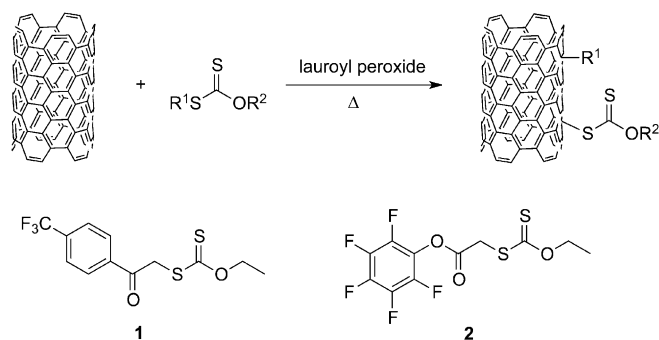


Radical Addition of Xanthates on Carbon Nanotubes as an Efficient Covalent Functionalization Method

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Carbon nanotubes (CNTs) attract wide interest because of their outstanding properties, leading to applications in various domains such as electronics, material engineering, gas storage, drug delivery and catalysis.^[1] CNTs are also used as nanoparticle (NP) supports for applications in sensors, fuel cells and composite materials.^[2] However, to implement carbon nanotubes in such applications, chemical modification is required. As a consequence, many efforts have been driven during the last decade by developing CNT chemical functionalization processes.^[3] These are usually grouped into three main routes: non-covalent, defect-site, and covalent sidewall functionalization. Among them, the most promising seems to be covalent functionalization because it produces highly functionalized nanotubes exhibiting good dispersion of strongly bonded moieties. Reported sidewall grafting reactions are mainly fluorination, cycloaddition, carbene or nitrene addition, and reactions involving radicals.^[4] The most frequently used radicals for CNT functionalization are obtained from the decomposition of diazonium salts or organic peroxides.^[5]

We report here a new approach for carbon nanotubes covalent functionalization by using xanthates as radical precursors. These compounds are known to react with non-activated olefins and arenes to create new carbon–carbon bonds through activation by a radical initiator.^[6] We based our hypothesis on the fact that CNTs may be regarded as polyolefins, capable of reacting with xanthates (Scheme 1). This approach is advantageous compared with the other radical methods cited above, since the mechanism is self-regulated due to a degenerative equilibrium; therefore, it allows the production of functionalized radicals in a controlled manner. Moreover, xanthate reagents are easily prepared and offer a wide range of functionalities. In this work, two model xanthates **1** and **2**, both fluorinated, have been selected for initial studies (Scheme 1), in combination with lauroyl peroxide (DLP) as the radical initiator. The first model was



Scheme 1. Functionalization of CNTs by xanthates **1** and **2**.

used to optimize reaction parameters, whereas the second one allowed us to obtain the activated-ester-functionalized CNTs, which may be further derivatized.

Covalent functionalization of single-walled nanotubes (SWNTs) involving fluorinated functions have already appeared elsewhere. Kawasaki et al.^[7] reported grafting yields of open and closed SWNTs by fluorination, that is, by reacting SWNTs samples with elemental fluorine gas at different temperatures (300–523 K) for different time periods (5 h–1 month). However, xanthate functionalization is advantageous because it is an easy process compared with fluorination since it does not imply gaseous reagents, high temperatures, or long reaction times. Moreover, xanthate functionalities are easily tuned, offering a large scope of products, whereas applications of fluorinated-SWNTs require post-functionalization to implement them in practical devices. Another typical example of SWNTs covalent fluorine-containing functionalization has been reported by Bahr et al.^[5a] This implies the well-known aryl diazonium salts reaction initiated by electrochemical reduction. It should be noted that this was performed on very small amounts of SWNTs (1–2 mg) of a small diameter selected for their higher reactivity.

The prime materials to be functionalized in the present study were multi-walled nanotubes (MWNTs) because they offer the advantages of being available to functionalize the external layer while being stabilized by the internal layers, and also resilient enough to be used in devices. However, we also used SWNTs as a tool because they allow spectroscopic characterization and distinct applications. TEM images of the pristine (*p*)-MWNTs used in this work revealed an average of 10 concentric graphene layers per tube (see Figure S1a and b in the Supporting Information).

