Noncovalent attachment of *pyro*-pheophorbide *a* to a carbon nanotube†

Jari S. Kavakka,[a] Sami Heikkinen,[a] Ilkka Kilpeläinen,[a] Marco Mattila,[b] Harri Lipsanen[b] and Juho Helaja*[c]

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Pyrene mediated noncovalent attachment of a chlorophyll derivative, *pyro*-pheophorbide *a*, to a soluble single wall carbon nanotube is reported and the resultant CD, UV-Vis absorbance, fluorescence and ^{1}H NMR spectra are discussed.

Several artificial bioinspired light absorbing molecular systems capable of photoinduced electron transfer (ET) have been reported in the literature.[1,2] Many of them mimic the donor–acceptor (DA) pair found in photosynthetic reaction centres, which initiate the charge separation process in photosynthesis. In photosynthesis, charge separation occurs between specifically arranged chlorophylls called "special-pairs". In synthetic mimicry, however, a number of artificial systems have been built, and even robustly constructed DA systems with porphyrin type electron donor and fullerene electron acceptor exhibit efficient charge separation.[3] This can be chiefly explained by the excellent electron acceptor properties of fullerenes. Carbon nanotubes (CNT) are also good electron acceptors, moreover, their nanowire structure make them attractive building blocks for solar cells and other electro-optical devices.[4] Recently, the charge separation event between CNT and porphyrin has been demonstrated in systems with covalent[5] or noncovalent[6] linkages between the DA.

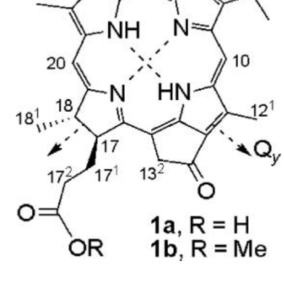
To the best of our knowledge, molecular systems in which chlorophyll or a chlorophyll derived compound acts as an electron donor, and a carbon nanotube as an electron acceptor, have not been reported. Herein we report the first synthetic approach to attaching chlorophyll derivative‡ of a biological origin to CNT. The electronic properties and structure of the system are studied by optical and ^{1}H NMR spectroscopic methods.

In general, CNT walls can be covalently functionalized by the same chemical approaches used for fullerenes.[7] Additionally, the flat aromatic wall in one and curved in another dimension provides a surface for hydrophobic interactions and, interestingly, for noncovalent π–π interactions with other flat aromatic rings.[8] Pyrene is already known to have such an affinity for CNT. In development of photovoltaic applications cationic 1-(trimethylammonium acetyl) pyrene dye has been successfully used to withdraw anionic porphyrin[8] or polymer[9] chromophore onto SWNT surface by combined van der Waals interactions and electrostatic forces. The pyrene–CNT attraction is so large that pyrene tethered proteins have been immobilised on single wall carbon nanotubes (SWNT).[10] The advantage in noncovalent binding is that CNT remains electronically intact and functionalization can be performed through self-assembly.

To study noncovalent biomaterial pigment attachment to CNT, we chose *pyro*-pheophorbide *a* **1a** (Scheme 1) as an integrable chlorophyll derivative because of its stability and processability. The chlorophyll mixture was isolated from green leaves and compound **1b** was obtained after chemical modification.[11,12]

The pyrene was linked to chlorin (**1a**) by tethering 1-pyrenemethanamine to the propionic acid residue of the *pyro*-pheophorbide with an amide bond to obtain dyad **2** after EDCI mediated coupling. The dyad **2** was dissolved in chloroform and non functionalized SWNT (insoluble) was dispersed in this mixture. After a short period, the green solution became colourless. Presumably dyad **2** forms adducts with SWNT, which precipitate instantly after mixing. CNT generally shows negligible solubility in organic solvents though it can be temporarily dispersed in some solvents by sonication. In order to make CNT soluble, and thus more practical for synthetic and spectroscopic applications, we functionalized the carboxy terminal of SWNT with pentyl esters according to a reported procedure.[13] When pyrene-*pyro*-pheophorbide *a* SWNT adduct (**3**) was prepared by simply dissolving compound **2** in chloroform solution and adding pentyl ester SWNT to the mixture (Scheme 2), the adduct obtained showed good stability and persistence in solution. Properties of **3** were studied with UV-Vis, CD, NMR, steady- and time-resolved fluorescence spectroscopy.

