder (Figure 1a,b). In addition, TEM pictures of r-SWNTs showed the presence of entangled bundles that were inhomogeneously coated with aggregates (Figure 1d to be compared to p-SWNTs depicted in Figure 1c). TGA of r-SWNTs (under Ar, 2 °C min^{-1} from 150 to 600 °C) indicated a weight loss of 50% relative to p-SWNTs (Figure 1e). Also, the FTIR spectrum exhibited two new strong vibration bands at 1757 and 1787 cm^{-1} (Figure 1f). These bands were shifted relative to PTAD by 10 and 18 cm^{-1}, respectively, and were assigned to C=O stretching. Interestingly, the same shifts were observed for cycloadduct **2**, which was obtained by treating PTAD with anthracene. Preliminary characterisation of r-SWNTs thus indicated drastic changes in the shape and nature of the nanotubes, which suggested chemical modification.

To determine whether covalent functionalisation had taken place on the surface of the nanotubes, the sample was further analysed by Raman spectroscopy. Indeed, the relative intensity of the D-band with respect to the G-band is commonly regarded as a probe for the conversion of sp^2 to sp^3 carbon atoms in the nanotube lattice.[11] Unfortunately, in our case, we were not able to detect any changes in the relative intensity of the so-called D-band, although low-frequency radial breathing modes (RBM) were shifted.

Taken together, these data indicate that the observed effect was not due to covalent functionalisation of the nanotubes but to another phenomenon that took place in their vicinity to produce aggregates. Interestingly, the formation of aggregates was inhibited in the absence of nanotubes that appear to act as initiators. To further understand the interactions between the two components, namely, SWNTs and PTAD, the reaction was repeated and monitored carefully. This time, we observed rapid evolution of small bubbles close to the nanotube surface immediately after the addition of PTAD, which could have originated from the release of nitrogen gas. To characterise the reaction product, the highly insoluble aggregates were isolated from the nanotubes by continuous solid–liquid extraction with THF in a Soxhlet apparatus. The aggregates were collected as a white powder, and the FTIR spectrum was nearly identical to that of r-SWNTs. We concluded from structural analysis that deaza dimer **4** of PTAD was the main product formed in the presence of SWNTs (Scheme 2). The conversion of TADs into their corresponding deaza dimer has already been described in the literature.[12] The reaction usually happens under either photolytic[12a] or thermal[12a,12c] conditions. Several mechanisms have been suggested and include radical anion chain reactions.[12b] As the process can also be activated by electron-donating species,[12a,12b,12e] we postulate here that carbon nanotubes could initiate the self-condensation of PTAD by acting as an electron source.

To support this hypothesis, we turned our attention to electron spin resonance (ESR) analysis of the reaction between PTAD and SWNTs. Given the lack of signal at room temperature, spectra were recorded at 4 K to ensure a better signal-to-noise ratio for the starting p-SWNTs.

The ESR signal of p-SWNTs (Figure 2a, full line) and that of the sample after PTAD addition evolve from a single component symmetrical spectrum (ΔB_{pp} = 0.35 mT) towards a more complex system (Figure 2a, dashed and dotted lines). These distorted lines consist of at least two visible overlapping lines, whose shape is obviously modified with respect to the starting state. Spectra are centred at g = 2.0027, which is very close to the free-electron value. Noteworthy is that the integrated intensity of these new lines increases with successive additions of PTAD. Given the uncertainty in the mass of the sample, the concentration of paramagnetic species was not assessed. Rather, a qualitative analysis was undertaken wherein the ESR signal simply decomposed into two lines. The difference spectra between r-SWNTs (after successive PTAD additions) and p-SWNTs

