Multiwalled carbon nanotubes in donor–acceptor nanohybrids—towards long-lived electron transfer products†

Dirk M. Guldi,[*a] **G. M. A. Rahman,**[a] **Norbert Jux,**[*b] **Domenico Balbinot,**[b] **Nikos Tagmatarchis**[c] **and Maurizio Prato**[*c]

Novel multiwalled carbon nanotube/metalloporphyrin nanohybrids are devised and probed as versatile donor–acceptor hybrids.

Nanoscale science, engineering, and technology are emerging fields where scientists and engineers are beginning to manipulate matter at the atomic and molecular scale level in order to obtain materials and systems with significantly improved properties.[1]

Here we probe for the first time interactions that are based on electron transfer chemistry between multiwalled carbon nanotubes (MWNT)[2]—having two or more concentric cylinders—and a polyanionic, water-soluble zinc tetraaryl porphyrin, using a pyrene salt as the glue.

As-obtained MWNT‡ were treated with an aqueous solution of 1-(trimethylammonium acetyl)pyrene (pyrene[+]), known to adhere to single wall carbon nanotubes (SWNT) *via* π–π interactions—see Scheme 1.[3,4] The resulting black suspension was stable for weeks without any apparent precipitation. A drop of this suspension was cast on a transmission electron microscopy grid (*i.e.,* a carbon copper grid, 3 mm, 200 mesh, coated with a formvar film) and analysed. Individual MWNT/pyrene[+] nanohybrids with diameters ranging between 20 and 30 nm with lengths of micrometers were identified (Fig. 1).

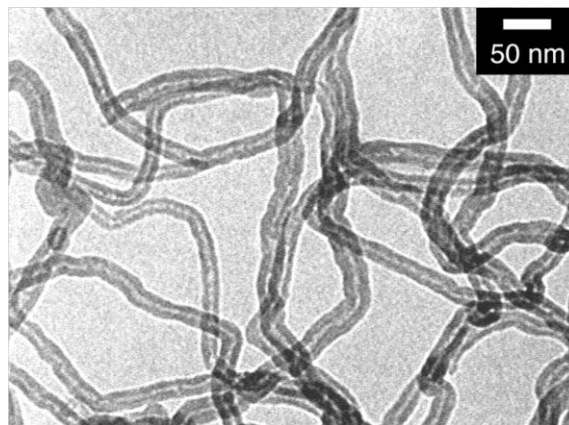UV-Vis and fluorescence studies—shown in Figs. 2 and 3—confirm the close interaction between the MWNT and the

Fig. 1 Transmission electron micrograph of water-soluble MWNT/pyrene[+] complex.

pyrene counterpart. The π–π transitions of pyrene[+] are red-shifted by about 1 nm in the presence of MWNT. In the visible and NIR, new transitions appear at 505, 630, 750, 850, 910 and 1100 nm, which are all MWNT centered. In steady state and time-resolved experiments, the strong pyrene[+] fluorescence is quenched by the presence of MWNT, an indication for fast and efficient energy trapping at the MWNT site. Relative to pyrene[+] alone, which exhibits a fluorescence lifetime of several ns, we note in MWNT/pyrene[+] the same lifetime, despite the steady-state quenching.
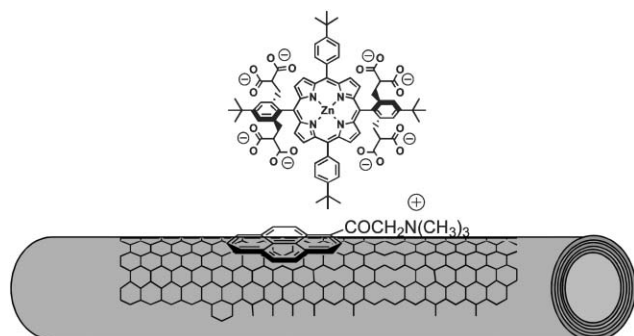
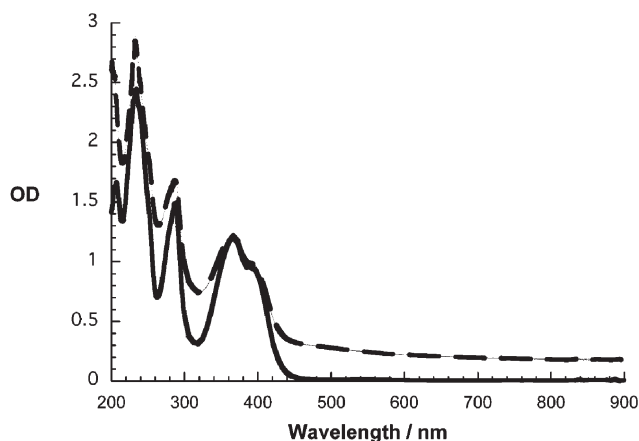**Scheme 1** MWNT/pyrene[+]/ZnP[8−] sketch.

