Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2012, **22**, 59–61
Mendeleev Communications

Synthesis of phthalocyanine *tert*-butyl ligand conjugates with fluorine-containing single-walled carbon nanotubes having mobile ether bonds

Alexander Yu. Tolbin,[a] Valery N. Khabashesku[b] and Larisa G. Tomilova*[a,c]

[a] *Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 524 9508; e-mail: tolbin@inbox.ru*
[b] *Department of Chemistry and Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX, 77005-1892, USA. E-mail: khval@rice.edu*
[c] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 0290; e-mail: tom@org.chem.msu.ru*

DOI: 10.1016/j.mencom.2012.03.001

The covalently bonded phthalocyanine conjugates with fluorinated single-walled carbon nanotubes (F-SWCNTs) were synthesized and characterized by Raman and IR spectroscopy and TGA/DTG.

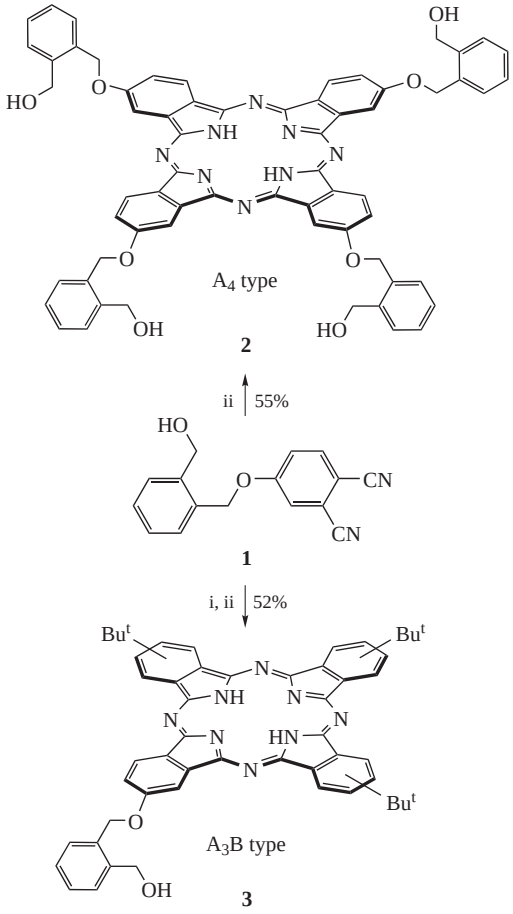
Phthalocyanines, which are synthetic analogues of natural porphyrins, are of interest due to their high chemical and thermal stability. These compounds display interesting electrical and electrochemical properties, which are important for applications in chemical sensors, liquid crystals, catalysis, nonlinear optics, optical data storage, nanotechnology[1,2] and as optical limiting materials due to their large optical non-linearities, ultrafast response times and ease of chemical modification.[3]

Carbon nanotubes (CNTs), representing a high aspect ratio one-dimensional π-conjugated nanoscale objects, possess a unique combination of mechanical, thermal and electrical properties, making this carbon allotrope a highly attractive material for applications as a reinforcing filler in polymers,[4,5] heat management components[6] and nanoelectronic devices.[7,8] For taking advantage of exceptional electrical characteristics of CNTs, recent advances[9,10] in linking specific groups or molecules to the nanotubes clearly show the strong potential of chemical functionalization not only for CNT solubilization and fine-tuning the tube electronic properties, but also to enable their assembly into more complex hybrid architectures required for integrated device operation.[11]

Peripherally functionalizated phthalocyanines having OH groups to modify their structures are of special interest for this purpose. Thus, the self-cyclization of phthalonitrile **1**[12] in the presence of MeOLi led us to target ligand **2** of A_4 type according to Scheme 1.†

The replacement of isoamyl alcohol in this synthesis[13] with *n*-hexanol has increased the yield of desired product **2** from 39 to 55%. Under similar conditions, the mixed cyclization of **1** with 4-*tert*-butylphthalonitrile[14,15] resulted in asymmetrically substituted phthalocyanine **3** of A_3B type.[16]

Benzyl alcohol fragments in compounds **2** and **3** opened the possibility to further modify F-SWCNT (C_2F) (Scheme 2).‡ Previously, nanotubes were suspended in DMF at 80 °C under ultrasonic irradiation. The reaction was conducted until the phthalocyanine color disappeared (UV-VIS control).