The UV-Vis spectra of **1b**, **2** and **3** were measured in chloroform. The reference compound Me-*pyro*-pheophorbide *a* (**1b**) and the dyad **2** gave identical spectra apart from the pyrene region in **2** (<350 nm). This is an indication that there is no



1a, R = H
1b, R = Me

Scheme 1 Green plant originated pheophorbibe *a*, **1a** and its methyl ester, **1b**. Partial chlorin ring atom numbering and approximate polarization axis (Q_x and Q_y).[14]

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[a] *Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, A.I Virtasen aukio 1, P.O. Box 55, FIN-00014, University of Helsinki, Finland*
[b] *Optoelectronics Laboratory, Micronova, Helsinki University of Technology, FIN-02150, Espoo, Finland*
[c] *Department of Chemistry, University of Helsinki, A.I Virtasen aukio 1, P.O. Box 55, FIN-00014, University of Helsinki, Finland. E-mail: juho.helaja@helsinki.fi; Fax: +358 9 191 50466; Tel: +358 9 19150430*

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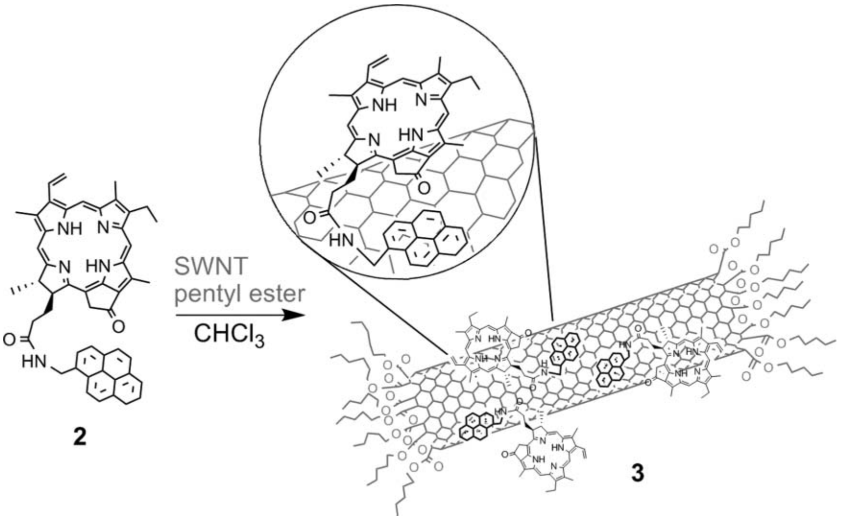

Scheme 2 Non-covalent pyrene guided pyrene-*pyro*-pheophorbide *a*, **2** attachment on SWNT.

significant electronic interaction between the aromatic rings in the dyad. In the case of prepared SWNT adduct **3**, a clear redshift of the Soret-band (415 → 420 nm) and blue shift of the Q_y-band (669 → 655 nm) in **3** were observed (Fig. 1). These changes in the electronic absorption spectrum suggest that the chlorin macrocycle is in close proximity to the surface of the SWNT.

Further evidence of the dyad **2** interaction with SWNT was obtained by CD spectroscopy (Fig. 2). The addition of SWNT pentyl ester into a chloroform solution of **2** caused several changes in the spectra, of which the most striking was the disappearance of the absorbance band at 539 nm, the chlorin ring Q_x band.[14] This indicates a change in the chlorin plane polarization which probably originates from interactions with SWNT.

Compounds **1b**, **2** and **3** were studied with ^{1}H NMR spectroscopy in CDCl$_3$ to monitor spectral changes induced by aromatic interactions. The ^{1}H spectra were assigned by 2D ^{1}H NMR techniques (TOCSY and NOESY). Only slight differences could be observed in the chemical shifts between the chlorin ring protons of **1b** and **2**. However, prominent changes were observed in the chlorin moiety when dyad **2** was measured with SWNT pentyl ester (Fig. 3). The sample was non-viscous, but all the proton signals were broadened due to the high molecular weight of the complex, and most of the chlorin ring protons show notable deshielding induced by aromatic interactions. The strongest deshielding (0.5 ppm) was observed for chlorin macrocycle protons 5 and 10 (Scheme 2 and Fig. 3). This was interpreted to originate from the close proximity of the SWNT, whose π orbitals are overlapping these parts of the chlorin ring.

