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PAPER

Screening interactions of zinc phthalocyanine–PPV oligomers with single wall carbon nanotubes—a comparative study†

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In this paper, the ability to disperse single wall carbon nanotubes (SWNT) of several different-nature poly(*p*-phenylene vinylene) (PPV) oligomers having pendant zinc phthalocyanines (ZnPc) has been investigated. Based on the quenching of the ZnPc and SWNT fluorescence in the supramolecular assemblies, it has been shown that parameters such as *p*/*n*-type character of the oligomer, size and the distance between the ZnPc moiety and the conjugated backbone play an important role in the strength of the interactions. Important results suggest that *n*-type oligomers as well as certain flexibility in the phthalocyanine arrangement are breakthroughs for immobilizing SWNT in THF, affording stable and homogeneous suspensions. Transient absorption measurements confirm that upon photoexcitation the photoexcited ZnPc triggers an intraensemble charge transfer to yield oxidized ZnPc and reduced SWNT.

Introduction

Single wall carbon nanotubes (SWNT) have become one of the most important one-dimension nanomaterials for optoelectronics applications due to their singular chemical, mechanical, thermal and electronic properties.[1] In addition, well ordered SWNT forming a homogeneous active layer has revealed to be indispensable in most of the devices.[2] However, the lack of solubility of the unfunctionalized SWNT makes them difficult to handle, arrange or organise in a controlled manner. Particularly, this fact becomes even more important in electronics and photovoltaics (PV) when combined with other types of donor or acceptor active units.[3]

Unfortunately, the covalent approach to functionalize SWNT walls and make them more soluble is responsible for partial saturation of the extended π-system, and therefore, for important modifications in both the electronic and spectroscopic characteristics that make them so particular.[4] In order to overcome this fact, another approach consisting in the supramolecular functionalization of SWNT by means of hydrophobic, π-stacking or van der Waals interactions has been widely investigated.[5] In this way, the attachment of, for example, polymers bearing photo- and electro-active molecules has proved to be a suitable procedure to preserve the tube properties, increase its solubility and control the organization between the donor and acceptor units.[6]

On the other hand, among the numerous industrial, chemical and technical applications of phthalocyanines (Pcs),[7] a particular interest as electron-donor molecules in the field of PV[8] is currently increasing. Factors such as (i) high light harvest at the maximum of the solar photon flux (around 700 nm), (ii) excellent photoconductivities, and (iii) reversible redox potentials are responsible for these conjugated macrocycles to hold such a prominent position. These properties turn the combinations of Pcs with SWNT into the focus of research. In this regard, the covalent functionalization of SWNT with phthalocyanines has been exploited using different approaches such as cycloaddition reactions.[9] Because of the aforementioned reasons, the supramolecular functionalization of SWNT using either pyrene[10] or conjugated poly(*p*-phenylene vinylene) oligomers (*o*PPV), bearing Pc's as pendant arms,[11,12] has already been investigated. The latter has been shown that the ability to immobilize on the sidewalls of SWNT—affording stable and homogeneous Pc–*o*PPV/SWNT suspensions—depends on the *n*-type character of the oligomer. The oligomers having an opposite *p*-type character failed to be efficient. As a proof of concept, when a metastable radical ion pair was formed upon photoexcitation of the Pc–*o*PPV (*n*-type)/SWNT assembly the isolation of the Pc with

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† Electronic supplementary information (ESI) available: Experimental and the synthetic details of the new compounds and transient absorption spectra of SWNT/**2** and **2** in the visible region. See DOI: 10.1039/c1jm10572h

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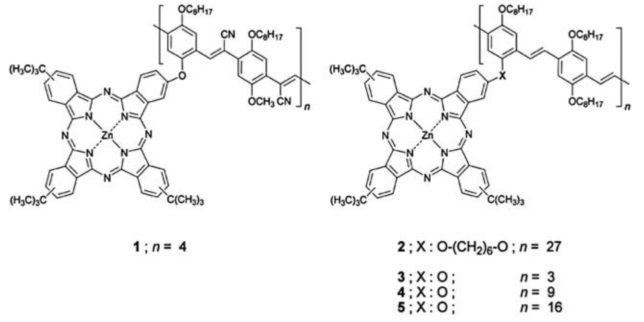


Fig. 1 ZnPc oligomers **1–5**.

regard to the carbon tube caused a ratio of charge separation rate to charge recombination rate of nearly 3 orders of magnitude.