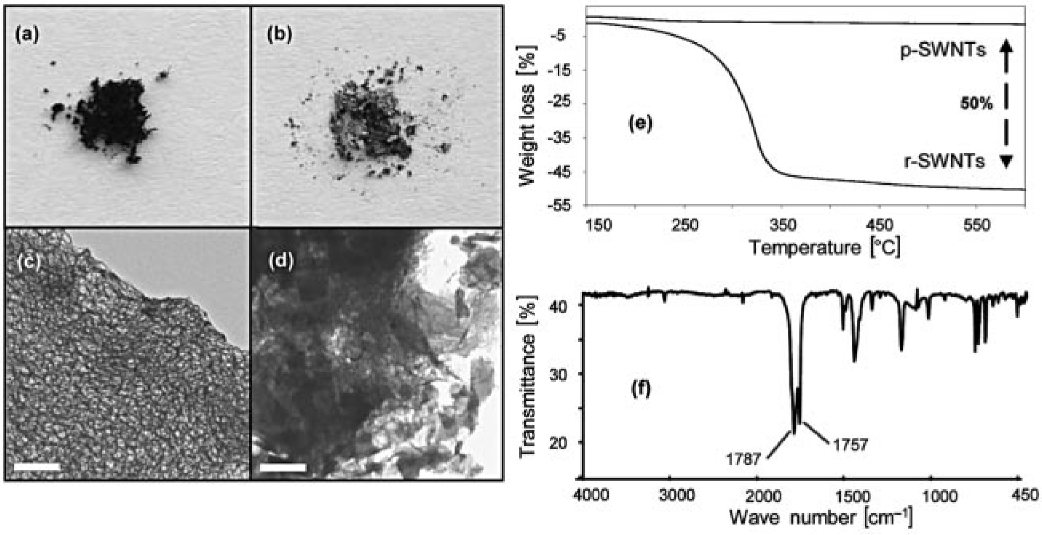
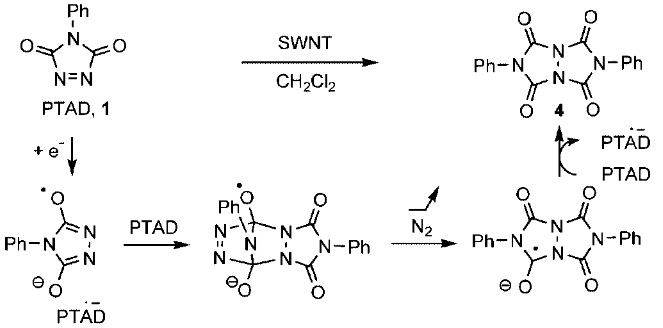


Figure 1. Pictures of (a) p-SWNTs and (b) r-SWNTs; TEM images of (c) p-SWNTs and (d) r-SWNTs (scale bar = 1 µm); (e) TGA of p-SWNTs and r-SWNTs and (f) FTIR spectrum of r-SWNTs.



Scheme 2. Postulated mechanism of deaza dimerisation of PTAD.

are depicted in Figure 2b. The same line shape is observed for r-SWNTs with a concomitant increase in the intensity upon successive additions of PTAD. The ESR spectra of r-SWNTs (Figure 2a) may be analysed as resulting from two species, i.e. the fraction of SWNTs having reacted with PTAD to afford the spectra shown in Figure 2b and the remaining unreacted fraction of p-SWNTs. Whatever the status of the new population, whether Curie-like localised or mobile conduction electrons as the Dysonian-like line shape may imply, there is an unambiguous increase in the apparent spin concentration. This indicates most likely a charge-transfer process originating from SWNTs to PTAD.[13]

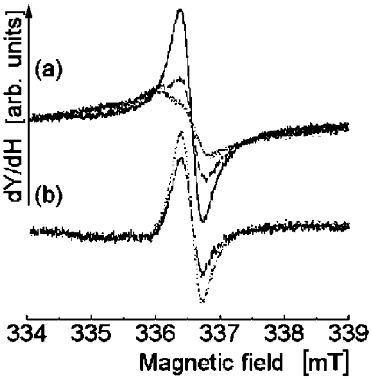


Figure 2. ESR spectra recorded at 4 K of SWNTs in the presence of PTAD: (a) typical spectrum before the addition of PTAD (–), after the 1st addition of PTAD (- - -) and then after the 2nd addition of PTAD (···); (b) difference signal between p-SWNTs and r-SWNTs, deduced from the spectra shown in (a).

Conclusions

We report here the reactivity of PTAD in the presence of carbon nanotubes. The latter initiate deaza dimerisation of PTAD, and ESR spectroscopy suggests that the reaction proceeds by electron transfer from SWNTs. This work represents a key example of the use of carbon nanotubes as electron donors.

Supporting Information (see footnote on the first page of this article): Experimental procedures for the reaction between SWNTs and PTAD.

Acknowledgments

C. M. M. thanks the “Délégation Générale pour l’Armement” for financial support. Dr. A. Yuen and Dr. E. Anglaret are gratefully acknowledged for helpful discussions.

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Received: June 1, 2007