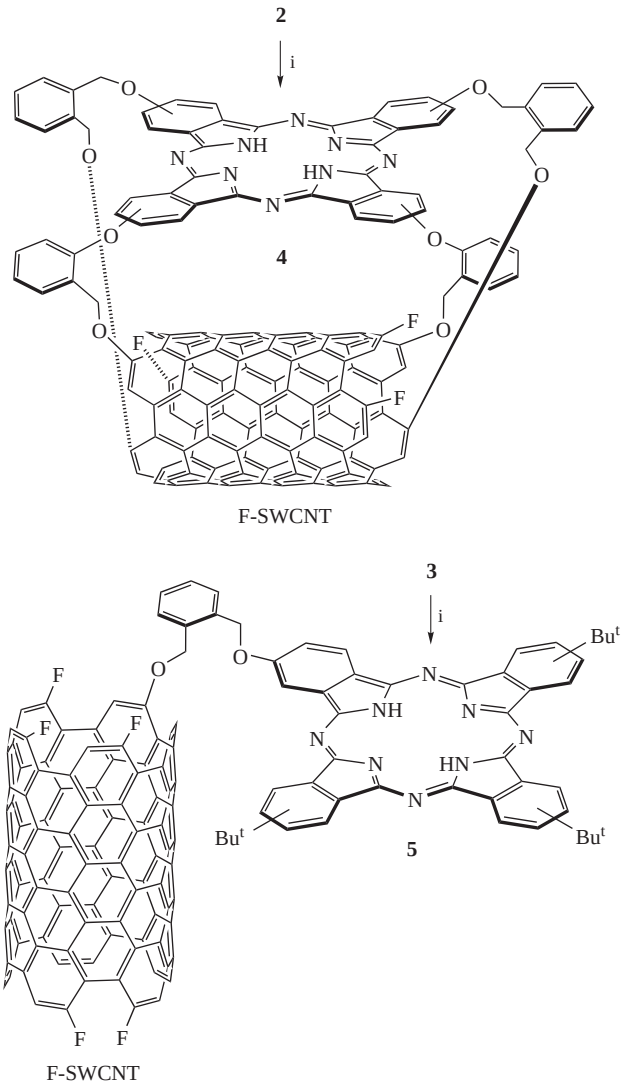


Scheme 1 *Reagents and conditions*: i, *tert*-butylphthalonitrile; ii, MeOLi/*n*-hexanol, reflux, 2.5 h.

With the use of IR spectroscopy, the covalent binding of phthalocyanines to the surface of F-SWCNT was proved. Thus, in the region of 1300–1000 cm^{-1}, we observed strong absorption, which is characteristic of ether bonds (Figure 1).

The TGA/DTG data also indicate the formation of covalent bonds between the phthalocyanine macrocycles and F-SWCNT surface (Figure 2). Thus, with gradually increasing the temperature in the range of 237–581 °C for phthalocyanines **2** and **3**

† *Synthesis of ligand* **2**. Lithium methoxide (252 mg, 6.65 mmol) was added to a solution of **1** (350 mg, 1.33 mmol) in *n*-hexanol (5 ml). The reaction was heated to reflux for 3 h. After reaction was finished, the solvent was evaporated, and crude products were treated with MeOH–H_2O (1:1) to give product **2**. Yield, 194 mg (55%). FT-IR (KBr, ν/cm^{-1}): 3400 (OH). MS (MALDI-TOF), *m*/*z* (%): 1058 $[M]^+$ (59), 817 $[M - 2C_8H_9O]^+$ (13), 698 $[M - 3C_8H_9O + H]^+$ (9), 577 $[M - 4C_8H_9O + H]^+$ (88). ^{1}H NMR (THF-d_8) δ: 4.94 (s, 8H, CH_2), 5.45 (s, 8H, CH_2OH), 7.10–7.42 (m, 16H, Ar), 7.48–7.86 (m, 12H, Ar). UV-VIS [THF, λ_{max}/nm (log ε)]: 343 (3.80), 665 (4.72), 704 (4.88).