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For the initial optimization experiments, each reaction was carried out on a 24 mg amount (2 mmol C atoms) of MWNTs with varying amounts of xanthates and DLP. TEM images (see Figure S1c and d in the Supporting Information) showed that the nanotube integrity was preserved after the functionalization procedure and XPS revealed non-negligible amounts of fluorine arising from the xanthate surface functionalization. Four different parameters were modified to optimize the grafting yield of xanthate **1** on MWNTs, namely the 1) xanthate concentration, 2) radical initiator concentration, 3) portionwise additions of radical initiator and 4) reaction time. Only the two former parameters were actually found to influence the functionalization level: the higher the xanthate and initiator concentrations, the higher the grafting yield (Figure 1). These experiments also showed

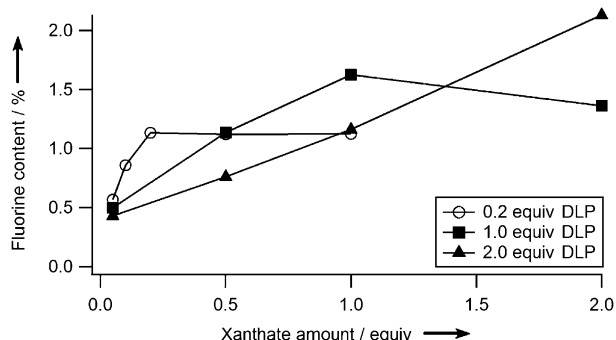


Figure 1. Fluorine surface concentrations determined by XPS as a function of the amount of xanthate **1**.

that the highest fluorine surface concentrations are obtained when xanthate and DLP are introduced in stoichiometric amounts. The number of DLP additions or the reaction time had negligible influence on the functionalization yield (see Figure S2 and Tables S1 and S2 in the Supporting Information). Taking into account the sulfur content of *p*-MWNTs, it should be noted that only the R¹ group of the starting xanthate is grafted onto the CNT, whereas the sulfur-containing moiety is not significantly present on the surface of the functionalized CNT (see Table S3 in the Supporting Information for numerical values). Measured F/S ratios are indeed very different from the theoretical value of 1.5 which would be observed if R¹ and R² moieties were grafted in stoichiometric proportions.

Similar experiments were carried out with xanthate **2** on MWNTs (Figure 2 and Tables S4 and S5 in the Supporting Information) and they led to the same conclusions, that is, negligible sulfur contents and highest fluorine rates for stoichiometric DLP/xanthate ratios. The fluorine amounts are slightly lower with xanthate **2** than with **1**, whereas F/S ratios are also different from the theoretical value (here 2.5).

The same methodology was applied to SWNTs under the optimized conditions for further characterizations by using spectroscopic techniques. In the case of SWNTs, the surface

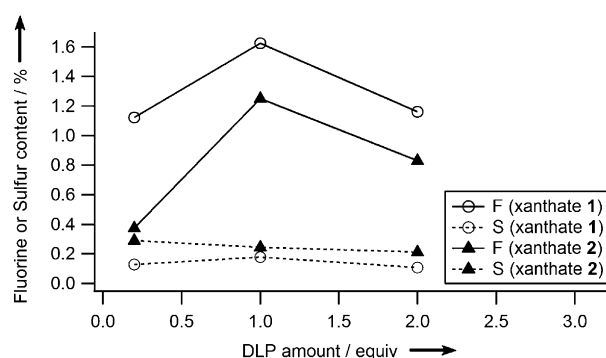


Figure 2. Fluorine and sulfur surface concentrations determined by XPS as a function of the amount of DLP for xanthates **1** and **2** (1 equiv).

F/C ratios obtained by XPS were higher (Table 1), which is in line with the absence of internal non-functionalizable carbon layers. Reported surface F/C ratios ranged from 0.23 to 0.51 in the case of direct fluorination of SWNTs,^[7] which is approximately 10–25 times higher than here (0.02). Fluorophenyl-functionalized SWNTs obtained by using aryl diazonium salts^[5a] presented a surface F/C atomic ratio of 0.037; this is very similar to our results.

Table 1. Comparison of F/C ratios obtained by XPS and EA.

