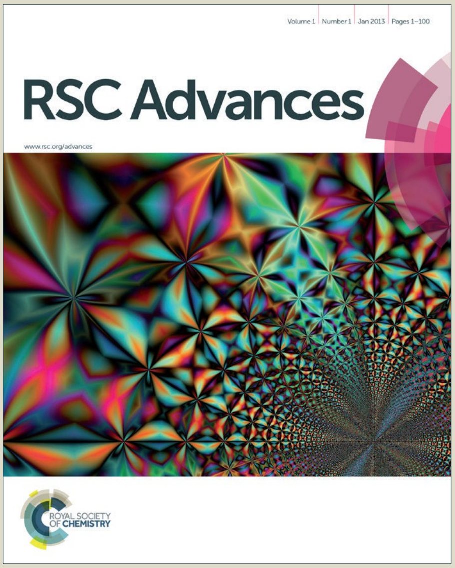
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

COMMUNICATION

Poly(methyl methacrylate) end-functionalized with hexabenzocoronene as an effective dispersant for multi-walled carbon nanotubes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Seung Pyo Jeong, Connor J. Boyle, and D. Venkataraman*

We demonstrate that MWCNTs can be dispersed in common organic solvents as single tubes using a *single* hexabenzocoronene (HBC) unit at the end of a poly(methyl methacrylate) (PMMA) chain. The concentration of the HBC-based additive needed to disperse MWCNTs is substantially lower than the concentration needed for existing additives.

Carbon nanotubes (CNTs) have generated considerable interest as components in many composite materials due to their excellent mechanical,[1, 2] electrical,[3, 4] and thermal properties.[5] To fabricate these materials, CNTs need to be dispersed in common solvents and that is not easy. CNTs have strong π-π intertube interactions, which make them insoluble in common solvents. CNTs can be dispersed in solvents without any treatment using ultrasonication but these dispersions typically contain large aggregates, and thus make the fabrication of CNT-based composite materials difficult.[6, 7] In order to render CNTs processable, the surfaces of the nanotubes need to be modified either covalently[8] or non-covalently.[9] Covalent functionalization of the CNT's surface through fluorination,[10] radical chemistry,[11] or other methods[8] does improve their solubility. For example, CNT/PMMA composites[12-16] have previously been prepared by grafting PMMA from MWCNT,[17] or by surface functionalization method such as diazonium salt[18] or UV/O_3 and acid treatment.[19, 20] But the surface modification can disturb or break the π-conjugation that is essential for the properties of CNTs. Therefore, non-covalent functionalization of the surface through π-stacking interactions is preferred.[21-27] However, this method generally requires a large concentration of the additives (either polycyclic aromatic hydrocarbons (PAHs) such as pyrene or polymers bearing several PAHs as side-chain units) to interact with the surface because interaction between each PAH unit and the CNT surface is weak.[28, 29] The use of large quantities of additives isolates CNTs from other components in materials, thus prevents us from exploiting the full potential of CNTs.

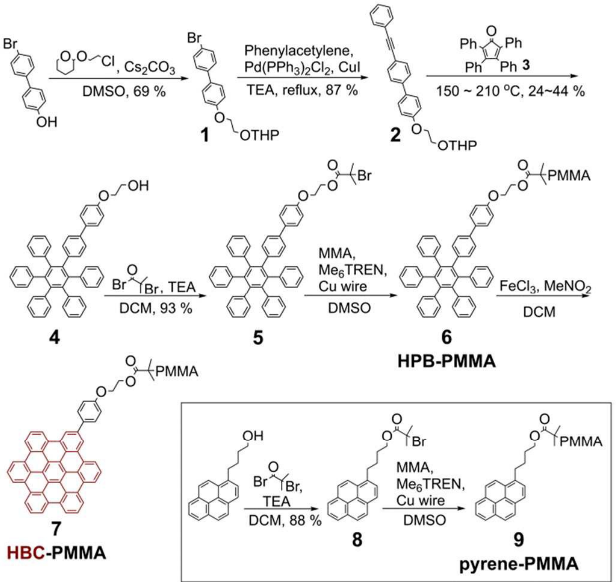
We are interested in using multi-walled carbon nanotubes (MWCNTs) for fabricating composite electronic materials. Since metallic behaviour is prevalent in MWCNTs,[30, 31] incorporating them in electronic materials allows us to efficiently transport electronic charges in the active layers of composites. For example, incorporation of CNTs in active layers of perovskite solar cells is known in boost open circuit voltages.[32] Incorporation of CNTs with conjugated polymers is also known to enhance thermolectric properties in organic thermoelectric devices.[33] It has also been shown that the surfactants and additives used to disperse CNTs, which are typically insulating, act as barriers for charge transport.[34] Since these systems are fabricated typically from organic solvents, we need a method that can disperse CNTs in these solvents with minimum amount of additives.

