

# Chemical improvement of surfaces. Part 2: Permanent hydrophobization of wood by covalently bonded fluoroorganyl substituents

Martin H.H. Drafz<sup>1</sup>, Sebastian Dahle<sup>2,3</sup>,  
Wolfgang Maus-Friedrichs<sup>2,3</sup>, Jan C. Namyslo<sup>1</sup>  
and Dieter E. Kaufmann<sup>1,\*</sup>

<sup>1</sup> Clausthal University of Technology, Institute of Organic Chemistry, Clausthal-Zellerfeld, Germany

<sup>2</sup> Clausthal University of Technology, Clausthal Centre of Materials Technology, Clausthal-Zellerfeld, Germany

<sup>3</sup> Clausthal University of Technology, Institute of Energy Research and Physical Technologies, Clausthal-Zellerfeld, Germany

\*Corresponding author.

Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstrasse 6, D-38678 Clausthal-Zellerfeld, Germany

E-mail: dieter.kaufmann@tu-clausthal.de

## Abstract

A recently developed esterification method in our laboratory was applied to permanent hydrophobization of wood surfaces. Specifically, the covalent attachment of fluoroorganyl substituents to wood hydroxy groups via benzotriazolyl-activated, substituted benzoic acids was in focus. Weight percent gain values from 10% to 28% were obtained on Scots pine (*Pinus sylvestris*) sapwood veneer chips. It proved feasible to lower the temperature for wood modification from 150°C to 120°C, or even to 70°C so that thermal decomposition of wood during modification can be neglected. The modified chips were analyzed by attenuated total reflection – infrared and X-ray photoelectron spectroscopy. Covalent attachment of the fluoro-benzoic acids led to a very high, permanent hydrophobicity of the wood surface, documented by outstanding contact angles of up to 143°.

**Keywords:** attenuated total reflection IR (ATR-IR); contact angle (CA); covalent fixation; esterification; fluorine; hydrophobation of wood surface; X-ray photoelectron spectroscopy (XPS).

## Introduction

Unmodified natural wood suffers from degradation by environmental influences and biological deterioration. Hydrophobization of wood surfaces is a means of combating these adversities (Hill et al. 2009). Permanent, protective modification of wood can be achieved by covalent attachment

of, for example, an organoboryl-function by means of an esterification with benzotriazole (Bzt)-activated benzoic acids (Namyslo and Kaufmann 2009). Hydrophobization is an effective approach as in most cases a certain moisture content of wood is a prerequisite for fungal decay (Haygreen and Bowyer 1982; Kazemi et al. 2001; Weigenand et al. 2008; Iaych et al. 2010). Hydrophobization of wood veneers can be improved by combining the Bzt-based wood esterification protocol with appropriate fluoroorganyl precursors, as demonstrated by infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), weight percentage gain (WPG) determinations and contact angle (CA) measurements.

The usefulness of XPS should be emphasized in this context (Dorris and Gray 1978; Jaic et al. 1996). This method was utilized to study the aging (Popescu et al. 2009; Bryne et al. 2010) and the oxidization of wood (Hon 1984), as well as to understand the effect of surface treatments (Williams and Feist 1984; Ostmeier et al. 1988; de Lange et al. 1992; Kazayawoko et al. 1999) not only on wood but also on pulp and paper (Barry and Koran 1990). The combination of XPS with other methods, especially with Fourier transform IR (FTIR) and CA measurements is very common (Felix and Gatenholm 1991; Mohammed-Ziegler et al. 2003; Stark and Matuana 2007; Bryne and Wälinder 2010; Bryne et al. 2010).

The investigation of wood surfaces with XPS yields not only quantitative results concerning chemical composition and C/O-ratios, but also the ratios of carbon atoms bonded as C-C, C-O, C=O and O-C-O. One of the limitations of the method is that stoichiometric calculations require detailed knowledge on the concentration depth profile, which is commonly assumed to be homogeneous (Ertl and Küppers 1985). Concentration depth profiles were determined, for example by peak-to-background intensity ratios (Johansson et al. 2004). Electrical charging may also cause errors. Sample degradation and surface contamination have to be considered, especially for ex-situ prepared samples (Johansson and Campbell 2004; Johansson et al. 2005). The amount of volatile organic compounds (VOC) can modify the results; special care is needed in sample handling, especially in connection with XPS measurements (Nguila Inari et al. 2011). Despite these effects, cellulose and lignin can be determined reliably (Gray et al. 2010).