Scheme 2 *Reagents and conditions*: i, F-SWCNT, DMF, DBU, 80 °C, 3.5 h.

[Figure 2(*a*) and (*b*)], two main maxima in DTG curves are observed (Table 1). Preliminary analysis led us to conclude that the destructive fragmentation of peripheral phthalocyanine substituents is the first stage of the process followed by the extreme degradation of macrocycles at the last decomposing stage. The mass loss in the region of 400–600 °C is characteristic of CNTs. At the same time, peaks in the DTG of phthalocyanines **2** and **3** may be attributed to the formation of corresponding ordered phases during the thermal processes. The strong difference in the nature of the DTG curves of conjugates **4** and **5** from starting

‡ *Synthesis of conjugates* **4** *and* **5**. To solutions of phthalocyanines **2** and **3** (0.04 mmol) in DMF (3 ml), F-SWCNT (C_2F, 0.93 mmol) and a catalytic amount of DBU were added. The mixtures were subjected to ultrasonic irradiation (320 W, 35 KHz) at 80 °C for 3.5 h. The reactions were controlled by UV-VIS spectroscopy and carried out until a phthalocyanine color disappeared. After the reactions finished, the mixtures were filtered off, washed with DMF and THF (3×30 ml) and dried at 40 °C.

For **4**: XPS elemental analysis data (%): C, 83.14; N, 5.77; O, 7.74; F, 3.34. FTIR (KBr, ν/cm^{-1}): 3413 (=NH), 2917, 2850 (C–H_{Ar}), 1045 (CH_2–O). Raman (780 nm, ν/cm^{-1}): 2570 (SWCNT–OPc), 1575 (G-band), 1292 (D-band). TGA [*in vacuo*, 53 K min^{-1}, loss% (T_{max}/°C)]: 30.48 (274, Pc elimination), 6.04 (588, rough destruction).

For **5**: FTIR (KBr, ν/cm^{-1}): 3434 (=NH), 2913, 2846 (C–H_{Ar}), 1084 1045 (CH_2–O). Raman (780 nm, ν/cm^{-1}): 2564 (SWCNT–OPc), 1560 (G-band), 1276 (D-band). TGA [*in vacuo*, 53 K min^{-1}, loss% (T_{max}/°C)]: 11.75 (210, Pc elimination), 5.39 (484, rough destruction).

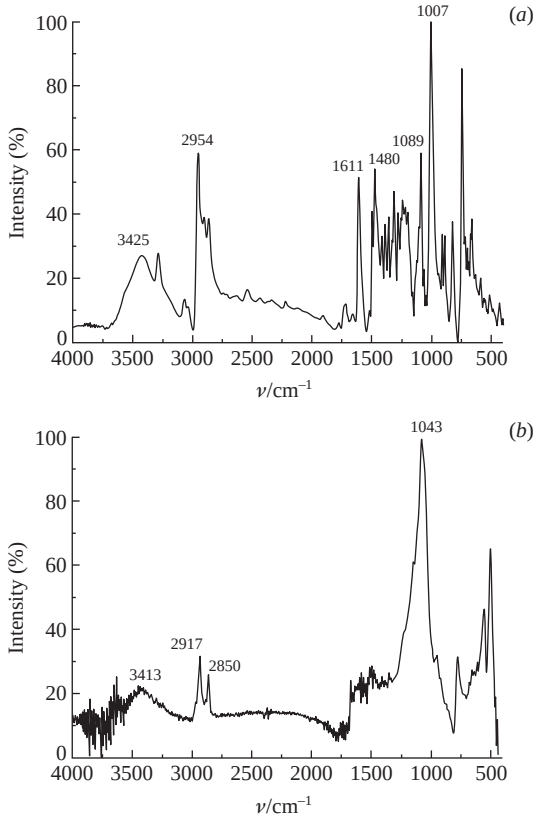


Figure 1 FTIR (KBr) spectra of (*a*) ligand **2** and (*b*) its conjugate with F-SWCNT.

phthalocyanines **2** and **3** provides evidence for the covalent bonding of macrocycles with the surface of F-SWCNT.