We hypothesized that if the non-covalent interaction between CNT's surface and PAH unit can be strengthened, then the concentration of the aromatic units needed to solubilize CNTs can be greatly reduced. We also reasoned that since MWCNTs have a larger diameter compared to SWCNTs, larger PAHs should be needed for stronger interactions with MWCNT surface than other smaller PAHs such as anthracene or pyrene. Herein we demonstrate that MWCNTs can be dispersed in common organic solvents using a *single* hexabenzocoronene (HBC) unit, one of the largest plane structures among PAHs, at the end of a polymer chain such as PMMA. We also show that the concentration of the HBC-based additive needed to disperse MWCNTs is substantially lower than the concentration needed for existing additives.

We first attempted to synthesize PMMA end-functionalized with HBC using an ATRP initiator or RAFT agent attached to an HBC unit. However, the poor solubility of HBC in typical organic solvents precluded both their structural characterization and solution processing. We therefore switched the strategy to first form the polymer by using a precursor to HBC as the initiator and then form the HBC unit. This strategy is outlined in Scheme 1.

Department of Chemistry, 710 N. Pleasant Street, University of Massachusetts Amherst, Amherst, MA 01003, USA. E-mail: dv@chem.umass.edu

† Electronic Supplementary Information (ESI) available: NMR, GPC, UV-Vis, SEM, TEM, DLS, Zeta potential, and dispersion test of MWCNT. See DOI: 10.1039/x0xx00000x



Scheme 1 Synthetic route of PMMA end-functionalized with either HBC or pyrene.

The syntheses and characterizations of molecules **1**-**6** were accomplished using established protocols and methods (ESI† for details). When **6** was subjected to Scholl oxidation, upon workup, a light brown colored solid, presumably **7**, was obtained that was soluble in common organic solvents. In ^{1}H NMR of this compound in $CDCl_3$, the peaks around 6.8 ppm attributable to protons on hexaphenylbenzene (HPB) in **6** were absent (Fig. 1a), which is consistent with the oxidation of the HPB unit. The ^{1}H NMR in tetrachloroethane–d_2 showed peaks at around 8.76, and 7.9 ppm attributable to the HBC end-group (ESI Fig. S7-2†). Moreover, new peaks of ^{13}C NMR after the conversion of HPB to HBC appear in the aromatic region around 120 ppm (ESI Fig. S7-3†), which are different from the peaks of HPB, indicating the oxidation of HPB to HBC.

To obtain further proof for the formation of HBC unit, we used UV-visible absorption spectra. E. Clar et al. had studied the UV-visible spectra of unsubstituted HBC in trichlorobenzene[35] and showed that there are three distinctive electronic absorption bands: (1) a peak around 440 nm with low extinction efficient termed as the α-band, (2) a peak with moderate extinction coefficient around 387 nm termed as the p-band, and (3) a peak around 360 nm with a large extinction absorption coefficient termed as the β-band. Although the exact location of these peaks change as a result of functionalization,[36, 37] the shape of the spectrum and the peak intensity ratios do not significantly change. The UV-vis spectra for **6** and **7** are shown in Fig. 1b. For **6**, we observed a peak around 290 nm, attributable to the HPB moiety,[38] and a peak at 255 nm attributable to PMMA (ESI S10†). In **7**, the peak around 290 nm is absent but new absorption bands appear from 340 nm to 450 nm. The new absorption bands are at 439 nm with low extinction coefficient, 388 nm with moderate extinction coefficient and 360 nm with a large extinction coefficient, attributable to the α, p and β bands of the HBC moiety. Moreover, the peaks attributable to the semi-fused HBC were not detected in the UV-vis spectra.[39] The ^{1}H NMR combined with UV-vis data strongly suggests the successful conversion of HPB to HBC, and are consistent with the expected chemical structure of **7**.

