Tuning the interaction between carbon nanotubes and dipole switches: the influence of the change of the nanotube–spiropyran distance

Tuning the interaction between carbon nanotubes and dipole switches: the influence of the change of the nanotube–spiropyran distance

P Bluemmel[1], A Setaro[1], C Maity[2], S Hecht[2] and S Reich[1]

[1] Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
[2] Department of Chemistry, Humboldt Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

E-mail: bluemmel@physik.fu-berlin.de and sh@chemie.hu-berlin.de

Abstract
The non-covalent functionalization of carbon nanotubes with spiropyran molecules, serving as optically addressable dipole switches, is reported. Two kinds of pyrene–spiropyran-based dyads with spacers of different lengths resulting in different switch–tube distances were investigated. While both surfactants were able to form stable carbon nanotube suspensions, the different distances between the switch and the tube affected both of the components' optical properties. In the case of the shorter spacer, the nanotubes' luminescence as well as the merocyanine absorption band were red-shifted and furthermore, the rate of the merocyanine $\rightarrow$ spiropyran thermal back isomerization was decreased.

S Online supplementary data available from stacks.iop.org/JPhysCM/24/394005/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

The functionalization of single-walled carbon nanotubes (SWCNTs) with switchable molecules, as a way of tuning the electronic properties of SWCNTs, recently became the subject of scientific investigation [1–3]. Molecular switches are chemical species possessing two or more (meta)stable configurations [4]. Upon optical, chemical or other stimuli the molecules undergo structural changes leading to alternation of their electronic properties.

Spiropyran/merocyanine is a unique molecular switch couple that undergoes dramatic changes of its dipole moment (by more than 10 D) upon irradiation with light [5, 6]. Following a non-covalent functionalization scheme, one could preserve the quantum nature of the tubes [7, 8] (which is demolished by a covalent approach, which strongly increases the defectivity of the carbon network forming the nanotube [9, 10]). Non-covalent functionalization is also expected to allow

reversible tuning of the SWCNTs' properties, such as the band structure, affecting the ballistic transport and exciton dynamics [11].

In the literature only a few attempts at photochromic functionalization have been reported thus far [1–3, 11, 13]. However, these studies either focused on covalent functionalization methods—inducing defects in the nanotubes—or targeted predeposited single nanotubes or nanotube films on substrates. Recently, we reported a method for producing stable suspensions of SWCNTs uniformly coated with a dipole switch made out of a spiropyran-based surfactant [14]. The SWCNTs' quantum nature could be maintained, as indicated by the bright infrared emission of the tubes, which had not been achieved before, neither through covalent nor through non-covalent functionalization approaches. As bulk amounts of SWCNTs can be efficiently isolated and steadily suspended in solution, this method moreover opens up the chance of performing systematic studies on the interaction
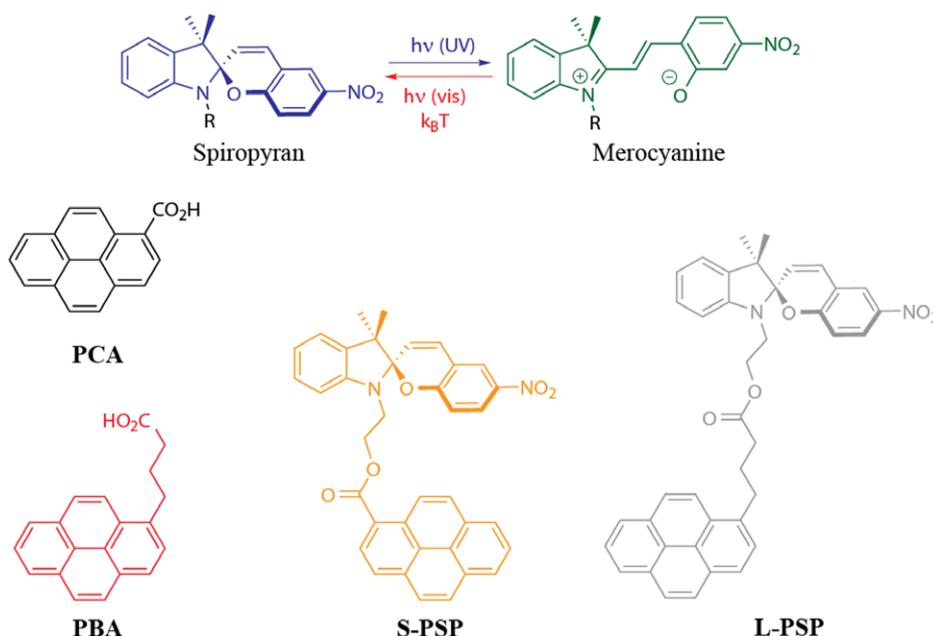
Figure 1. Photochromic equilibrium between the ring-closed spiropyran and its corresponding ring-opened merocyanine form as well as molecular structures of pyrene-1-carboxylic acid (**PCA**), pyrene-1-butyric acid (**PBA**), and the pyrene–spiropyran dyads with a short spacer (**S-PSP**) and longer spacer (**L-PSP**).