As a consequence of the aforementioned results, we have focused on the study of a longer PPV oligomer with the Pc separated from the conjugated backbone and comparing it with the previous ones having the Pc unit directly attached to the oligomer chain in order to shed light onto the interactions taking place among the different components. Specifically, the oligomers subject of this study are, on one hand, *p*-type PPV with varying number of repeat units **3–5**[11,12] or with a hexyl spacer that links ZnPc to the PPV backbone **2**, and, on the other hand, *n*-type (CN-functionalized) short PPV **1**[11,12] as depicted in Fig. 1.

Strong interactions between *n*-type PPV and SWNT have already been documented, but the fact that also *p*-type PPVs interact with SWNT is surprising and warrants further investigations.[12] To this end, inserting alkane spacers between ZnPc and the PPV backbone brings about structural flexibility, which emerges as a decisive factor in the interactions with SWNT.

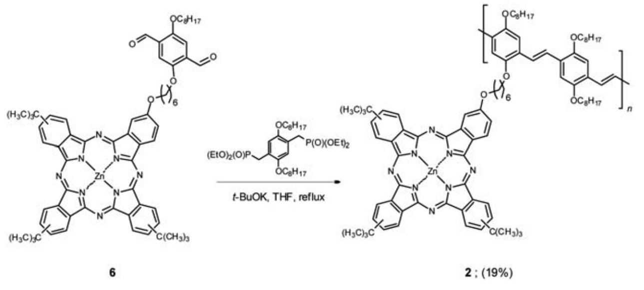
Synthesis

Compounds **1** and **3** as well as **4–6** were prepared as described previously by us, elsewhere.[11,12] Oligomer **2** was synthesized following a related procedure, that is, by a Wadsworth–Horner–Emmons reaction of dialdehyde **6** and 2,5-di-*n*-octyloxy-1,4-xylene-bis(diethylphosphonate)ester[13] with *t*BuOK, in refluxing THF (Scheme 1). Subsequent separation on a SEC (size exclusion chromatography) column afforded the corresponding main fraction named as compound **2**, in a moderate yield (19%).

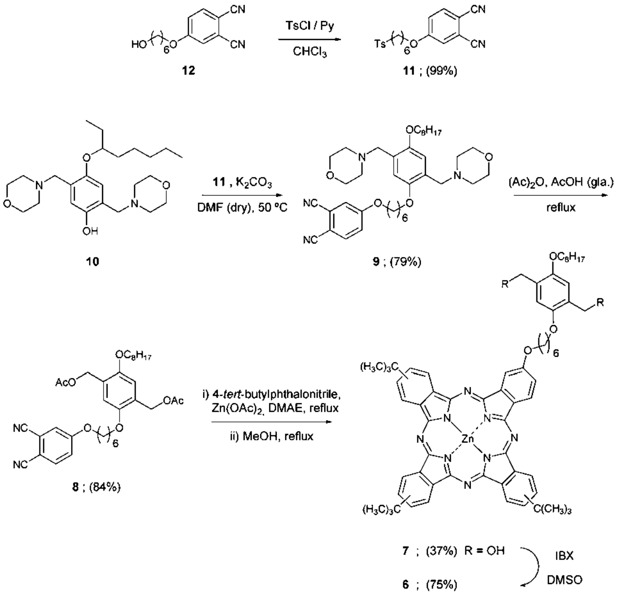
The synthesis of the key phthalocyanine **7** was accomplished by cross-condensation of **8** with 4-*tert*-butylphthalonitrile in the presence of Zn(AcO)$_2$ followed by methanolysis. Phthalonitrile **8** was prepared from phthalonitrile precursor **12**[14] after tosylation, and used like that for the alkylation of **10**[11] affording in this way the derivative **9**. The subsequent substitution of the morpholine rings by acetoxy groups led to bis(acetoxy)phthalonitrile **8**. A further step consisting of an oxidation of the bis(hydroxymethyl) phthalocyanine **7** by means of periodinane IBX[15] provided the diformylphthalocyanine **6** in an 18% overall yield (Scheme 2).