The present study is based on our previous work and experiences concerning wood modification and the study of surfaces by XPS (Klarhöfer et al. 2005, 2007, 2010). In particular, the studies of Namyslo and Kaufmann (2009), Part 1 of this series focusing on organoboron compounds, are continued here by extending the experiments with fluorine

and other bromine-containing reactants. The interpretation of the results is supported by studies on lignin and cellulose, as well as their precursors (Klarhöfer et al. 2008; Klarhöfer 2009).

## Materials and methods

### General procedures

Nuclear magnetic resonance (NMR) instrument: Bruker Avance III 600 or Avance 400 (Bruker, Ettlingen, Germany) with 600 or 400 MHz proton frequency.  $^1\text{H}$ -NMR spectra in  $\text{CDCl}_3$  were referenced to TMS at 0.0 ppm and  $^{13}\text{C}$ -NMR spectra to the solvent signal center at 77.0 ppm ( $\text{CDCl}_3$ ). In case of  $\text{DMSO}-d_6$ , the solvent peak was set to 2.50 ppm ( $^1\text{H}$ ) and 39.50 ppm ( $^{13}\text{C}$ ), respectively.  $^{15}\text{N}$ -NMR spectra refer to external  $\text{CH}_3\text{NO}_2$  (0.0 ppm).  $^{19}\text{F}$ -NMR spectra were referenced to internal  $\text{Cl}_3\text{CF}$  (0.0 ppm).  $^{15}\text{N}$  and  $^{19}\text{F}$  NMR spectra were measured at their appropriate resonance frequencies on the aforementioned spectrometers;  $^{15}\text{N}$  chemical shifts were obtained from 1D spectra in inverse-gated decoupling mode or from inverse-detected, 2D  $^1\text{H}$ ,  $^{15}\text{N}$ -HMBC spectra. All coupling constants are given in Hz. Multiplicities are abbreviated as usual: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

IR instrument: Vector 22 FTIR (Bruker, Bremen, Germany) equipped with a 'Specac Golden-Gate' Diamond-ATR/KRS5 unit applying the samples as solids. The post-processing of the spectra was limited to the rubber band baseline-correction with 64 points implemented in the Software OPUS 6.5 (Bruker) between 4000 and  $400\text{ cm}^{-1}$ .

Mass spectrometer: Varian 320 MS (Varian, Darmstadt, Germany) equipped with a triple quadrupole with direct inlet and electron impact ionization (EI). The source temperature was set to  $200^\circ\text{C}$ .

XPS measurements: at room temperature; base pressure of  $5 \times 10^{-11}$  hPa (Frerichs et al. 2006); hemispherical analyzer (VSW HA100) in combination with a commercial non-monochromatic X-ray source (Specs RQ20/38C); X-ray photons irradiated the surface under an angle of  $80^\circ$  to the surface normal; diameter of the illuminated spot: several mm. The Al  $\text{K}_\alpha$  line (photon energy 1486.6 eV) was used. Energy resolution: 1.1 eV emitted under an angle of  $10^\circ$  to the surface normal. For quantitative XPS analysis, peak fitting with Gauss-type profiles was applied: OriginPro 7G (OriginLab, Northampton, MA, USA) including the PFM fitting module, which is based on the Levenberg-Marquardt algorithms to achieve the best agreement possible between experimental data and fit. For fitting optimization, Voigt-profiles have been applied to various oxidic and metallic systems, but for most systems the Lorentzian contribution converges to 0. Therefore, all XPS peaks are fitted with Gaussian curves. Photoelectric cross sections were applied as calculated by Scofield (1976) with asymmetry factors (Reilman et al. 1976; Powell and Jablonski 2010a). The inelastic mean free paths (IMFP) in polyethylene from the NIST database (Powell and Jablonski 2010b) (with the dataset of Tanuma et al.) were used as model system instead of the unknown IMFPs in wood. The energy dependent transmission function of our hemispherical analyzer is taken into account together with IMFPs, cross sections and asymmetry factors when calculating stoichiometry. Prior to these measurements, the veneer chips were cut into pieces of approximately  $10 \times 10 \times 0.6\text{ mm}^3$ . These samples were mounted on cartridges of molybdenum or titanium, depending on which was advantageous according to the expected sample composition.