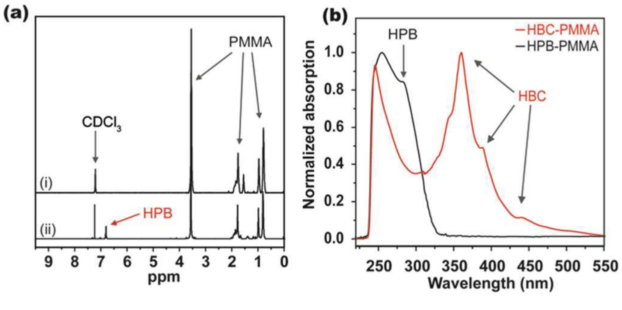


Fig. 1 (a) ^{1}H NMR spectra of (i) HBC-PMMA and (ii) HPB-PMMA. (b) Normalized UV-vis absorption spectra of HPB-PMMA and HBC-PMMA.

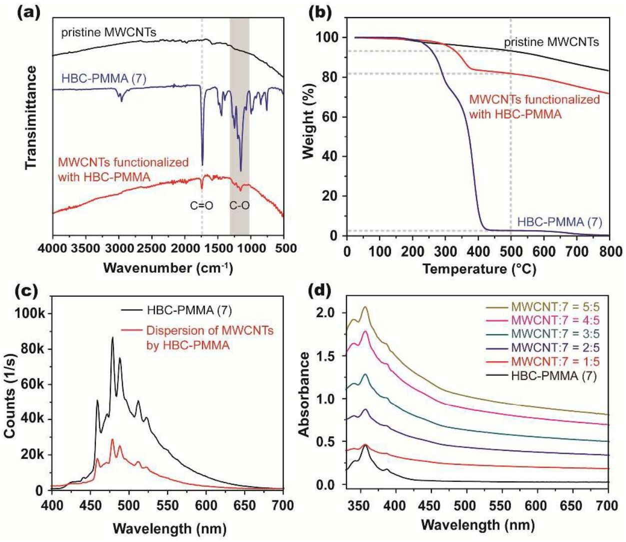


Fig. 2 (a) FT-IR spectra of pristine MWCNTs, HBC-PMMA, and HBC-PMMA/MWCNTs composite. (b) TGA curves of pristine MWCNTs, HBC-PMMA, and HBC-PMMA/MWCNTs composites. (c) Fluorescence spectra of HBC-PMMA (0.05 mg/mL) and dispersion of MWCNT (0.05 mg/mL) with HBC-PMMA (0.05 mg/mL) in acetone. (d) UV-Vis absorbance spectra of dispersion of MWCNTs in the different concentration ratio of MWCNTs (0.01, 0.02, 0.03, 0.04, and 0.05 mg/mL) and HBC-PMMA (0.05 mg/mL) in acetone.

All the peaks attributable to PMMA in **6** in the ^{1}H NMR were also present in **7** and no additional peaks were observed indicating that the PMMA chain remains unaltered during the Scholl oxidation step. This conclusion is consistent with the observation that the M_n of **6** was found to be 15.0 kDa/mol and M_n for **7** was found to be 14.6 kDa/mol (ESI Fig. S7-5†).

Next, to probe the effectiveness of **7** (HBC-PMMA) to bind to MWCNTs, we suspended commercial S-purified MWCNTs grown by CVD (outer diameters of 40-60 nm and lengths of 1-2 μm) in acetone containing 6.8 μM of **7** (Fig. 3e). As a test solvent, acetone was selected due to no ability of dispersion of CNTs. The suspension was sonicated in an ultrasonic bath for 1 min. The dispersion was left undisturbed for 1 day and was centrifuged. The residue was then collected, washed with acetone, and centrifuged. This process was repeated twice to remove any unbound **7**. The solid was dried