Compound **2** is soluble in polar solvents such as THF or DMF, which makes easier the purification and characterization in solution by ^{1}H-NMR, UV-Vis, FT-IR, and GPC (gel permeation chromatography) techniques. ^{1}H-NMR spectroscopy showed broad signals due to the presence of isomers from both Pc and PPV moieties. The signals (in THF-d_8) at 9.7–8.0 ppm are ascribed to the two types of hydrogen atoms surrounding the Pc core and are split into two groups. The phenyl rings of the conjugated polymer are observed at 7.9–7.3 ppm. At 7.2–6.4 ppm, the vinylene linkers within the PPV backbone resonance showing the usual shift for *trans*-isomer vinylenes. Finally, the signals between 4.6 and 4.2 ppm and 4.2 and 3.6 ppm were assigned to the methylene groups linked to the oxygen. The *trans*-configuration of the vinylene linkers was also confirmed by FT-IR with a δ_{oop}(C=C–H) at 979 cm^{-1}. Absorption spectroscopy of **1** reveals the known features of ZnPc. In particular, these are strong Soret bands around 350 nm, and Q bands at around 675 nm. In addition, a broad band is seen around 480 nm, which is ascribed to the PPV backbone (Fig. 2).

The GPC results in THF using polystyrene standards are summarized in Table 1 for all the series. These data allow estimating the length of the polymeric chains with regard to their weight-average molecular weight in mass (M_w). Moreover, the number-average molecular weight, taking the size distributions of the chains (M_n) into account, was determined. The ratio M_w/M_n provided insight into the regularity in size or dispersion (polydispersity, PDI). It is important to remark that in all the compounds each repeat unit contains two PPV units and one Pc.



Scheme 1 Synthesis of oligomer **2**.



Scheme 2 Synthetic pathway of diformylphthalocyanine **2**.

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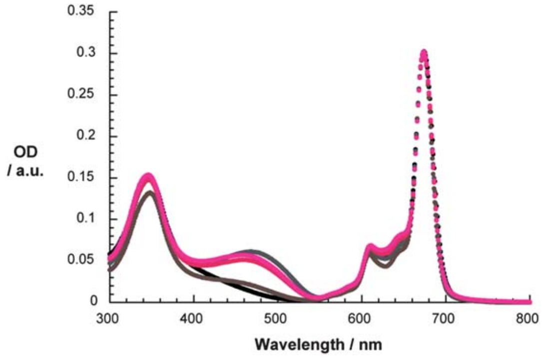

Fig. 2 Room temperature absorption spectra of **1–5** in THF, normalized for identical Q band absorption maxima at 675 nm. **1**: black; **2**: grey; **3**: brown; **4**: red; and **5**: magenta. Please note that due to the different number of repeat units of oligomers **1–5**, no concentrations are given.

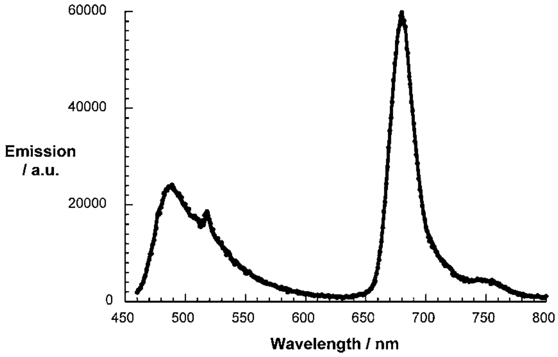

Fig. 3 Room temperature fluorescence spectrum of **2** in THF upon 450 nm excitation of PPV with optical density at the excitation wavelength of 0.01 (1.7×10^{-8} M).

Table 1 GPC results of oligomers **1–5** in THF and size estimated based on M_n data

Entry	M_w	M_n	PDI	Size based on M_n (repeating units)
1	8495	5730	1.482	*ca.* 4
2	37 896	12 883	2.941	*ca.* 27
3	7211	5132	1.405	*ca.* 3
4	21 823	6365	3.429	*ca.* 9
5	32 038	11 882	2.696	*ca.* 16

Results and discussion

The absorption features of the different oligomers (**1–5**) are a combination of those of ZnPc and PPVs. In particular, ZnPc reveals two major absorption bands in THF, namely the Soret band with a maximum at 350 nm and the Q band with the maximum at 675 nm. PPVs show broad absorptions in the region between 400 and 500 nm—see Fig. 2. Oligomer **1**, for example, shows just a weak PPV absorption, whilst in the remaining oligomers the intensity of the PPV centered absorption increases with the number of repeat units. Interestingly, **2**, in which the ZnPc/PPV distance has been enlarged, the PPV absorption is red-shifted.