It is important to pay attention to the similarity of the destructive processes of conjugates **4** and **5**. Initially, we observed the thermal elimination of phthalocyanine macrocycles (total mass losses of about 30 and 10%, respectively) followed by the destruction of the nanotubes with a mass loss of about 6%. The final phase for all compounds, apparently, may be carbon black, which is indirectly indicated by the absence of peaks in DTG above 600 °C.

The Raman spectra (780 nm) of the initial F-SWCNT, as well as conjugates **4** and **5**, are shown in Figure 3. Thus, during the substitution of fluorine atoms, the ratio of the D and G bands decreases in the spectra, which is consistent with experimental data.[17] At the same time, the intensity of D bands decreases because of a decrease in the fluorine content of the conjugates. The presence of additional peaks at 2564 and 2570 cm^{-1}, respectively, was due to the formation of additional covalent bonds (ether linkages of phthalocyanine ligands with CNTs).

Thus, the conjugates of *tert*-butyl substituted phthalocyanines with F-SWCNT were synthesized. Owing to highly ordered surfaces, the compounds may be promising catalysts.

Table 1 TGA data for compounds **2**–**5**.

Compound	Temperature range/°C	Half-period temperature decomposition/°C (DTG)	Weight loss (%)
2	237–357	321	16.33
	357–491	395	11.77
	491–847	553	13.19
3	253–363	363	8.70
	363–581	581	35.28
4	121–538	274	30.48
	538–785	588	6.04
5	131–260	210	11.75
	439–551	484	5.39

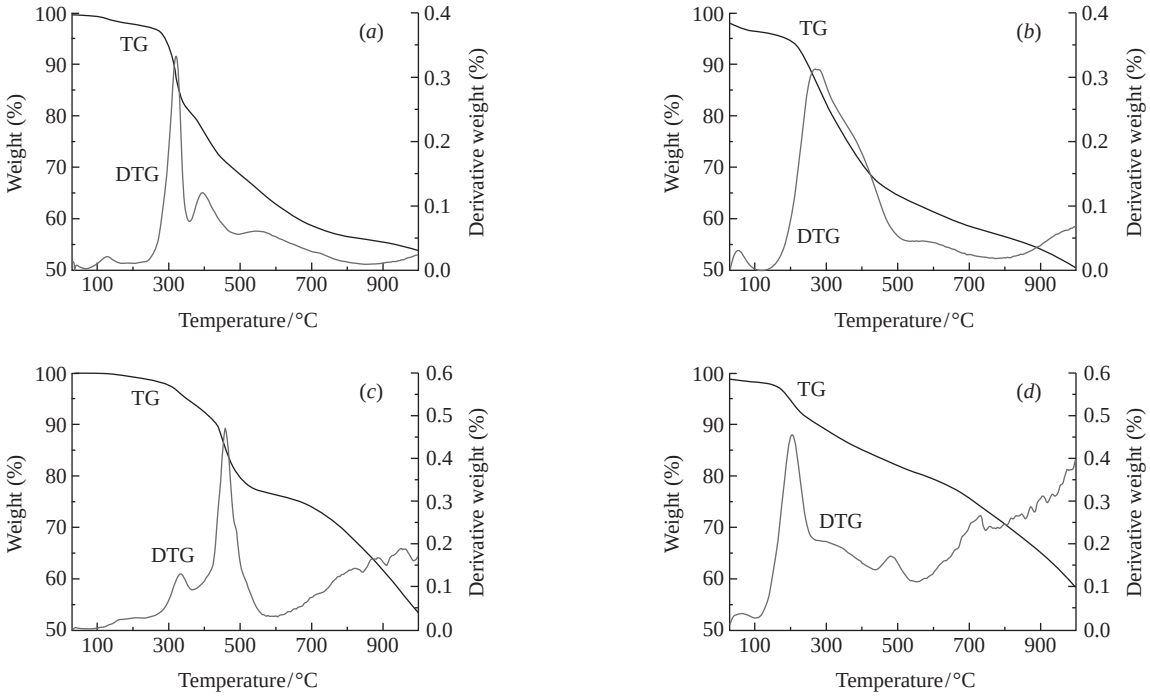


Figure 2 TGA curves for phthalocyanine ligands (*a*) **2** and (*c*) **3** and (*b*), (*d*) corresponding conjugates with F-SWCNT.