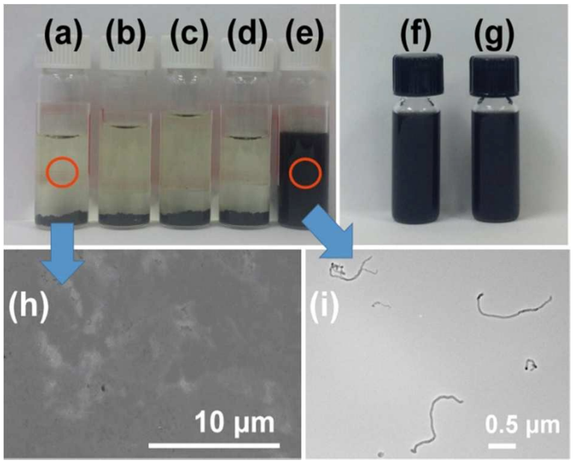


Fig. 3 Dispersion test of (a) MWCNTs (0.1 mg/mL) in acetone, (b) MWCNTs (0.1 mg/mL) with PMMA (1 mg/mL) in acetone, (c) MWCNTs (0.1 mg/mL) with HPB-PMMA (1 mg/mL) in acetone , (d) MWCNTs (0.1 mg/mL) with pyrene-PMMA (0.1 mg/mL) in acetone, (e) MWCNTs (0.1 mg/mL) with HBC-PMMA (0.1 mg/mL) in acetone, (f) MWCNTs (0.1 mg/mL) with HBC-PMMA (0.1 mg/mL) in toluene, and (g) The solution of 'f' after heating at 60 °C for 10 days. (h) SEM image of air dried sample on silicon wafer after the drop of solution of MWCNTs (0.1 mg/mL) in acetone, and (i) TEM image of air dried sample on Cu grid after the drop of solution of MWCNTs (0.01 mg/mL) with HBC-PMMA (0.05 mg/mL) in acetone.

under vacuum overnight and the FT-IR spectra of the solid showed peaks attributable to PMMA, such as at 1734 cm^{-1} and 1147 cm^{-1} (Fig. 2a).[40, 41] These peaks are absent in pristine MWCNT. We therefore concluded that **7** was strongly bound to MWCNTs. From comparing the thermogravimetric traces of pristine MWCNT, **7** and MWCNT:**7** (Fig. 2b), we calculated that the amount of **7** in the MWCNT:**7** composite was around 11 wt% (~8×10^{-6} mol of **7** per 1 g of the composite). Sonication of MWCNT, MWCNT with PMMA, or MWCNT with **6** in acetone did not result in stable dispersions indicating that the HBC unit in **7** was necessary to disperse MWCNTs. Moreover, the absorbance of MWCNT:**7** is increased by increasing the concentration of MWCNTs at the same concentration of **7**. (Fig. 2d, ESI S11†) More importantly, the fluorescence of HBC (Fig. 2c) was quenched after the addition of MWCNTs, strongly indicating that there is an interaction of HBC and the surface of MWCNTs.

To compare the effectiveness of HBC versus pyrene, a commonly used additive, to bind to MWCNTs, we synthesized PMMA end-functionalized with pyrene (pyrene-PMMA, **9**) (M_n: 12,772, M_w: 15,090, $Đ$: 1.18). Sonicating MWCNT with 7.8 μM of **9** in acetone did not result in stable dispersions (Fig. 3d). This observation is consistent with the expectation that the larger aromatic core of HBC can bind strongly to MWCNTs compared to smaller PAHs such as pyrene.[28, 42]

We found that MWCNT can be dispersed in any solvent in which **7** is soluble. For example, we are able to make stable dispersions of MWCNT in toluene (ESI S12†). We also found that these dispersions are stable for more than 6 months at ambient temperature. Moreover, heating the dispersions at 60 °C for 10 days did not result in any aggregation, indicating that the interaction between HBC and MWCNT surface is strong. We confirmed by SEM and TEM (Fig. 3i, ESI Fig. S15 and Fig. S16) that MWCNTs were well separated from each otherand each MWCNT had a width of less than 100 nm (ESI Fig. S15†).

Conclusion

We have demonstrated that MWCNTs can be dispersed in organic solvents using PMMA end-functionalized with HBC. These dispersions are stable for over six months under ambient conditions. They are also stable at elevated temperatures, indicating strong binding between the HBC unit and MWCNT. In our direct comparison of pyrene-PMMA to HBC-PMMA as MWCNT dispersants, pyrene-PMMA was unable to stabilize MWCNT dispersions under the same conditions that HBC-PMMA forms stable dispersions, highlighting the important role of the type of PAH in stabilizing these dispersions. We anticipate that this strategy will not only be useful for compatibilizing MWCNT with PMMA to improve the already remarkable properties of MWCNT/PMMA blends, but can easily be modified to substitute PMMA for another polymer during polymerization to obtain any desired MWCNT/polymer blend or MWCNT dispersion in any solvent for the selected polymer. Our strategy of using HBC as a binding unit to disperse MWCNTs therefore opens up new opportunities for fabricating composite materials containing CNTs.