CA measurements: Dataphysics OCA 15plus (DataPhysics Instruments, Filderstadt, Germany). For each measurement 3  $\mu\text{l}$  of distilled water was applied on the surface. For each sample at least five different positions were analyzed.

All solvents were dried according to standard methods and were freshly distilled prior to use. Anhydrous *N,N*-dimethylformamide (DMF) and all other chemicals were used as purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany) or Fluorochem (Hadfield, UK). Wood samples were obtained from the Section of Wood Biology and Wood Products (Georg-August-University Göttingen, Göttingen, Germany).

### Organic precursors

**1H-Benzotriazol-1-yl(phenyl)methanone (6)** Under an inert atmosphere, a solution of 6.048 g (50.7 mmol) 1H-benzotriazole and 1.3 ml (17.9 mmol) thionyl chloride in 15 ml anhydrous  $\text{CH}_2\text{Cl}_2$  was added dropwise to a suspension of 2.000 g (16.4 mmol) benzoic acid in 10 ml anhydrous  $\text{CH}_2\text{Cl}_2$  within 30 min. After stirring for 16 h, water (10 ml) was added. The water layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $5 \times 30\text{ ml}$ ). The combined organic layers were washed with water ( $5 \times 100\text{ ml}$ ) to be dried afterwards ( $\text{Na}_2\text{SO}_4$ ). Evaporation to dryness gave 3.176 g (79%) of **6**.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.40 (d,  $J$ =8.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 8.23–8.21 (m, 2 H,  $\text{H}_{\text{arom}}$ ), 8.18 (d,  $J$ =8.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 7.74–7.68 (m, 2H,  $\text{H}_{\text{arom}}$ ,  $\text{H}_{\text{arom,Bzt}}$ ), 7.61–7.54 (m, 3H,  $\text{H}_{\text{arom}}$ ,  $\text{H}_{\text{arom,Bzt}}$ ).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ =166.8 ( $\text{C}_{\text{quat}}$ , 1 C, C=O), 145.8 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 133.7 (+, 1 C,  $\text{C}_{\text{arom}}$ ), 132.3 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 131.7 (+, 2 C,  $\text{C}_{\text{arom}}$ ), 131.5 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom}}$ ), 130.5 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 128.4 (+, 2 C,  $\text{C}_{\text{arom}}$ ), 126.3 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 120.2 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 114.8 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ). MS (20 eV);  $m/z$  (%): 223.1 [ $M^+$ ] (10), 195.0 [ $M-\text{N}_2$ ] $^+$  (80), 105.0 [ $M-\text{Bzt}$ ] $^+$  (100). IR (ATR): 3102, 3068, 2980, 2656, 1703, 1598, 1580, 1487, 1449, 1378, 1360, 1319, 1305, 1286, 1244, 1227, 1183, 1153, 1129, 1108, 1094, 1049, 1036, 1003, 972, 954, 938, 883, 791, 772, 750, 715, 694, 682, 657, 634, 617, 584, 564, 530, 457, 434.