between the dipole switch and SWCNT surface, ruling out most other competing effects, such as intra-bundle tube–tube interaction and interaction with the substrate.

Here, we investigate the spacer length dependence of the interaction between the spiropyran switch and the SWCNTs. A pyrene anchor group was chosen to attach the switch compounds to the SWCNTs, as it has been proven to efficiently stick on the SWCNT sidewall through $\pi-\pi$ stacking interaction [15]. To investigate the effect of varying the nanotube–switch distance, we synthesized two pyrene–spiropyran dyads with a short spacer (**S-PSP**: ∼0.6 nm) and a long spacer (**L-PSP**: ∼1.0 nm), connecting pyrene anchor and spiropyran/merocyanine switch moieties (figure 1).

2. Synthesis and switching behavior of the pyrene–spiropyran dyads

The desired pyrene–spiropyran dyads were synthesized via carbodiimide-mediated coupling of pyrene carboxylic acid derivatives, i.e. pyrene-1-carboxylic acid and pyrene-1-butanoic acid with 1-(2-hydroxyethyl)-3,3-dimethyl-6'-nitroindolespirobenzopyran. The latter was synthesized from 2,3,3-trimethylindole via alkylation with 2-bromoethanol, followed by deprotonation with aqueous sodium hydroxide solution and final condensation with 5-nitro-2-hydroxybenzaldehyde (see the supporting information available at stacks.iop.org/JPhysCM/24/394005/mmedia).

Spiropyrans have two perpendicular π electron systems linked through a tetrahedral spiro carbon atom. Upon irradiation, the C_{spiro}–O bond of the closed form is broken and the formerly sp^3-hybridized spiro carbon atom adopts sp^2 hybridization and becomes planar to form the extended

π conjugated system of the ring open merocyanine form, which is thus strongly colored. When the UV light source is removed, the molecules thermally revert to the initial colorless spiropyran isomer. In solution the ring-closed spiropyran form exhibits an absorption maximum in the UV range between 320 and 380 nm. Irradiation of this absorption band causes ring opening and conversion to the merocyanine form which displays a broad and red-shifted absorption in the visible region of the spectrum between 450 and 650 nm. The absorption spectra of pyrene–spiropyran dyads are the mere superposition of the absorption spectra of the pyrene anchor and spiropyran switch components (see supporting information available at stacks.iop.org/JPhysCM/24/394005/mmedia). From the optical spectra it seems that there is negligible interaction between pyrene and spiropyran moieties in the ground state.