Finally, the compounds were studied with fluorescence spectroscopy. In steady-state measurements the reference compound **1b** and dyad **2** gave nearly identical spectra. In the case of **3**, the relative intensity decreased by a factor of 0.4 and the fluorescence was blue shifted (666 → 656 nm) compared to **2**. The time-resolved fluorescence measurements indicated an identical lifetime, τ = 6.7 ns, for **1b** and dyad **2**. The lifetime shortened to 3.6 ns for **3**, which indicates a different quenching mechanism for this system. The faster decay of Q_y-band singlet fluorescence in the presence of SWNT suggest that pyrene tethered chlorophyll singlet excited

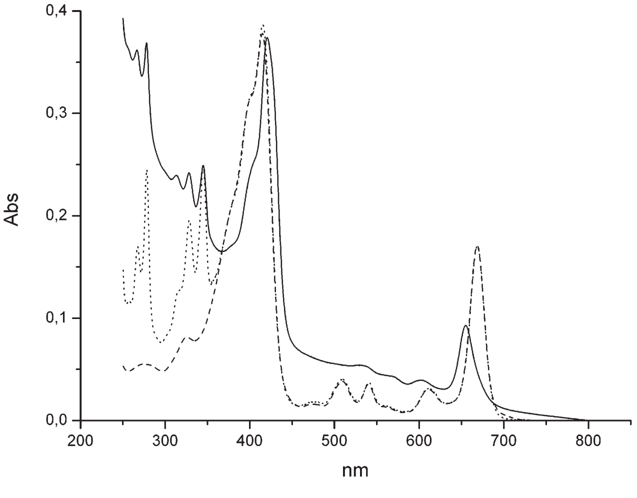

Fig. 1 UV/Vis absorbance spectra of **1b** (dash line), pyrene-*pyro*-pheophorbide *a*, **2** (dotted line) and **3** pentyl ester (solid line) measured in CHCl$_3$.

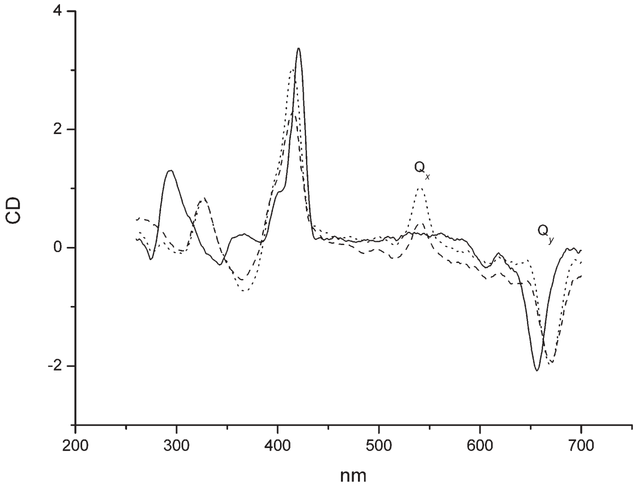

Fig. 2 CD spectra of **1b** (dash line), pyrene-*pyro*-pheophorbide *a*, **2** (dotted line) and **3** pentyl ester (solid line) measured in CHCl$_3$.