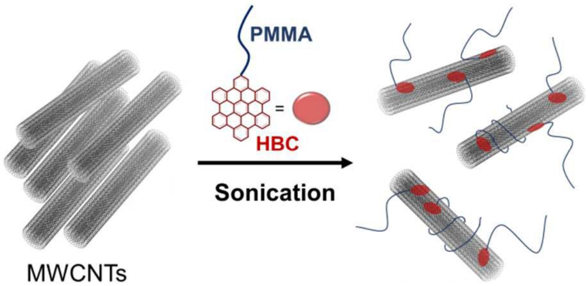
Acknowledgements

The authors acknowledge SEM use through the W.M. Keck Electron Microscopy Lab, which is partially supported by U. S. National Science Foundation MRSEC on Polymers, award DMR-0820506. The Field Emission Scanning Electron Microscope was purchased with funds provided by U. S. National Science Foundation MRI-0923105.

Notes and references

1 M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly and R. S. Ruoff, Science, 2000, **287**, 637-640.
2 J. N. Coleman, U. Khan, W. J. Blau and Y. K. Gun'ko, Carbon, 2006, **44**, 1624-1652.
3 T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi and T. Thio, Nature, 1996, **38**2, 54-56.
4 P. R. Bandaru, J. Nanosci. Nanotechno., 2007, **7**, 1239-1267.
5 A. A. Balandin, Nat. Mater., 2011, **10**, 569-581.
6 N. Karousis, N. Tagmatarchis and D. Tasis, Chem. Rev., 2010, **110**, 5366-5397.
7 D. Tasis, N. Tagmatarchis, A. Bianco and M. Prato, Chem. Rev., 2006, **10**6, 1105-1136.
8 C. A. Dyke and J. M. Tour, J. Phys. Chem. A, 2004, **108**, 11151-11159.
9 Y. L. Zhao and J. F. Stoddart, Accounts Chem. Res., 2009, **42**, 1161-1171.
10 E. T. Mickelson, C. B. Huffman, A. G. Rinzler, R. E. Smalley, R. H. Hauge and J. L. Margrave, Chem. Phys. Lett., 1998, **296**, 188-194.
11 Y. M. Ying, R. K. Saini, F. Liang, A. K. Sadana and W. E. Billups, Org. Lett., 2003, **5**, 1471-1473.
12 C. McClory, T. McNally, M. Baxendale, P. Potschke, W. Blau and M. Ruether, Eur. Polym. J., 2010, **46**, 854-868.
13 F. Mammeri, J. Teyssandier, C. Connan, E. Le Bourhis and M. M. Chehimi, RSC Adv., 2012, **2**, 2462-2468.
14 N. K. Shrivastava, P. Kar, S. Maiti and B. B. Khatua, Polym. Int., 2012, **61**, 1683-1692.