Irradiation of the pyrene–spiropyran dyads in tetrahydrofuran (THF) solution with light of 350 nm (3.5 eV) wavelength leads to the formation of new absorption bands at around 570 nm (2.2 eV) as well as at 380 nm (3.3 eV), both characteristic of the ring-opened merocyanine form (figure 2). The absorption band of the pyrene moiety with its typical vibronic fine structure remains unchanged. UV irradiation led to the opening of the spiropyran moiety to its corresponding merocyanine form. The spectral perturbation resulting from UV irradiation of the dyads decays with time after irradiation ceases and the original spectrum is recovered. The decay is exponential and is ascribed to thermal closing of the merocyanine to regenerate the spiro form, i.e. so called T-type photochromism [4]. Hence in THF and at room temperature the spiropyran is the most stable form of the molecule. The transformations between ring-closed spiropyran isomer and ring-opened merocyanine isomer are reversible.
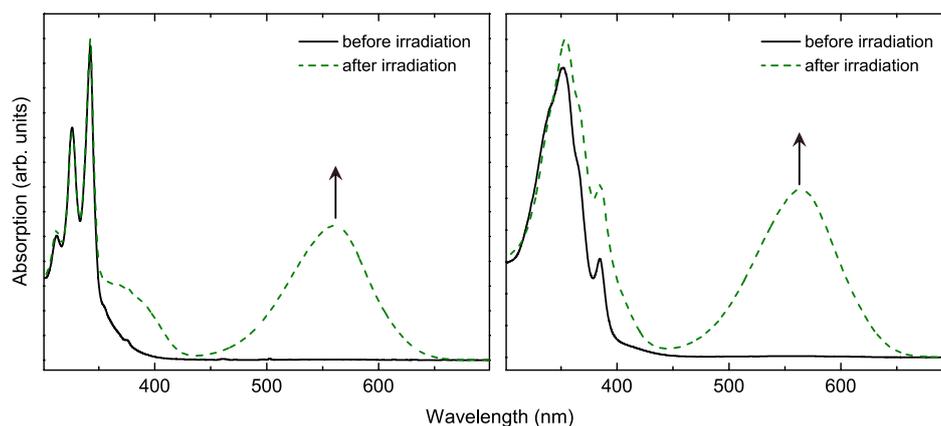
Figure 2. Absorption spectra of spiropyran dyads in THF ($c = 1 \times 10^{-5}$ M): (left) UV/visible spectra of **L-PSP**, recorded before (black line) and after (green dashed line) irradiation with light of 350 nm wavelength; (right) UV/visible spectra of **S-PSP**, recorded before (black line) and after (green dashed line) irradiation with light of 350 nm wavelength. In both pictures the merocyanine absorption bands at 380 nm and 570 nm is observed after UV irradiation.
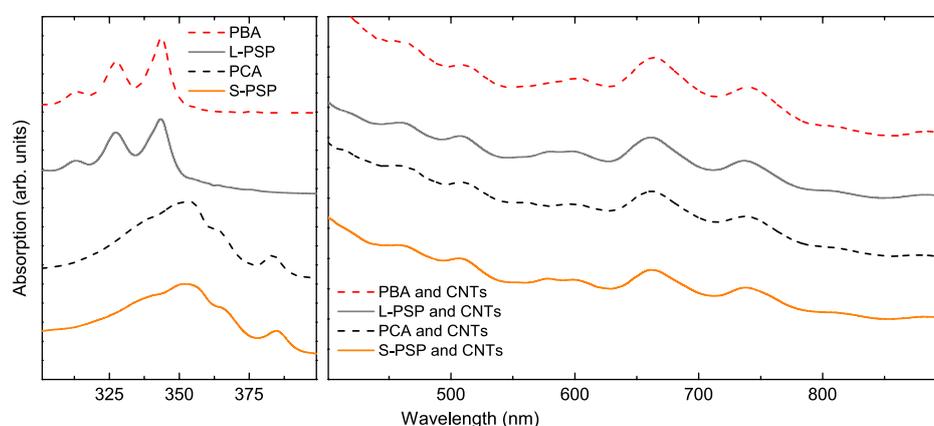

Figure 3. Absorption spectra of **PCA**, **PBA**, **S-PSP**, and **L-PSP** (left) as well as their suspensions with SWCNTs (right) in THF at 25 °C: the spectra on the left show that the characteristic pyrene absorption in the UV region is clearly visible and not altered by the presence of the switch (left). The visible region shows the M_{11} and S_{22} absorption bands of the SWCNTs stabilized as a suspension by the pyrene–spiropyran dyads (right).

3. Characterization of SWCNTs functionalized with pyrene–spiropyran dyads

Investigation of the UV/visible absorption spectra of **PCA**, **PBA**, **S-PSP** and **L-PSP** in THF solution shows that the pyrene anchor group's characteristic absorption bands seen in **PCA** and **PBA** are not significantly altered in the presence of the spiropyran switching moiety, i.e. **S-PSP** and **L-PSP**, respectively (figure 3, left).