**1H-Benzotriazol-1-yl(4-bromophenyl)methanone (7)** Under an inert atmosphere, a solution of 14.240 g (120.0 mmol) 1H-benzotriazole and 3.2 ml (44 mmol) thionyl chloride in 150 ml anhydrous  $\text{CH}_2\text{Cl}_2$  was added dropwise to a suspension of 8.050 g (40 mmol) 4-bromobenzoic acid in 60 ml anhydrous  $\text{CH}_2\text{Cl}_2$  within 30 min. After stirring for 16 h, water (100 ml) was added. The organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 70\text{ ml}$ ). The combined organic layers were washed with water and brine to be dried ( $\text{MgSO}_4$ ) afterwards. Evaporation to dryness gave the raw material which was washed with MeOH to give 10.117 g (84%) of pure **7**.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =8.39 (ddd,  $J$ =8.3, 1.9, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 8.18 (ddd,  $J$ =8.3, 1.9, 1.0 Hz,  $\text{H}_{\text{arom,Bzt}}$ ), 8.15–8.11 (m, 2 H,  $\text{H}_{\text{arom}}$ ), 7.77–7.70 (m, 3 H,  $\text{H}_{\text{arom,Bzt}}$ ,  $\text{H}_{\text{arom}}$ ), 7.57 (ddd,  $J$ =8.3, 7.2, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ =165.8 ( $\text{C}_{\text{quat}}$ , 1 C, C=O), 145.8 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 133.2 (+, 2 C,  $\text{C}_{\text{arom}}$ ), 132.3 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 131.9 (+, 2 C,  $\text{C}_{\text{arom}}$ ), 130.6 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 130.2 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom}}$ ), 129.2 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom}}$ ), 126.6 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 120.3 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 114.8 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ). MS (20 eV);  $m/z$  (%): 301.0 [ $M^+$ ], 273.1 [ $M-\text{N}_2$ ] $^+$ , 183.0 [ $M-\text{Bzt}$ ] $^+$ . IR (ATR): 3117, 3092, 3063, 1702, 1607, 1586, 1481, 1448, 1427, 1395, 1367, 1320, 1306, 1283, 1245, 1224, 1182, 1145, 1125, 1039, 1001, 966, 933, 886, 834, 771, 748, 739, 681, 665, 645, 623, 586, 569, 539, 475, 457, 430, 411.

**1H-Benzotriazol-1-yl(4-fluorophenyl)methanone (8)** Under an inert atmosphere, a solution of 7.907 g (66.4 mmol) 1H-benzotriazole and 1.71 ml (23.6 mmol) thionyl chloride in 20 ml anhydrous  $\text{CH}_2\text{Cl}_2$

was added dropwise to a suspension of 3.000 g 4-fluorobenzoic acid in 30 ml anhydrous  $\text{CH}_2\text{Cl}_2$  within 30 min. After stirring for 16 h, water (20 ml) was added. The resulting mixture was neutralized by means of 10% aqueous NaOH. The water layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3×50 ml). The combined organic layers were washed with water (4×100 ml) and brine (100 ml) to be dried ( $\text{Na}_2\text{SO}_4$ ) afterwards. Evaporation to dryness gave 4.954 g (96%) of **8**.  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.41 (ddd,  $J$  = 8.2, 1.8, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 8.33–8.32 (m, 2 H,  $\text{H}_{\text{arom}}$ ), 8.20 (ddd,  $J$  = 8.2, 1.8, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 7.74 (ddd,  $J$  = 8.3, 7.2, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 7.59 (ddd,  $J$  = 8.3, 7.2, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 7.32–7.27 (m, 2 H,  $\text{H}_{\text{arom}}$ ).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.2 ( $\text{C}_{\text{quat}}$ , d,  $J$  = 237.4 Hz, 1 C, C-F), 165.3 ( $\text{C}_{\text{quat}}$ , 1 C, C=O), 145.7 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 134.7 ( $\text{C}_{\text{quat}}$ , d,  $J$  = 9.8 Hz, 2 C,  $\text{C}_{\text{arom}}$ ), 132.4 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 130.5 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 127.6 ( $\text{C}_{\text{quat}}$ , d,  $J$  = 3.1 Hz,  $\text{C}_{\text{arom}}$ ), 126.4 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 120.3 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 115.8 ( $\text{C}_{\text{quat}}$ , d,  $J$  = 22.9 Hz, 2 C,  $\text{C}_{\text{arom}}$ ), 114.8 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ).  $^{19}\text{F-NMR}$  (564 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -108.9. **MS** (20 eV);  $m/z$  (%): 241.3 [ $\text{M}^+$ ] (20), 213.2 [ $\text{M-N}_2$ ] (+) (100), 123.1 [ $\text{M-Bzt}$ ] (+) (70). **IR** (ATR): 3075, 1707, 1602, 1508, 1485, 1450, 1411, 1366, 1318, 1301, 1287, 1242, 1228, 1163, 1153, 1130, 1100, 1077, 1039, 1004, 966, 935, 890, 862, 845, 813, 779, 770, 749, 670, 658, 629, 609, 576, 562, 519, 498, 430, 411.