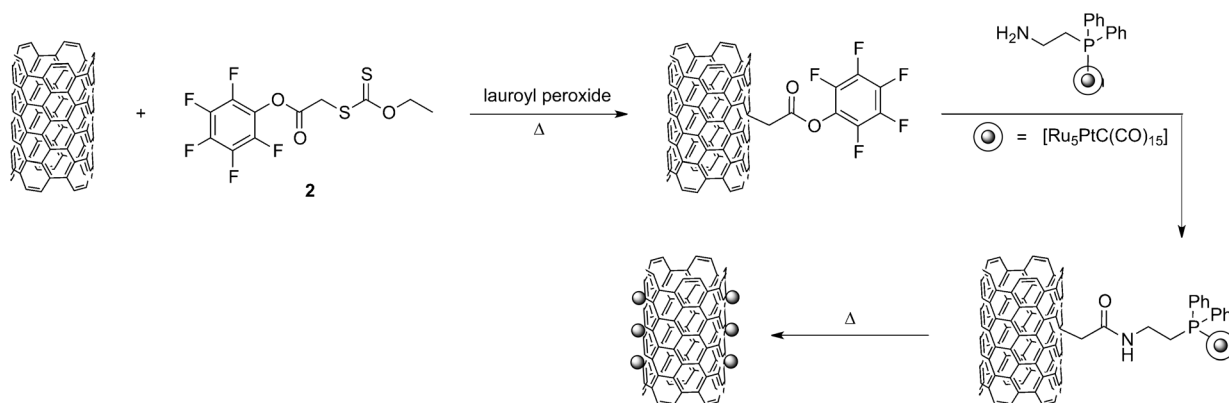
	F/C molar ratios	
	<i>f</i> -MWNTs (1:1:1) ^[a]	<i>f</i> -SWNTs (1:1:1) ^[a]
XPS	0.0131	0.0189
EA	0.0076	0.0198

[a] (Xanthate **2**/DLP/C from nanotube) equivalents.

XPS is used as a routine technique for the quantitative analysis of functionalized nanotubes throughout the literature. However, its information depth is of the same order of magnitude than MWNT diameters. Therefore, a bulk elemental analysis (EA) is required to obtain more reliable quantitative concentrations in each heteroelement within the sample. EA indeed revealed a smaller F/C ratio than XPS in the case of MWNTs, meaning that XPS only probes a fraction of the concentric carbonaceous layers. This hypothesis is confirmed by the fact that in the case of SWNTs, which comprise only one graphene layer, the F/C ratios obtained by XPS and EA are in agreement.

The covalent nature of the bond between the R¹ moiety and the nanotube framework was proven using Raman spectroscopy and thermogravimetric analysis (TGA). Indeed the Raman spectrum of functionalized (*f*)-SWNTs exhibits a large increase of the so-called D band, attributed to sp³-hybridized carbon atoms, located at 1277 cm⁻¹, compared with the Raman spectrum of pristine nanotubes (Figure 3). TGA revealed a mass loss at higher temperature in the *f*-SWNTs case than with a *p*-SWNTs/xanthate physical mixture (see Figure S3 in the Supporting Information).

The grafted fragments were used as tethers for clusters to probe their reactivity. These clusters can be used as molecular precursors of NPs. Molecular clusters can be modified by



Scheme 2. Reaction scheme for the post-functionalization of carbon nanotubes. Filled sphere = metallic core, empty circle = ligand shell.

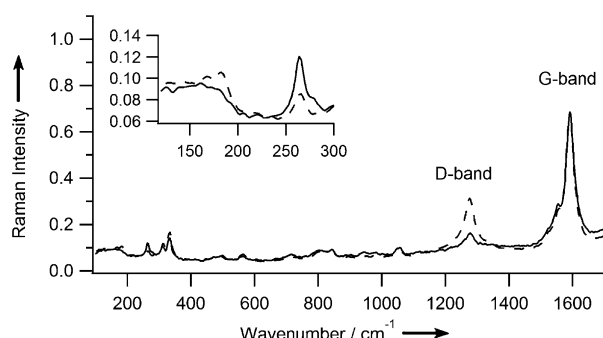


Figure 3. Raman spectra ($\lambda = 1064$ nm) of pristine- (—) and functionalized- (---) SWNTs. Inset shows a magnification of the radial breathing modes.

ligand exchange to introduce in their coordination sphere a reactive fragment capable of covalently binding to a functionalized surface. Moreover, when multimetallic, they are excellent precursors of bimetallic nanoparticles. Given that xanthate **2** contains an activated ester function, an amine-containing ligand was selected (Scheme 2). The cluster $[\text{Ru}_5\text{PtC}(\text{CO})_{16}]$ was treated with 2-(diphenylphosphino)-ethylamine and the $\text{NH}_2(\text{CH}_2)_2\text{PPh}_2\text{Ru}_5\text{PtC}(\text{CO})_{15}$ adduct was obtained.