When SWCNT suspensions stabilized by either **PCA**, **PBA**, **S-PSP**, or **L-PSP** were measured, the typical M_{11} and S_{22} absorption bands of carbon nanotubes in the visible spectral region could clearly be discerned (figure 3, right). All four different suspensions exhibit similar spectral contributions from the different absorption bands indicating similar sample compositions. Note that the merocyanine's characteristic absorption maximum at 570 nm is absent in the **S-PSP** and **L-PSP** spectra (orange and gray line in figure 3, right) and hence the switches have not undergone a ring-opening reaction upon complexation with the SWCNTs.

By obtaining the photoluminescence excitation (PLE) maps of the **S-PSP**- and **L-PSP**-stabilized SWCNT suspension, it is possible to conveniently determine the approximate chirality distribution of the semiconducting carbon nanotubes within the sample based on the relative luminescence intensities [8]. For SWCNT samples using either of the two molecules, a very similar distribution of nanotubes has been observed (figure 4). In both samples the most abundant species are the (8, 4) and (7, 6) tubes, while all other chiralities show more or less similar contributions. This nicely illustrates the fact that the binding interaction between the molecules and nanotubes remains very similar, exhibiting more or less the same composition in the isolation and solubilization process based on the use of pyrene as an anchor group. This was expected, as changes in the anchoring moiety have been shown to affect the sample composition [16, 17].

Although the spacer length does not affect the intensity distribution of the various nanotubes, a shift in the positions of the peaks within the PLE charts was observed between the two samples. The luminescence energies of both the (7, 5) and
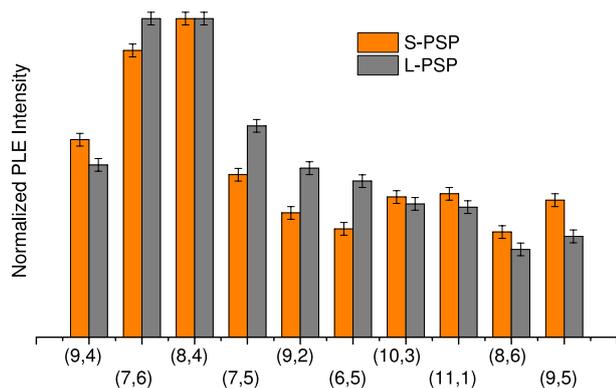
Figure 4. Contributions of SWCNTs of different chiralities in suspensions using either **S-PSP** or **L-PSP** as surfactants as revealed from the photoluminescence excitation (PLE) maps obtained.
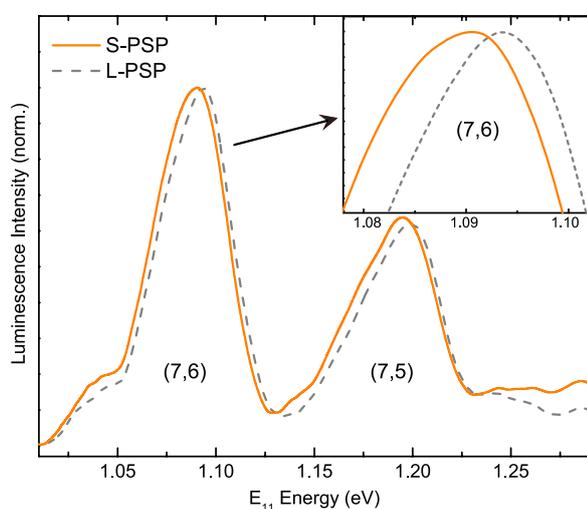

Figure 5. Normalized luminescence spectra of SWCNT samples coated either with **S-PSP** or **L-PSP** in THF upon excitation at 650 nm (1.907 eV): in the case of the longer spacer (**L-PSP**) a slight but reproducible red shift of 3 meV as compared to **S-PSP** is observed (see the inset).

(7, 6) tubes, functionalized with either **S-PSP** or **L-PSP**, differ by 3 meV (figure 5). This is expected, as the charge carriers in the nanotubes couple to the dipole moment of spiropyran, and alter the electronic properties of the tubes [11]. As the distance becomes smaller, the coupling strength increases and the effect becomes more pronounced. Please note that the dependence of this shift on the different morphology of the anchors (the **PCA** and **PBA** parts of the molecules, respectively) can be ruled out, as can be seen in figure S7 of the supporting information (available at stacks.iop.org/JPhysCM/24/394005/mmedia), where no peak shift can be observed.