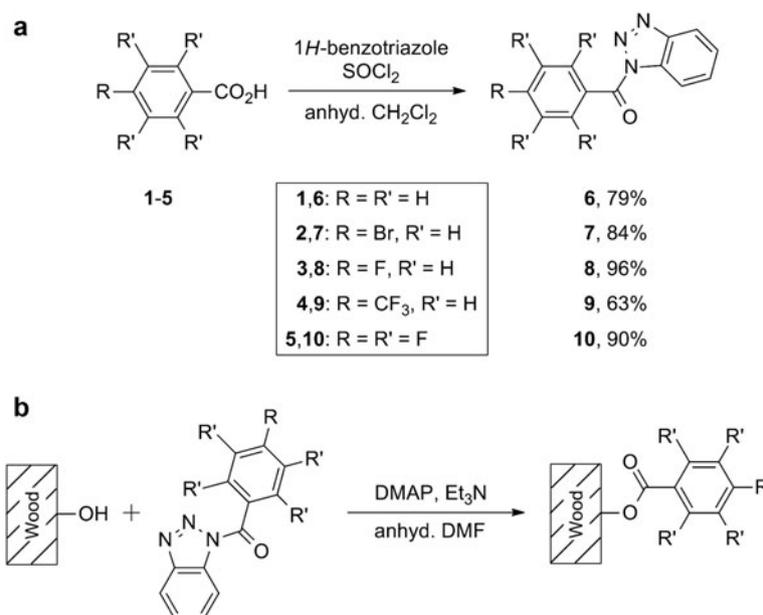
#### 1H-Benzotriazol-1-yl[4-(trifluoromethyl)phenyl]methanone (9)

Under an inert atmosphere, a solution of 11.078 g (93.0 mmol) 1H-benzotriazol and 2.40 ml (33 mmol) thionyl chloride in 50 ml anhydrous  $\text{CH}_2\text{Cl}_2$  was added dropwise to a suspension of 5.704 g (30 mmol) 4-(trifluoromethyl)benzoic acid in 50 ml anhydrous  $\text{CH}_2\text{Cl}_2$  within 30 min. After stirring for 16 h, 30 ml of water were added. The resulting mixture was neutralized by means of 10% aqueous NaOH. The water layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3×50 ml). The combined organic layers were dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to dryness. Purification by column chromatography (10:1, petrol ether:ethyl acetate) gave 5.476 g (63%) of **9**.  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.40 (ddd,  $J$  = 8.3, 1.8, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 8.33 (d,  $J$  = 8.3 Hz, 2 H,  $\text{H}_{\text{arom}}$ ), 8.19 (ddd,  $J$  = 8.3, 1.8, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 7.85 (d,  $J$  = 8.3 Hz, 2 H,  $\text{H}_{\text{arom}}$ ), 7.74 (ddd,  $J$  = 8.3, 7.1, 1.0 Hz, 1 H,

$\text{H}_{\text{arom,Bzt}}$ ), 7.58 (ddd,  $J$  = 8.3, 7.1, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.6 ( $\text{C}_{\text{quat}}$ , 1 C, C=O), 145.8 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 134.9 ( $\text{C}_{\text{quat}}$ , q,  $J$  = 33.0 Hz, 1 C,  $\text{C}_{\text{arom}}$ ), 132.1 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 132.0 (+, 2 C,  $\text{C}_{\text{arom}}$ ), 130.8 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 130.5 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom}}$ ), 126.7 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 125.5 (+, q,  $J$  = 3.5 Hz, 2 C,  $\text{C}_{\text{arom}}$ ), 123.5 (q,  $J$  = 272.9 Hz, 1 C,  $\text{CF}_3$ ), 120.4 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 114.8 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ).  $^{15}\text{N-NMR}$  (61 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -122.1, -15.2, 6.3.  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -63.8. **MS** (20 eV);  $m/z$  (%): 291.2 [ $\text{M}^+$ ] (20), 263.2 [ $\text{M-N}_2$ ] (+) (100), 173.1 [ $\text{M-Bzt}$ ] (+) (90). **IR** (ATR): 3067, 2923, 2853, 1710, 1619, 1605, 1596, 1514, 1485, 1451, 1429, 1399, 1326, 1312, 1287, 1246, 1226, 1196, 1167, 1150, 1128, 1111, 1052, 1019, 1001, 960, 938, 889, 861, 844, 777, 761, 748, 716, 696, 658, 646, 630, 611, 570, 539, 489, 478, 464, 431, 414.