This adduct was then reacted with MWNTs functionalized with xanthate **2**, to covalently attach the precursor to the CNT. This was performed in solution followed by filtering. A control experiment was carried out with pristine-MWNT in the presence of a Ru_5Pt cluster solution: 0% loading of the cluster on the non-functionalized carbon surface was ob-

served. The final NP/CNT nanocomposite was obtained by treatment at 350°C ; this temperature being determined by TGA analysis of the pure cluster. After such a treatment, the material is converted into bimetallic NPs, stripped off the ligands, and supported on CNTs.

The samples at each step in the preparation of the nanostructured material were characterized by XPS and EA (Table 2). Before activation, the cluster was indeed tethered to the tube surface, as evidenced by the decrease of fluorine content with concomitant appearance of Ru and Pt. The Ru/Pt ratio being close to the theoretical value of 5 indicates that the cluster keeps its integrity. After activation, no more fluorine remains, meaning that the organic moiety has been released upon heating. The Ru/Pt ratio obtained by XPS after activation demonstrates some surface rearrangements; whereas the Ru/Pt ratio close to 5 obtained by EA shows that the global composition is preserved. Finally, also according to the EA results, the final sample of NP/CNT contains about 2 wt % of metal (Ru + Pt), which is sufficient for most applications.

Those samples were also characterized by secondary ion mass spectrometry (SIMS, Figure S4a–d in the Supporting Information). The pure cluster SIMS spectrum (Figure S4a) revealed a typical fragmentation pattern for clusters (successive CO losses). Before heating (Figure S4b), the supported cluster revealed peaks arising from the metallic core of the cluster. Finally, after activation, only a few peaks arising from the cluster core still appear, namely Ru–Ru and Ru–Pt fragments.

After thermal treatment the supported clusters were also characterized by TEM. The micrograph (Figure 4) showed

Table 2. Characterization by XPS and EA of samples at each step of NP/CNT preparation.

	C	F	Element content		Ru	Pt	Ru/Pt	Molar ratios	
			P	N				Ru/C ^[c]	Pt/C ^[c]
f-MWNTs	95.10 ^[a]	1.25 ^[a]	N/A	N/A	N/A	N/A	N/A	N/A	N/A
cluster	95.12 ^[a]	0.72 ^[a]	0.06 ^[a]	0.28 ^[a]	0.28 ^[a]	0.06 ^[a]	4.7	0.30	0.06
supported									
activated	97.55 ^[a]	0.01 ^[a]	0.05 ^[a]	0.23 ^[a]	0.34 ^[a]	0.05 ^[a]	6.8	0.35	0.05
NP/CNT	89.24 ^[b]	N/A	0.14 ^[b]	0.60 ^[b]	1.35 ^[b]	0.62 ^[b]	4.2	0.18	0.04

[a] XPS (at %). [b] EA (wt %). [c] $\times 100$.

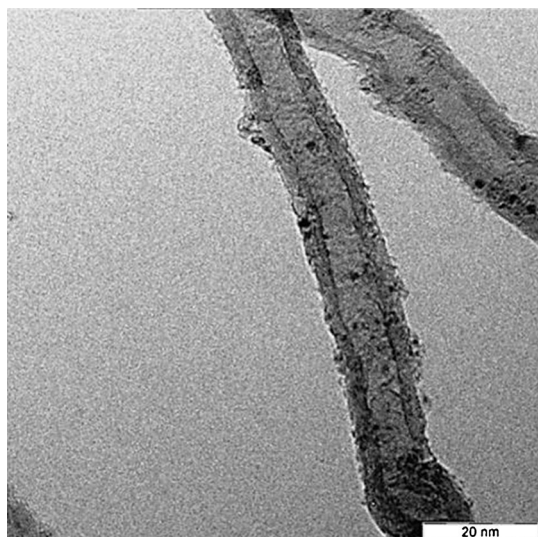


Figure 4. TEM image of nanoparticles supported on CNT.

that homogeneously dispersed metallic nanoparticles of 1–2 nm in size were obtained. This is lower than previous published results of Ru–Pt NPs supported on CNTs.^[8] Retro-spectively, this also proves the homogeneity of xanthate functionalization.