Fig. 2 Absorption spectra of pyrene[+] (solid line) and MWNT/pyrene[+] (dashed line) in H_2O in the 200–900 nm range.

† Electronic supplementary information (ESI) available: spectrophotometric and kinetic details. See http://www.rsc.org/suppdata/cc/b4/b418406h/
*dirk.guldi@chemie.uni-erlangen.de (Dirk M. Guldi)
jux@chemie.uni-erlangen.de (Norbert Jux)
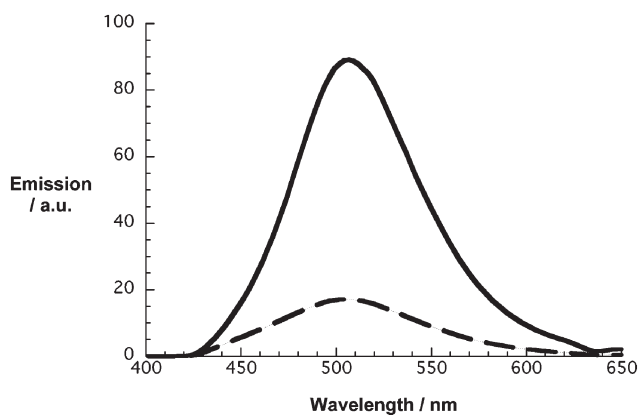prato@units.it (Maurizio Prato)

Fig. 3 Fluorescence spectra of pyrene$^+$ (solid line) and MWNT/pyrene$^+$ (dashed line) in water with matching absorption at the 360 nm excitation wavelength – OD$_{360 \text{ nm}}$ = 0.5.

Fig. 4 Fluorescence spectra of a dilute aqueous solution of ZnP^{8-} (2.9×10^{-6} M) upon adding MWNT/pyrene$^+$—complementary to Figure S3. Excitation wavelength is 429 nm.

Consequently, we must assume that this long-lived component originates from non immobilized pyrene$^+$, while for grafted pyrene$^+$ the corresponding value is masked by our instrumental time resolution of around 100 ps.§

For the realisation of a supramolecular photoactive self-assembly, the MWNT/pyrene$^+$ system was combined with the zinc complex of 5,15-bis-[2′,6′-bis-{2″,2″-bis-(carboxy)-ethyl}methyl-4′-*tert*-butyl-phenyl]-10,20-bis-(4′-*tert*-butyl-phenyl)porphyrin as octasodium salt (ZnP^{8-}). The trimethylammonium group of pyrene$^+$ was used as an electrostatic anchor to bind the anionic ZnP^{8-} electron donor.[5] Such a supramolecular organization—see Scheme 1—was probed in titration experiments where dilute aqueous solutions of ZnP^{8-} ($\sim 10^{-6}$ M) were mixed with variable concentrations of MWNT/pyrene$^+$. We analysed the ZnP^{8-} absorption features (Fig. S1), namely, *Soret*- and *Q*-bands upon adding variable MWNT/pyrene$^+$ concentrations. Firstly, the ZnP^{8-} transitions are red-shifted (*i.e.*, 426 → 431 nm; 560 → 563 nm; 600 → 603 nm). Secondly, the ZnP^{8-} absorption decreases in intensity. Thirdly, an isosbestic point develops at 429 nm, which was used for the fluorescence experiments, since all samples show here the same absorbance. Finally, it should be mentioned that the pyrene$^+$-centered absorptions are also characterized by shifts. However, these shifts occur to the blue (*i.e.*, 233 → 229 nm; 288 → 287 nm; 366 → 363 nm), which might indicate an appreciable transfer of electron density to MWNT.