15 M. Naraghi, G. H. Bratzel, T. Filleter, Z. An, X. D. Wei, S. T. Nguyen, M. J. Buehler and H. D. Espinosa, Adv. Funct. Mater., 2013, **23**, 1883-1892.
16 T. Gegenhuber, A. H. Groschel, T. I. Lobling, M. Drechsler, S. Ehlert, S. Forster and H. Schmalz, Macromolecules, 2015, **48**, 1767-1776.
17 H. Roghani-Mamaqani, V. Haddadi-Asl, M. Ghaderi-Ghahfarrokhi and Z. Sobhkhiz, Colloid Polym. Sci., 2014, **292**, 2971-2981.
18 F. Mammeri, J. Teyssandier, C. Darche-Dugaret, S. Debacker, E. Le Bourhis and M. M. Chehimi, J. Colloid. Interf. Sci., 2014, **433**, 115-122.
19 S. Kim, A. A. Kafi, E. Bafekpour, Y. I. Lee, B. Fox, M. Hussain and Y. H. Choa, J. Nanomater., 2015, DOI:10.1155/2015/130270.
20 S. N. Tripathi, S. Singh, R. S. Malik and V. Choudhary, Macromol. Symp., 2014, **341**, 75-89.
21 R. Murphy, J. N. Coleman, M. Cadek, B. McCarthy, M. Bent, A. Drury, R. C. Barklie and W. J. Blau, J. Phys. Chem. B, 2002, **106**, 3087-3091.
22 W. H. Zhong and J. P. Claverie, Carbon, 2013, 51, 72-84.
23 J. H. Zou, S. I. Khondaker, Q. Huo and L. Zhai, Adv. Funct. Mater., 2009, **19**, 479-483.
24 P. Petrov, F. Stassin, C. Pagnoulle and R. Jerome, Chem. Commun., 2003, 2904-2905.
25 M. Kuhnast, C. Tschierske and J. Lagerwall, Chem. Commun., 2010, **46**, 6989-6991.
26 C. H. Liu, Y. Y. Liu, Y. H. Zhang, R. R. Wei, B. R. Li, H. L. Zhang and Y. Chen, Chem. Phys. Lett., 2009, **471**, 97-102.
27 S. Gotovac, Y. Hattori, D. Noguchi, J. Miyamoto, M. Kanamaru, S. Utsumi, H. Kanoh and K. Kaneko, J. Phys. Chem. B, 2006, **110**, 16219-16224.
28 J. Yoo, H. Ozawa, T. Fujigaya and N. Nakashima, Nanoscale, 2011, **3**, 2517-2522.
29 S. Debnath, Q. Cheng, T. G. Hedderman and H. J. Byrne, J. Phys. Chem. C, 2008, **112**, 10418-10422.
30 Y. Ando, X. Zhao, H. Shimoyama, G. Sakai and K. Kaneto, Int. J. Inorg. Mater., 1999, **1**, 77-82.
31 Y. J. Kim, T. S. Shin, H. D. Choi, J. H. Kwon, Y. C. Chung and H. G. Yoon, Carbon, 2005, **43**, 23-30.
32 Z. Li, P. P. Boix, G. Xing, K. Fu, S. A. Kulkarni, S. Batabyal, W. Xu, A. Cao, T. C. Sum, N. Mathews and L. H. Wong, Nanoscale, 2015, DOI:10.1039/C1035NR06177F.
33 D. Kim, Y. Kim, K. Choi, J. C. Grunlan and C. H. Yu, ACS Nano, 2010, **4**, 513-523.
34 K. D. Harris, S. Xiao, C. Y. Lee, M. S. Strano, C. Nuckolls and G. B. Blanchet, J. Phys. Chem. C, 2007, **111**, 17947-17951.
35 E. Clar, C. T. Ironside and M. Zander, J. Chem. Soc., 1959, 142-147.
36 Z. H. Wang, M. D. Watson, J. S. Wu and K. Mullen, Chem. Commun., 2004, 336-337.
37 D. J. Jones, B. Purushothaman, S. M. Ji, A. B. Holmes and W. W. H. Wong, Chem. Commun., 2012, **48**, 8066-8068.
38 T. Renouard, L. Gherghel, M. Wachtler, F. Bonino, B. Scrosati, R. Nuffer, C. Mathis and K. Mullen, J. Power Sources, 2005, **139**, 242-249.
39 Y. Y. Lu and J. S. Moore, Tetrahedron Lett, 2009, **50**, 4071-4077.
40 G. R. Duan, C. X. Zhang, A. M. Li, X. Yang, L. Lu and X. Wang, Nanoscale Res. Lett., 2008, **3**, 118-122.
41 Z. H. Guo, L. L. Henry, V. Palshin and E. J. Podlaha, J. Mater. Chem., 2006, **16**, 1772-1777.
42 C. S. Huang, R. K. Wang, B. M. Wong, D. J. Mcgee, F. Leonard, Y. J. Kim, K. F. Johnson, M. S. Arnold, M. A. Eriksson and P. Gopalan, ACS Nano, 2011, **5**, 7767-7774.



We demonstrate that single MWCNTs can be dispersed in organic solvents using a poly(methyl methacrylate) (PMMA) end-functionalized with hexabenzocoronene.