In conclusion, we have proven that xanthate is capable of reacting with the CNT surface thanks to a radical mechanism. Only the moiety containing no sulfur is grafted on the tube surface. Two different xanthates were used and have shown a similar behavior when varying the reaction parameters. Reactions involving SWNTs have proven the covalent nature of such functionalization. The activated ester groups introduced on CNTs from xanthate reactants were further implemented as an anchor for molecular clusters, which after activation led to supported bimetallic NPs of 1–2 nm in size. This new approach of CNT functionalization by xanthates offers the advantages of easy processing and versatility, which could lead to a large variety of adducts towards applications in a multitude of domains.

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- [1] a) Y.-L. Zhao, J. F. Stoddart, *Acc. Chem. Res.* **2009**, *42*, 1161–1171; b) Y. Lee, K. E. Geckeler, *Adv. Mater.* **2010**, *22*, 4076–4083; c) G. Pastorin, *Pharm. Res.* **2009**, *26*, 746–769; d) M. Prato, K. Kostarelos,

- A. Bianco, *Acc. Chem. Res.* **2008**, *41*, 60–68; e) Z. Liu, S. Tabakman, K. Welscher, H. Dai, *Nano Res.* **2009**, *2*, 85–120.
- [2] a) G. G. Wildgoose, C. E. Banks, R. G. Compton, *Small* **2006**, *2*, 182–193; b) V. Tzitzios, V. Georgakilas, E. Oikonomou, M. Karakassides, D. Petredis, *Carbon* **2006**, *44*, 848–853.
- [3] a) D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* **2006**, *106*, 1105–1136; b) X. Peng, S. S. Wong, *Adv. Mater.* **2009**, *21*, 625–642; c) N. Karousis, N. Tagmatarchis, D. Tasis, *Chem. Rev.* **2010**, *110*, 5366–5397.
- [4] a) M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weiss, F. Jellen, *Angew. Chem.* **2001**, *113*, 4132–4136; *Angew. Chem. Int. Ed.* **2001**, *40*, 4002–4005; b) A. Hirsch, *Angew. Chem.* **2002**, *114*, 1933–1939; *Angew. Chem. Int. Ed.* **2002**, *41*, 1853–1859; c) V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **2002**, *124*, 760–761; d) V. Georgakilas, N. Tagmatarchis, D. Pantarotto, A. Bianco, J.-P. Briand, M. Prato, *Chem. Commun.* **2002**, 3050–3051; e) M. Holzinger, J. Abraham, P. Whelan, R. Graupner, L. Ley, F. Hennrich, M. Kappes, A. Hirsch, *J. Am. Chem. Soc.* **2003**, *125*, 8566–8580; f) K. S. Coleman, S. R. Bailey, S. Fogden, M. L. H. Green, *J. Am. Chem. Soc.* **2003**, *125*, 8722–8723; g) M. Alvaro, P. Atienzar, P. de La Cruz, J. L. Delgado, H. Garcia, F. Langa, *J. Phys. Chem. B* **2004**, *108*, 12691–12697; h) S. Banerjee, T. Hemraj-Benny, S. S. Wong, *Adv. Mater.* **2005**, *17*, 17–29; i) J. Li, H. Grennberg, *Chem. Eur. J.* **2006**, *12*, 3869–3875; j) C. Ménard-Moyon, N. Izard, E. Doris, C. Mioskowski, *J. Am. Chem. Soc.* **2006**, *128*, 6552–6553; k) B. Ballesteros, G. de La Torre, C. Ehli, G. M. A. Rahman, F. Agullo-Rueda, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2007**, *129*, 5061–5068; l) F. G. Brunetti, M. A. Herrero, J. de M. Munoz, S. Giordani, A. Diaz-Ortiz, S. Filippone, G. Ruaro, M. Meneghetti, M. Prato, E. Vazquez, *J. Am. Chem. Soc.* **2007**, *129*, 14580–14581; m) B. Ballesteros, S. Campidelli, G. de La Torre, C. Ehli, D. M. Guldi, M. Prato, T. Torres, *Chem. Commun.