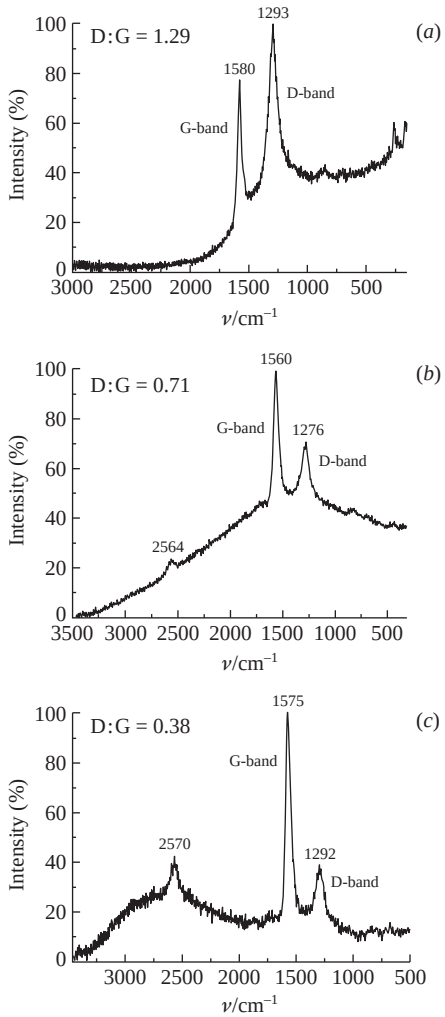


Figure 3 Raman spectra (780 nm laser) of (*a*) starting F-SWCNT and conjugates (*b*) **5** and (*c*) **4**.

This work was supported by the Russian Foundation for Basic Research (grant no. 05-03-33202) and the Programme for Fundamental Studies of the Presidium of the Russian Academy of Sciences ‘Development of Methods for Synthesising Chemical Compounds and Creating New Materials’.

References

1 M. Hanack and M. Lang, *Adv. Mater.*, 1994, **6**, 819.
2 S. Huang, L. Dai and A. W. H. Mau, *J. Phys. Chem. B*, 1999, **103**, 4223.
3 Y. Liu, Y. Chen, L. Z. Cai, J. Wang, Y. Lin, J. J. Doyle and W. J. Blau, *Mater. Chem. Phys.*, 2008, **107**, 189.
4 P. M. Ajayan, L. S. Schadler, C. Giannaris and A. Rubio, *Adv. Mater.*, 2000, **12**, 750.
5 M. X. Pulikkathara, O. V. Kuznetsov, I. R. G. Peralta, X. Wei and V. N. Khabashesku, *Nanotechnology*, 2009, **20**, 195602.
6 S. Shenogin, A. Bodapati, L. Xue, R. Ozisik and P. Keblinski, *Appl. Phys. Lett.*, 2004, **85**, 2229.
7 A. N. Cleland, *Nature*, 2004, **431**, 251.
8 M. Chlao, *Nature*, 2004, **428**, 481.
9 V. N. Khabashesku, W. E. Billups and J. L. Margrave, *Acc. Chem. Res.*, 2002, **35**, 1087.
10 V. N. Khabashesku and M. X. Pulikkathara, *Mendeleev Commun.*, 2006, 61.
11 R. S. B. K. Kerenm, E. Buchstab, U. Sivan and E. Braun, *Science*, 2003, **302**, 1380.
12 A. Yu. Tolbin, A. V. Ivanov, L. G. Tomilova and N. S. Zefirov, *J. Porphyrins Phthalocyanines*, 2003, **7**, 162.
13 A. Yu. Tolbin and L. G. Tomilova, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 2350 (*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 2433).
14 M. Hanack, J. Metz and G. Pawlowski, *Chem. Ber.*, 1982, **34**, 2836.
15 B. W. Larner and A. T. Peters, *J. Chem. Soc.*, 1952, 680.
16 A. Yu. Tolbin, V. E. Pushkarev, G. F. Nikitin and L. G. Tomilova, *Tetrahedron Lett.*, 2009, **50**, 4848.
17 D. McIntosh, V. N. Khabashesku and E. V. Barrera, *Chem. Mater.*, 2006, **18**, 4561.

Received: 25th October 2011; Com. 11/3820