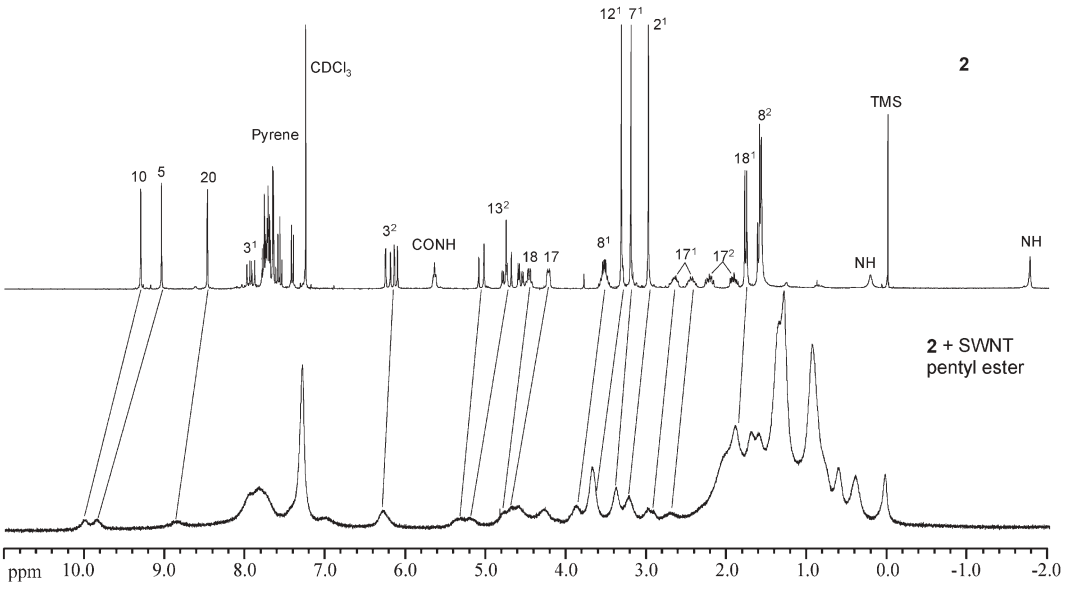

Fig. 3 ^{1}H NMR spectra of dyad **2** (above) and dyad **2** + SWNT pentyl ester (**3**) (below) measured in $CDCl_3$. The signals which could be reliably assigned in the spectrum (based on TOCSY and NOESY spectra) below are noted with lines.

state, Chl*-pyrene@SWNT, decays additionally *via* $\text{Chl}^{\bullet+}$-pyrene@$\text{SWNT}^{\bullet-}$ charge separated state. At present, we are looking for further prove for the mechanism by time-resolved absorbance measurements.

In summary, the pyrene guided van der Waals driven attachment of tethered chlorin to soluble SWNT walls was successfully conducted with a self-assembling approach. The presented technique can be potentially used in integration of biopigment material to CNT based electronic component material. Currently, we are extending our studies towards a wider range of chlorins to prepare bioderived self-assembling materials for electro-optical applications such as photovoltaic cells[1] and field effect transistors.[15]

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Notes and references

‡ The chlorophylls were extracted from spinach and purified according to reported procedure.[10] The Me-*pyro*-pheophorbide *a* (demethoxycarbonyl-pheophorbide *a*), **1b**, was prepared from corresponding pheophorbide by heating in pyridine.[11] The synthesis of dyad **2**: 50 mg (9.35×10^{-2} mmol) of **1a** was mixed with 18 mg (9.35×10^{-2} mmol) of EDCI in THF, 24 mg (1.03×10^{-1} mmol) of 1-methylaminopyrene was poured in and stirred over 16 h at RT. After aqueous workup the dried residue was purified with SiO_2 column chromatography to afford the product (28 mg, 3.74×10^{-2} mmol, 40%). R_f(ethyl acetate) = 0.29; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.31, 9.04, 8.53 (each 1H, s, 10-, 5-, 20-H), 7.93 (1H, dd, $^3J_{cis}$ = 11.4 Hz, $^3J_{trans}$ = 17.7 Hz, 3^1-H), 7.79–7.40 (9H, m, pyrene-ArH), 6.22 (1H, dd, $^2J_{gem}$ = 1.5 Hz, $^3J_{trans}$ = 18.3 Hz, 3^2_{trans}-H), 6.12 (1H, dd, $^2J_{gem}$ = 1.5 Hz, $^3J_{cis}$ = 11.4 Hz, 3^2_{cis}-H), 5.64 (1H, t, ^3J = 4.8 Hz, P1-NH), 5.06 (1H, d, $^2J_{gem}$ = 20.4 Hz, 13^2-H_A), 4.72 (1H, d, $^2J_{gem}$ = 20.4 Hz, 13^2-H_B), 4.77 (1H, dd, $^2J_{gem}$ = 14.4 Hz, ^3J = 4.8 Hz, P2-H_A), 4.57 (1H, dd, $^2J_{gem}$ = 14.4 Hz, ^3J = 4.8 Hz, P2-H_B), 4.47 (1H, dq, $^3J_{18,17}$ = 1.8 Hz, $^3J_{18,18}1$ = 6.9 Hz, 18-H), 4.23 (1H, m, 17-H), 3.52 (2H, m, 8^1-CH_2), 3.32, 3.20, 2.98 (each 3H, s, 2^1-, 7^1-, 12^1-H), 2.65–1.91 (each 1H, m, 17^1-, 17^2-CH_2), 1.77 (3H, d, $^3J_{18}1_{,18}$ = 7.2 Hz, 18^1-CH_3), 1.60 (3H, t, $^3J_82_{-8}1$ = 7.8 Hz, 8^2-CH_3). ESI HRMS: *m*/*z* 748.3652 (M^+H), calc.: 748.3658.