* **2007**, 2950–2952; n) S. J. Pastine, D. Okawa, B. Kessler, M. Rolandi, M. Llorente, A. Zettl, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2008**, *130*, 4238–4239; o) V. Georgakilas, A. B. Bourlinos, R. Zboril, C. Trapalis, *Chem. Mater.* **2008**, *20*, 2884–2886; p) W. Zhang, A. U. Shaikh, E. Y. Tsui, T. M. Swager, *Chem. Mater.* **2009**, *21*, 3234–3241; q) W. Zhang, J. K. Sprafke, M. Ma, E. Y. Tsui, S. A. Sydlík, G. C. Rutledge, T. M. Swager, *J. Am. Chem. Soc.* **2009**, *131*, 8446–8454; r) P. Singh, S. Campidelli, S. Giordani, D. Bonifazi, A. Bianco, M. Prato, *Chem. Soc. Rev.* **2009**, *38*, 2214–2230; s) E. J. Lawrence, G. G. Wildgoose, L. Aldous, Y. A. Wu, J. H. Warner, R. G. Compton, P. D. McNaughton, *Chem. Mater.* **2011**, *23*, 3740–3751; t) G. Giambastiani, S. Cicchi, A. Giannasai, L. Luconi, A. Rossin, F. Mercuri, C. Bianchini, A. Brandi, M. Melucci, G. Ghini, P. Stagnaro, L. Conzatti, E. Passaglia, M. Zoppi, T. Montini, P. Fornasiero, *Chem. Mater.* **2011**, *23*, 1923–1938.
- [5] a) J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, J. M. Tour, *J. Am. Chem. Soc.* **2001**, *123*, 6536–6542; b) S. E. Kooi, U. Schlecht, M. Burghard, K. Kern, *Angew. Chem.* **2002**, *114*, 1409–1411; *Angew. Chem. Int. Ed.* **2002**, *41*, 1353–1355; c) H. Peng, L. B. Alemany, J. L. Margrave, V. N. Khabashesku, *J. Am. Chem. Soc.* **2003**, *125*, 15174–15182; d) H. Peng, P. Reverdy, V. N. Khabashesku, J. L. Margrave, *Chem. Commun.* **2003**, 362–363; e) J. L. Hudson, M. J. Casavant, J. M. Tour, *J. Am. Chem. Soc.* **2004**, *126*, 11158–11159; f) C. A. Dyke, J. M. Tour, *J. Am. Chem. Soc.* **2003**, *125*, 1156–1157; g) C. A. Dyke, J. M. Tour, *Nano Lett.* **2003**, *3*, 1215–1218; h) Z. Peng, A. H. Holm, L. T. Nielsen, S. U. Pedersen, K. Daasbjerg, *Chem. Mater.* **2008**, *20*, 6068–6075; i) G. Schmidt, S. Gallon, S. Esnouf, J.-P. Bourgoin, P. Chenevier, *Chem. Eur. J.* **2009**, *15*, 2101–2110.
- [6] Reviews a) B. Quiclet-Sire, S. Z. Zard, *Chem. Eur. J.* **2006**, *12*, 6002–6016; b) B. Quiclet-Sire, S. Z. Zard, *Pure Appl. Chem.* **2011**, *83*, 519–551; c) B. Quiclet-Sire, S. Z. Zard, *Chimia* **2012**, *66*, 404–412; d) M. El Qacemi, L. Petit, B. Quiclet-Sire, S. Z. Zard, *Org. Biomol. Chem.* **2012**, *10*, 5707–5719. For recent examples, see e) M.-G. Braun, B. Quiclet-Sire, S. Z. Zard, *J. Am. Chem. Soc.* **2011**, *133*, 15954–15957; f) B. Quiclet-Sire, N. Tölle, S. N. Zafar, S. Z. Zard, *Org. Lett.* **2011**, *13*, 3266–3269; g) M.-G. Braun, R. Heng, S. Z. Zard, *Org. Lett.* **2011**, *13*, 1230–1233; h) M.-G. Braun, S. Z. Zard, *Org. Lett.* **2011**, *13*, 776–779; i) L. Debien, B. Quiclet-Sire, S. Z. Zard, *Org. Lett.* **2011**, *13*,

- 5676–5679; j) B. Hawkins, V. L. Paddock, N. Tölle, S. Z. Zard, *Org. Lett.* **2012**, *14*, 1020–1023; k) B. Quiclet-Sire, N. Diem My Tran, S. Z. Zard, *Org. Lett.* **2012**, *14*, 5514–5517.
- [7] S. Kawasaki, K. Komatsu, F. Okino, H. Touhara, H. Kataura, *Phys. Chem. Chem. Phys.* **2004**, *6*, 1769–1772.
- [8] a) Y.-L. Yao, Y. Ding, L.-S. Ye, X.-H. Xia, *Carbon* **2006**, *44*, 61–66; b) J. Li, Y. Liang, Q. Liao, X. Zhu, X. Tian, *Electrochim. Acta* **2009**, *54*, 1277–1285.

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