In steady-state fluorescence experiments with ZnPc and **1–5**, very similar fluorescence patterns emerged that exhibit a pronounced maximum at around 680 nm. Excitation of **1** and **3–5** into the PPV absorption at 480 nm did not lead to any appreciable PPV fluorescence. Instead, intense phthalocyanine fluorescence is seen. To unravel the mechanism of producing the ZnPc fluorescence, excitation spectra were taken. The excitation spectra were exact matches of the ground state absorption of the PPV and ZnPc with maxima at 400–500 and 675 nm, respectively. An excited state deactivation *via* an energy transfer from the donating PPV to the accepting ZnPc is taking place.

Notably, **2**, which features a somewhat larger PPV/ZnPc distance, reveals a different trend—see Fig. 3. Here, we note dual fluorescence, that is, a PPV and a ZnPc centered fluorescence with maxima at 490 and 680 nm, respectively. The reason assigned to this behaviour is an incomplete energy transfer between the two constituents. Fluorescence quantum yields further confirm this notion. The ZnPc fluorescence quantum yield—upon exclusive PPV excitation at 480 nm—is 0.021 for **1** and between 0.076 and 0.045 for **3–5**, while a lower value of 0.028 has been determined for **2**. Comparing the fluorescence quantum yields upon ZnPc excitation at 610 nm, the following trend is observed. The fluorescence quantum yield for the ZnPc reference is in the order of 0.3[16] and decreases steadily with the length of the oligomer chain—see Table 2. A similar trend is seen when inspecting the fluorescence lifetimes. Longer chain lengths result in shorter fluorescence lifetimes. The explanation for these findings implies interactions between neighboring ZnPc as commonly observed in aggregates of ZnPc.[17] As the chain lengths increase, the ZnPc/ZnPc interactions intensify.

To test the interactions between ZnPc–PPV oligomers **1–5** and SWNT, in THF suspended SWNT were titrated with small amounts of the dissolved oligomers. The SWNT suspensions were prepared following our recently published procedure.[10,12]

For all of the oligomers, interactions with SWNT are discernible. For example, in the visible region, the Q band absorptions of ZnPc red-shift from 675 nm to 695 nm–see Fig. 4. In addition, the ZnPc fluorescence is quenched following the addition to the SWNT suspensions. As a complement to the aforementioned, in the near-infrared SWNT absorptions red-shift as well upon addition of ZnPc–PPV oligomers **1–5**. In line with this observation, the near-infrared fluorescence of SWNT is susceptible to parallel red-shifts, when photoexcited with a Nd: YAG laser at 532 nm. However, upon further addition of the ZnPc–PPV oligomers, the fluorescence features of ZnPc reappear, a finding, which is due to free, non-SWNT bound ZnPc–PPV oligomer in solution. This is accompanied by a shoulder in the absorption spectra at around 675 nm, which matches the Q band absorption seen in experiments lacking SWNT—see Fig. 4. Notable differences between the different ZnPc–PPV oligomers do not emerge.

Further studies on interactions between the ZnPc–PPV oligomers and SWNT necessitated the preparation of more stable and more concentrated suspensions of SWNT.[10,12,18] Importantly, the simple use of the procedure developed for **1**[12] fails for **2–5**, but nevertheless we managed to modify our procedure to prepare a stable suspension of SWNT with all of the ZnPc–PPV oligomers. To ensure that comparable amounts of SWNT are added, a pre-suspension of SWNT in THF was

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Table 2 Overview of the number of repeat units of the compounds. Fluorescence quantum yields (Φ_{PPV} 480 nm excitation; Rhodamine 6G reference; Φ_{ZnPc} 610 nm excitation; ZnPc reference; THF) and fluorescence lifetimes (647 nm excitation, 684 nm detection, THF)

Compound	Pc units per molecule	Φ_{PPV}	Φ_{ZnPc}	τ_{ZnPc}/ns	Relative weight
ZnPc	1	—	0.30	3.49	1.00
1	4	0.021	0.23	3.21	0.90
2	27	0.028	0.07	2.85	0.96
3	3	0.076	0.18	3.42	0.99
4	9	0.045	0.13	3.13	0.99
5	16	0.032	0.04	3.03	0.98