1 D. Gust, T. A. Moore and A. L. Moore, in *Artificial Photosynthesis*, ed. A. E. Collings, C. Critchley, Wiley-VHC, 2005, Weinheim, pp. 187–210.
2 G. D. Moore, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, **34**, 40; T. Konishi, A. Ikedab and S. Shinkai, *Tetrahedron*, 2005, **61**, 4881–4899.
3 T. Konishi, A. Ikedab and S. Shinkai, *Tetrahedron*, 2005, **61**, 4881–4899.
4 M. Meyyappan and D. Srivastava, in *Handbook of Nanoscience, Engineering and Technology*, ed. W. A. Goddard, III, D. W. Brenner, S. E. Lyshevski and G. J. Iafrate, CRC Press, 2003, Boca Raton, pp. 497–523.
5 D. Baskaran, J. W. Mays, X. P. Zhang and M. S. Bratcher, *J. Am. Chem. Soc.*, 2005, **127**, 6916–6917.
6 D. M. Guldi, G. N. A. Rahman, J. Ramey, M. Marcaccio, D. Paolucci, F. Paolucci, S. Qin, W. T. Ford, D. Balbinot, N. Jux, N. Tagmatarchis and M. Prato, *Chem. Commun.*, 2004, 2034–2035; D. M. Guldi, G. M. A. Rahman, M. Prato, N. Jux, S. Qin and W. Ford, *Angew. Chem., Int. Ed.*, 2005, **44**, 2015–2018.
7 D. Tasis, N. Tagmatarchis, A. Bianco and M. Prato, *Chem. Rev.*, 2006, **106**, 1105–1136.
8 D. M. Guldi, G. N. A. Rahman, F. Zerbetto and M. Prato, *Acc. Chem. Res.*, 2005, **38**, 871–878.
9 G. M. A. Rahman, D. M. Guldi, R. Cagnoli, A. Mucci, L. Schenetti, L. Vaccari and M. Prato, *J. Am. Chem. Soc.*, 2005, **127**, 10051–10057.
10 R. J. Chen, Y. Zhang, D. Wang and H. Dai, *J. Am. Chem. Soc.*, 2001, **123**, 3838–3839.
11 K. Iriyama, M. Shiraki and M. Yoshiura, *J. Liq. Chromatogr.*, 1979, **2**, 255–276.
12 F. C. Pennington, H. H. Strain, W. A. Svec and J. J. Katz, *J. Am. Chem. Soc.*, 1964, **86**, 1418–1426.
13 M. Alvaro, P. Atienzar, P. de la Cruz, J. L. Delgado, H. Garcia and F. Langa, *Chem. Phys. Lett.*, 2004, **386**, 342–345.
14 C. Houssier and K. Sauer, *J. Am. Chem. Soc.*, 1970, **92**, 779–791.
15 D. S. Hecht, R. J. A. Ramirez, M. Briman, E. Artukovic, K. S. Chichak, J. F. Stoddart and G. Grüner, *Nano Lett.*, 2006, **6**, 2031–2036.