Malic *et al* calculated the dipole moment of spiropyran to be 6.2 D, while the dipole moment of merocyanine is 13.9 D, consistent with the experimental observations [11, 12]. It is important to note that the direction of the dipole moment changes upon isomerization. The dipole moments of spiropyran and merocyanine are approximately orthogonal
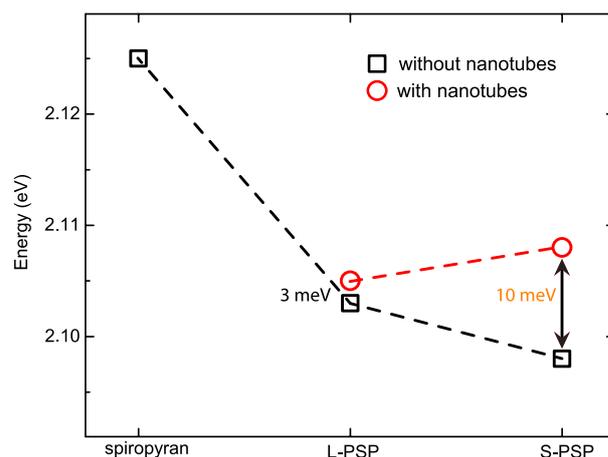

Figure 6. Positions of the merocyanine absorption band upon UV irradiation with 366 nm for the parent spiropyran (without SWCNTs) and for the pyrene–spiropyran dyads (**L-PSP** and **S-PSP** in the presence and absence of SWCNTs). Note that all samples were prepared in the same solvent (THF).

and, thus, the component of the spiropyran dipole moment in the merocyanine direction is almost zero.

Up to now, we have investigated only the interaction of the spiropyran dyad with the nanotubes. Upon switching, the spiropyran converts to the merocyanine form, which is a planar molecule with an extended π-system that should interact more strongly with the tubes. The interaction between the tubes and the attached switches is expected to alter upon irradiation and, importantly, the intensity of such interaction should in principle be dependent on their relative distance, i.e. the spacer length [11].

After UV-induced switching to the ring-opened merocyanine form, two effects were observed in the absorption spectra: first, the position of the merocyanine absorption band around 570 nm changes depending on the spacer length (figure 6). Considering the parent spiropyran as a pyrene–spiropyran dyad with infinite spacer length and comparing the position of the merocyanine band with the dyads of long and short spacer length, a systematic red shift of the absorption band with decreasing spacer length was observed, which is most likely due to the increasing interaction between the merocyanine's and the pyrene's π-systems. Note that, as all samples were prepared in THF, solvent effects can be ruled out as a source of the red shifts. Second, complexation to the carbon nanotubes seems to reverse the pyrene-induced red shift to a certain extent. The peaks shift back toward their original positions in the blue after nanotube functionalization. This opposing effect is most likely due to the dominating pyrene–SWCNT π–π interaction, leading to a lower disturbance of the merocyanine π-system.

Perhaps most interestingly, the tube–dipole distance not only affects the electronic properties of the switch molecule by tuning the spectral position of the merocyanine absorption band, but also influences the kinetic behavior of the isomerization processes (table 1). The switching behaviors of the spiropyran moiety are very similar for the two compounds,

Table 1. Switching dynamics of the spiropyran–merocyanine switching system in both the presence and the absence of SWCNTs. Shown are the times for the photochemical ring-opening reaction ($t_{\text{spiro}\rightarrow\text{mero}}$) and the thermal ring-closing isomerization ($t_{\text{mero}\rightarrow\text{spiro}}$).

	S-PSP		L-PSP	
	Without SWCNTs	With SWCNTs	Without SWCNTs	With SWCNTs
$t_{\text{spiro}\rightarrow\text{mero}}$ (s)	31 ± 2	32 ± 2	35 ± 6	29 ± 1
$t_{\text{mero}\rightarrow\text{spiro}}$ (s)	39 ± 2	48 ± 2	32 ± 5	36 ± 2