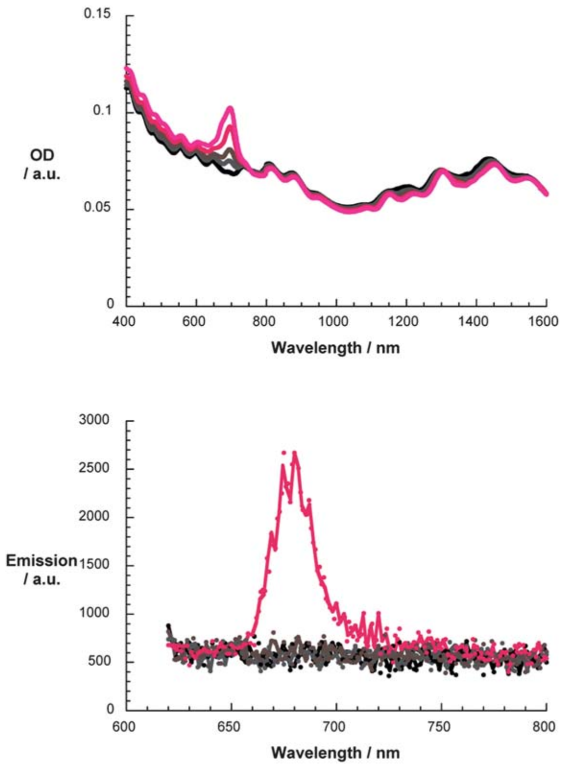

Fig. 4 Upper part – titration of SWNT suspended in THF with **2**. Black—absorption spectrum of pure SWNT, grey—absorption spectrum of 2.9 × 10^{-9} M of **2** with SWNT, brown—absorption spectrum of 5.8 × 10^{-9} M of **2** with SWNT, red—absorption spectrum of 1.1 × 10^{-8} M of **2** with SWNT, and purple—absorption spectrum 1.7 × 10^{-8} M of **2** with SWNT. Lower part: corresponding fluorescence spectra after 610 nm excitation.

prepared. We started with 0.2 mg of solid SWNT and 3 mL of THF, which are sonicated for 10 minutes to disperse the SWNT. Although these SWNT suspensions are largely heterogeneous, it guarantees the use of equal amounts of SWNT. Next, 0.2 mL of this pre-suspension were added to 8 mL of THF solutions of ZnPc–PPV oligomers **1–5** that exhibit identical Q band absorptions of ZnPc. This was followed by 10 minutes of ultrasonication and recording absorption spectra. Going through several repetitions of these steps we could realize stable SWNT suspensions, which contain SWNT immobilized ZnPc–PPV oligomers. To this end, stability tests were carried out for up to a week without showing notable SWNT aggregation. A further increase of the SWNT concentration initiated aggregation, precipitation, *etc.* The number of repeat units in the PPV backbone is not decisive, only the shortest oligomer **3** seems to be slightly favored to yield stable suspensions. The overall limiting factor is the weak nature of the π–π-interactions to drive the PPV immobilization onto SWNT. Repulsive forces as they result between *p*-type PPV[19] and *p*-type SWNT[20] further contribute to the overall limitations. **1**, on the hand, has been shown to be efficient SWNT suspender due to the strong *n*-type character of the PPV of SWNT.[12,19] A closer inspection at **2–5** reveals an interesting trend—see Fig. 5. SWNT suspensions with **2** show a superior stability when compared to those prepared with **3–5**, although never reaching the performance of **1**. A likely rationale involves the structural flexibility of **2**, which enables the PPV backbone to interact better with the curved SWNT surface and, in turn, secures an enhanced stability of the resulting suspensions. The stability of the SWNT suspensions was further tested by centrifugation to remove the non-debundled SWNT. **1** and **2** give rise to acceptable stabilities upon centrifugation for 15 minutes at 9.6 kG, whilst **3–5** failed these tests. Here, only residual amounts of SWNT remain in suspensions.

To get deeper insights into the SWNT/ZnPc–PPV oligomer hybrids, the suspensions prepared by the aforementioned procedure were subjected to fluorescence measurements, in which the near-infrared fluorescence of SWNT is recorded at various excitation wavelengths, the so-called 3D fluorescence plot. These experiments are decisive, since they generate comparable fluorescence landscapes of SWNT upon variable excitation, namely between 550 and 800 nm, by a Xe-lamp.[21] A SWNT/SDBS suspension in D_2O, in which the SWNT are capped by SDBS and, in turn, lack the electronic communication with the environment (*i.e.*, ZnPc–PPV), was used as a reference. The fact that different solvents were used in these assays should