Similarly, the strong ZnP^{8-} fluorescence (Φ = 0.04)[6] is another marker to demonstrate intracomplex interactions with MWNT, especially considering the electron acceptor character of nanotubes. Therefore, we ran sets of fluorescence experiments parallel to the above-mentioned absorption measurements. Relative to ZnP^{8-} alone a number of important observations are gathered in Fig. 4 when adding MWNT/pyrene$^+$. The strong ZnP^{8-} fluorescence decreases in a non-linear, exponential fashion upon addition of MWNT/pyrene$^+$. Also, during the titration, the fluorescence maxima shift gradually to the red (*i.e.*, 612 → 614 nm; 665 → 667 nm), tracking the changes seen in the absorption spectra.¶

To gather independent confirmation for the trend seen in the steady-state fluorescence studies, we monitored the ZnP^{8-} fluorescen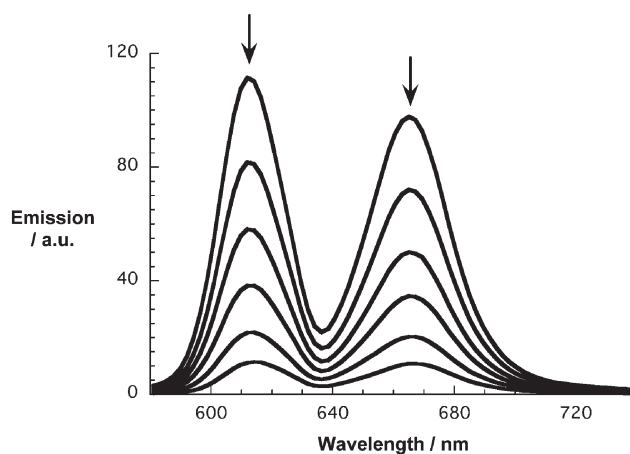ce deactivation at several wavelengths (*i.e.*, 612 and 665 nm). In the absence of any quencher the fluorescence–time profiles were best fitted (*i.e.*, χ^2-value of at least 1) by a mono-exponential expression. From such a fitting procedure a lifetime of 2.1 ± 0.2 ns was determined. In the presence of MWNT/pyrene$^+$ we realize that acceptable χ^2-values were only obtained when treating the decay traces with a multi-exponential fitting function. In particular, we see a long-lived and a short-lived constituent with lifetimes of 2.1 ± 0.2 ns and 0.2 ± 0.02 ns, respectively. This trend holds throughout the titration with the only variable being the pre-exponential factors of both constituents. Fig. S2 and Table S1 provide summaries for a few selected examples. The pre-exponential factors decrease steadily for the long, 2.1 ns component, while they increase simultaneously for the short, 0.2 ns component. At the titration end point, where the concentration of free ZnP^{8-} is presumably negligible, the first pre-exponential factor disappears.¶

The conclusion of absorption and fluorescence experiments is that mixing ZnP^{8-} with MWNT/pyrene$^+$ results in the coulombic complex formation of photo- and electroactive MWNT/pyrene$^+$/ZnP^{8-} nanohybrids. Therefore, the initial and final spectra of the titration experiments correspond to ZnP^{8-} and MWNT/pyrene$^+$/ZnP^{8-}, respectively, which differ in a number of aspects. The fluorescence quenching is predominantly static with a unimolecular deactivation rate (*i.e.*, (5.0 ± 0.5) × 10^9 s^{-1}) that corresponds to an intra-complex electron transfer reaction. The association is labile and readily reverted by increasing the ionic strength or protonating the carboxylic functionalities of ZnP^{8-}.

The fluorescence experiments prompted us to examine the photophysics of MWNT/pyrene$^+$/ZnP^{8-} nanohybrids by transient absorption changes, recorded after 532 nm laser pulse (*i.e.*, nanosecond), and compare them to those of the corresponding ZnP^{8-}. Turning first to the question of the reference ZnP^{8-}: at early times (*i.e.*, 50–100 ns), strong transitions were found in the visible, which are ascribed to the triplet excited state absorption feature.[7] The most important signature of the triplet is a maximum around 860 nm.

For MWNT/pyrene$^+$/ZnP^{8-} (Fig. 5), the transient absorption changes, recorded at the conclusion of the nanosecond excitation are not superimposable with those recorded for ZnP^{8-}, that is, the
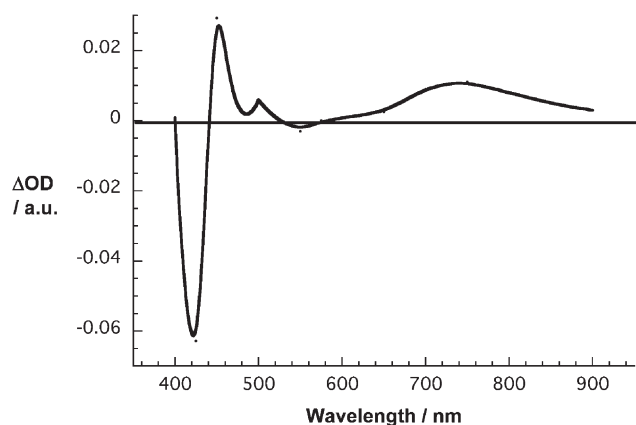
Fig. 5 Differential absorption spectrum (VIS and NIR) obtained upon nanosecond flash photolysis (532 nm) of MWNT/pyrene$^+$/ZnP^{8-} in nitrogen saturated solutions with a time delay of 100 ns.