i.e. **S-PSP** and **L-PSP**, in neat solution, while they change drastically in the presence of the nanotubes. For the dyad molecule with the long spacer, the tube–switch distance seems to be large enough to confer only little change on the dynamics, whereas for the dyad molecule with the short spacer, the time necessary to achieve the thermal ring-closing isomerization is increased by 25%. This can be attributed to the stabilizing effect of the SWCNT outer surface on the merocyanine form due to enhanced π–π interactions, if the spacer is short enough. In contrast, the effect on the photochemical forward reaction, converting the spiropyran to the merocyanine, is negligible within experimental error. However, as carbon nanotubes give rise to scattering and inner filter effects, this is not self-evident and further investigations of the quantum yields are necessary to gain more insight into the fundamental isomerization processes. Furthermore, it has to be pointed out that all the dynamical behaviors observed are averages over the ensembles of functionalized molecules present in our suspensions. Quantitative estimation of the switching rate at the single-molecule level based on these experiments cannot be performed and will be a subject of future research.

4. Conclusion

The functionalization of SWCNTs with two pyrene–spiropyran dyads with different spacer lengths has been accomplished and the influence of variation of the tube–spiropyran separation has been investigated. As both molecules utilize pyrene as a non-covalent anchor for adsorbing onto the surface of carbon nanotubes, the relative compositions of the nanotube chirality distributions inside the samples are similar using the two surfactants.

Although the distributions of the peak intensities of the nanotubes in the suspensions are affected only by the morphology of the anchor, the different distances between anchor and dipole switch alter the positions of the peaks themselves: a slight red shift (about 3 meV) between the

emissions of nanotubes coated with **S-PSP** and **L-PSP** was observed.

In addition the spiropyran itself is affected by the distance to the nanotubes. The red-shifted merocyanine absorption band at 570 nm implies a stronger π–π interaction of the merocyanine isomer and the nanotube sidewall when decreasing the spacer length of the dyad. Furthermore, we found that at shorter distances carbon nanotubes are able to stabilize the merocyanine form of the switch molecules, which slows down the merocyanine $\rightarrow$ spiropyran thermal back isomerization.

References

[1] Guo X F, Huang L M, O'Brien S, Kim P and Nuckolls C 2005 *J. Am. Chem. Soc.* **127** 15045–7
[2] Zhou X, Zifer T, Wong B M, Krafcik K L, Léonard F and Vance A L 2009 *Nano Lett.* **9** 1028–33
[3] Simmons J, In I, Campbell V, Mark T, Léonard F, Gopalan P and Eriksson M 2007 *Phys. Rev. Lett.* **98** 1–4
[4] Feringa B 2001 *Molecular Switches* ed B Feringa (New York: Wiley) p 476
[5] Russew M-M and Hecht S 2010 *Adv. Mater.* **22** 3348–60
[6] Guo X, Zhang D, Wang T and Zhu D 2003 *Chem. Commun.* **7** 914–5
[7] Reich S, Thomsen C and Ordejón P 2002 *Phys. Rev.* B **65** 155411
[8] Bachilo S M, Strano M S, Kittrell C, Hauge R H, Smalley R E and Weisman R B 2002 *Science* **298** 2361–6
[9] Hirsch A and Vostrowsky O 2005 *Top. Curr. Chem.* **245** 193–237
[10] Balasubramanian K and Burghard M 2005 *Small* **1** 180–92
[11] Malic E, Weber C, Richter M, Atalla V, Klamroth T, Saalfrank P, Reich S and Knorr A 2011 *Phys. Rev. Lett.* **106** 1–4
[12] Atassi Y, Chauvin J, Delaire J A, Delouis J-F, Fanton-Maltey I and Nakatani K 1998 *Pure Appl. Chem.* **70** 2157–66
[13] Del Canto E, Flavin K, Natali M, Perova T and Giordani S 2010 *Carbon* **48** 2815–24
[14] Setaro A, Bluemmel P, Maity C, Hecht S and Reich S 2012 *Adv. Funct. Mater.* **22** 2425–31
[15] Chen R J, Zhang Y, Wang D and Dai H 2001 *J. Am. Chem. Soc.* **123** 3838–9
[16] Setaro A, Popeney C S, Trappmann B, Datsyuk V, Haag R and Reich S 2010 *Chem. Phys. Lett.* **493** 147–50
[17] Marquis R, Greco C, Sadokierska I, Lebedkin S, Kappes M M, Michel T, Alvarez L, Sauvajol J-L, Meunier S and Mioskowski C 2008 *Nano Lett.* **8** 1830–5