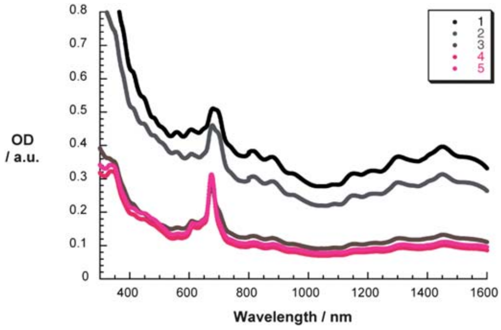

Fig. 5 Absorption spectra of stable suspensions of SWNT/**1–5** in THF with the highest possible amount of dispersed SWNT prior to their precipitation. Oligomer solutions exhibited similar Q band absorption of **1–5** at the starting point of the preparation procedure—see Fig. 2.

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not invalidate the interpretation. All of the suspensions were of comparable SWNT absorptions all throughout the excitation area. Resembling the absorption features, all SWNT characteristic fluorescence maxima are red-shifted in SWNT/**1–5** relative to SWNT/SDBS. Although **1–5** evoke no particular differences in terms of red-shifts, significant changes are seen in terms of fluorescence intensities.

In fact, the fluorescence intensities at an excitation wavelength of 725 nm—see Fig. 6—show the weakest quenching of SWNT fluorescence for the longest ZnPc–PPV oligomer, that is, **5**, followed by **4** and **3**. Phthalocyanines that are in contact with the surface of SWNT by either covalent or non-covalent[9b,10,12,22] binding reveal quenched fluorescence due to charge transfer interactions. Due to the fact that an excess of oligomer was omnipresent during these assays, we postulate that the immobilization of ZnPc–PPV oligomers **1–5** onto the SWNT surface is at its maximum. Taking this into consideration we rationalize the weaker SWNT fluorescence quenching, especially for the longer ZnPc–PPV oligomers to fewer ZnPc immobilized onto SWNT. Due to sterical reasons, smaller ZnPc–PPV oligomers have more possibilities to attach to the SWNT surface. **1** and **2** show a comparable quenching of the SWNT fluorescence. The latter is nearly as strong as that seen for **3**. For **1** and **2**, high SWNT surface coverage arises either from a favored *n*-type/*p*-type interaction between **1** and SWNT or from an efficient interaction of SWNT and **2** due to its structural flexibility. All of the aforementioned results were independently corroborated by fluorescence spectra recorded upon 532 nm Nd:YAG laser excitation.

Lastly, we turned to transient absorption measurements. The low concentration of SWNT suspensions containing oligomers **3–5** rendered their investigations difficult. Thus, we focused our work exclusively on the characterization of SWNT/**2** in comparison to the results published recently for SWNT/**1**.[12] During the preparation of SWNT suspensions in THF—by following the aforementioned procedure—special care was taken to avoid free ZnPc–PPV oligomer in solution. To this end, the ZnPc Q band absorption at 695 nm served as a convenient marker for SWNT immobilized ZnPc–PPV. The differential absorption spectra of SWNT/**2**, obtained upon laser excitation at 387 nm, show great similarities with those seen for SWNT/**1** (Fig. 7). Initially after photoexcitation, a broad maximum in the 500 to 620 nm range and a minimum located at around 700 nm, reflecting the ZnPc singlet excited state absorption and the ground state bleaching, are discernible—see Fig. S1†. The ground state bleach deactivates rapidly within 6.1×10^{12} s^{-1}, while in Fig. S2† showing non-SWNT bound ZnPc–PPV oligomer **2**, a slow intersystem crossing to the ZnPc triplet excited state is observable. Inspecting the near-infrared region sheds light on SWNT based features. In particular, bleaching of the SWNT's van Hove singularities evolves as a minimum at around 1350 nm and as shoulders at around 1160 and 1280 nm. However, taking the fact of the diluted SWNT suspension into account, no further features have been identified. All of the SWNT centered features decay very fast—1.6×10^{12} s^{-1}—a value that matches quite well with the singlet excited state decay of ZnPc. Together with the decay of the ZnPc and SWNT characteristics, the SWNT exNIR bands shift towards shorter wavelengths and an 840 nm maximum evolves. The earlier feature, namely a blue shift of about 10 to 20 nm of the SWNT absorption features, is indicative for the formation of the charge transfer product, that is, reduced SWNT—see Fig. 7, while the latter reflects the well-known absorption of the ZnPc radical cation,[12,23] for which we have determined a lifetime of around 100 ps. Such a short lifetime relates to the short distance between the electron donating ZnPc and the SWNT sidewalls. Interesting is the comparison with SWNT/**1**—similar lifetimes corroborate our assumption that the nature of the PPV oligomer plays no