triplet excited state. Instead, the newly formed species shows a broad peak in the 650–900 nm region, the characteristic fingerprint of the one-electron oxidized ZnP^{8-} π-radical cation.[8] The decay curves of the new absorption—see Fig. S3—were well fitted by a single exponential decay component. In particular, lifetimes that are on the order of microseconds (5.8 ± 0.2 μs) were derived. The better delocalization of electrons in MWNT—relative to analogous SWNT nanohybrids (*i.e.*, SWNT/pyrene$^+$/ZnP^{8-}) and a lifetime of 0.4 μs[4]—decelerates the decay dynamics of the electron transfer product.

In retrospect, our strategy to devise novel MWNT donor–acceptor ensembles clearly demonstrates *i*) the electron acceptor character of MWNT and *ii*) the stabilization of an efficiently formed charge-separated state.[9] Particularly beneficial for delocalizing the charges in MWNT appears the large number of concentric cylindrical graphitic tubes.

Dirk M. Guldi,*[a] **G. M. A. Rahman,**[a] **Norbert Jux,***[b]
Domenico Balbinot,[b] **Nikos Tagmatarchis**[c] **and Maurizio Prato***[c]
[a]*Institute for Physical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058, Erlangen, Germany.*
E-mail: dirk.guldi@chemie.uni-erlangen.de
[b]*Institute for Organic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91054, Erlangen, Germany.*
E-mail: jux@chemie.uni-erlangen.de
[c]*Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127, Trieste, Italy. E-mail: prato@units.it*

Notes and references

‡ MWNT were obtained from Nanostructured & Amorphous Materials, Inc., www.nanoamor.com, outer/inner diameter 20–30/5–10 nm, purity 95%.
§ Femtosecond resolved transient spectroscopy suggests an ultrafast deactivation of several ps.
¶ Parallel experiments with zinc 5,10,15,20-tetrakis-(2′,6′-bis-(*N*-methylene-(4″-*tert*-butylpyridinium))-4′-*tert*-butylphenyl)porphyrin octabromide (ZnP^{8+}) did not show any appreciable interactions.

1 *Introduction to Nanotechnology*, C. P. Poole and F. J. Owens, eds., Wiley-Interscience, Weinheim, 2003; *Nanophysics and Nanotechnology: An Introduction to Modern Concepts in Nanoscience*, E. L. Wolf, ed., John Wiley & Sons, New York, 2004.
2 P. Harris, *Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century*, Cambridge University Press, Cambridge, 2001; *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*, M. S. Dresselhaus, G. Dresselhaus, P. Avouris, eds., Springer, Berlin, 2001; *Carbon Nanotubes: Basic Concepts and Physical Properties*, VCH, Weinheim, 2004; Special issue on Carbon Nanotubes, *Acc. Chem. Res.*, 2002, **35**, 997.
3 N. Nakashima, Y. Tomonari and H. Murakami, *Chem. Lett.*, 2002, 638; A. B. Artyukhin, O. Bakajin, P. Stroeve and A. Noy, *Langmuir*, 2004, **20**, 1442.
4 D. M. Guldi, G. M. A. Rahman, N. Jux, N. Tagmatarchis and M. Prato, *Angew. Chem., Int. Ed.*, 2004, **43**, 5526.
5 D. M. Guldi and M. Prato, *Chem. Commun.*, 2004, 2517.
6 S. L. Muov, I. Carmichael and G. L. Gordon, *Handbook of Photochemistry*, Dekker, New York, 1993.
7 J. Rodriguez, C. Kirmaier and D. Holten, *J. Am. Chem. Soc.*, 1989, **111**, 6500.
8 D. M. Guldi, P. Neta and P. Hambright, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2013 and references cited therein; C. Luo, D. M. Guldi, H. Imahori, K. Tamaki and Y. Sakata, *J. Am. Chem. Soc.*, 2000, **122**, 6535.
9 Previous mentions of porphyrins with CNTs—but not in the context of photoinduced charge transfer—are found in: H. Murakami, T. Nomura and N. Nakashima, *Chem. Phys. Lett.*, 2003, **378**, 481; H. Li, B. Zhou, Y. Lin, L. Gu, W. Wang, K. A. S. Fernando, S. Kumar, L. F. Allard and Y.-P. Sun, *J. Am. Chem. Soc.*, 2004, **126**, 1014.