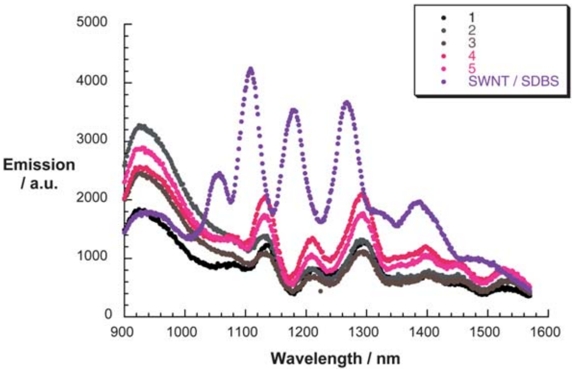

Fig. 6 SWNT NIR fluorescence spectra of SWNT/**1–5** in THF upon Xe-lamp 725 nm excitation of SWNT/**1–5** and SWNT/SDBS/D$_2$O reference. All samples show similar absorption at 725 nm.

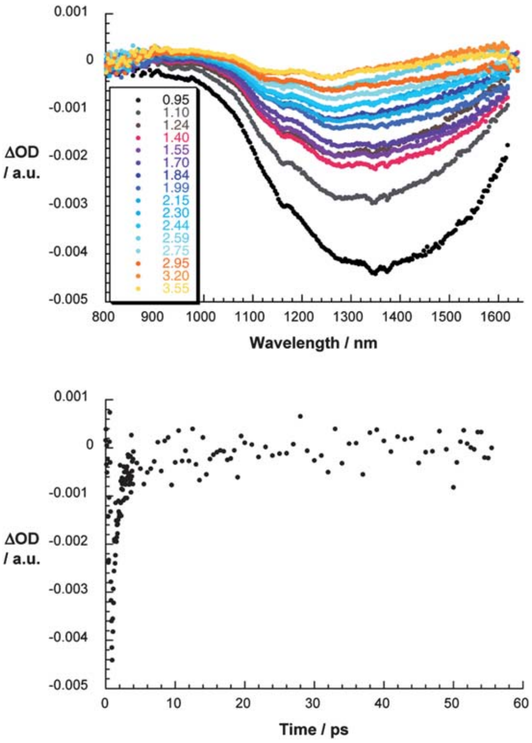

Fig. 7 Upper part—differential absorption spectra (near-infrared) obtained upon femtosecond laser flash photolysis (387 nm) of SWNT/**2** in THF at room temperature with several time delays between 0.95 and 4.0 ps representing the bleaching of the SWNT van Hove singularities and formation of reduced SWNT. Lower part—the absorption time profile of the above spectra at 1350 nm.

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significant or only a minor role in impacting the charge transfer properties.

Conclusions

In summary, we have developed a novel synthetic route of a key diformylphthalocyanine **6** as a monomer for the preparation of conjugated PPV oligomers having the Pc connected to the conjugated backbone through a flexible spacer. With the comparative study among oligomers of different lengths, *p*/*n*-type character, and separation between the Pc and the conjugated backbone, we have documented the interactions of ZnPc–PPV oligomers with the surface of SWNT. We were able to show that either electronic modifications (**1**) or implementation of structural flexibility (**2**) in simple ZnPc–PPV oligomers is indispensable to realize highly concentrated and stable SWNT suspensions. On the contrary, oligomers of a varied number of repeat units did not show significant differences regarding the stability of the suspensions. When inspecting, however, the quenching of the SWNT fluorescence in the near-infrared the length of the ZnPc–PPV oligomer (**3–5**) matters. In particular, shorter oligomers cover more of the SWNT surface leading to a stronger SWNT fluorescence quenching. The structurally modified oligomers, such as **1** and **2**, reveal the strongest SWNT fluorescence quenching. This is primarily due to facilitated immobilization onto SWNT, that is either based on *n*-type/*p*-type interactions in the case of **1** or the structural flexibility in the case of **2**. Time-resolved transient absorption measurements verified charge transfer that evolves from the photoexcited ZnPc to SWNT yielding a 100 ps stable charge transfer product. In terms of charge transfer, the nature of the PPV backbone has at best a minor role.

Acknowledgements

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