#### 1H-Benzotriazol-1-yl(pentafluorophenyl)methanone (10)

Under an inert atmosphere, a solution of 3.483 g (29.2 mmol) 1H-benzotriazol and 0.75 ml (10.3 mmol) thionyl chloride in 20 ml anhydrous  $\text{CH}_2\text{Cl}_2$  was added dropwise to a suspension of 2.000 g (9.4 mmol) pentafluorobenzoic acid in 20 ml anhydrous  $\text{CH}_2\text{Cl}_2$  within 30 min. After stirring for 16 h, water (20 ml) was added. The resulting mixture was neutralized by means of 10% aqueous NaOH. The water layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3×50 ml). The combined organic layers were washed with water (4×100 ml) and brine (1×100 ml) to be dried ( $\text{Na}_2\text{SO}_4$ ) afterwards. Evaporation to dryness gave 2.656 g (90%) of **10**.  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.40 (ddd,  $J$  = 8.3, 1.8, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 8.22 (ddd,  $J$  = 8.3, 1.8, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 7.81 (ddd,  $J$  = 8.3, 7.2, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ), 7.65 (ddd,  $J$  = 8.3, 7.2, 1.0 Hz, 1 H,  $\text{H}_{\text{arom,Bzt}}$ ).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 156.9 ( $\text{C}_{\text{quat}}$ , 1 C, C=O), 146.5 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 144.4 (m, 2 C,  $\text{C}_{\text{arom}}$ ), 143.8 (m, 1 C,  $\text{C}_{\text{arom}}$ ), 137.7 (m, 2 C,  $\text{C}_{\text{arom,Bzt}}$ ), 131.3 (+, 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 130.8 ( $\text{C}_{\text{quat}}$ , 1 C,  $\text{C}_{\text{arom,Bzt}}$ ), 127.4 (+, 1 C,  $\text{C}_{\text{arom}}$ ), 120.8 (+, 1 C,  $\text{C}_{\text{arom}}$ ), 114.2 (+, 1 C,  $\text{C}_{\text{arom}}$ ), 109.3 ( $\text{C}_{\text{quat}}$ , m, 1 C,  $\text{C}_{\text{arom}}$ ).  $^{19}\text{F-NMR}$  (564 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -137.6 to -137.7 (2 F,  $\text{F}_{\text{ortho}}$ ), -147.2 to -147.3 (1 F,  $\text{F}_{\text{para}}$ ), -159.3 to -159.4 (2 F,  $\text{F}_{\text{meta}}$ ). **MS** (20 eV);  $m/z$  (%): 313.2 [ $\text{M}^+$ ] (30), 285.2 [ $\text{M-N}_2$ ] (+) (65), 195.1 [ $\text{M-Bzt}$ ] (+) (100). **IR** (ATR): 3101, 2961, 1716, 1652, 1625, 1597, 1526, 1504, 1483, 1450, 1426, 1389,



**Figure 1** Synthesis of activated benzoic acids (a), followed by the general wood modification procedure (b).

**Table 1** Modification parameters, ATR-IR values and contact angles obtained upon modification.

Modification reagents	Modification parameters			Results of ATR-IR		Contact angles	
	Temp. (°C)	WPG (%)	QCO (mmol g <sup>-1</sup> )	v(C=O) (cm <sup>-1</sup> )	δ(aromatics) (cm <sup>-1</sup> )	(°)	Std. dev. ± (°)
Untreated				1733	-/-	-/-	-/-
6	120	10.4	1.0	1720	709	-/-	-/-
7	120	26.9	1.5	1719	754	97.3	9.2
8	120	12.5	1.0	1720	764	122.9	7.7
9	120	19.2	1.1	1726	773	123.3	4.9
10	70	28.4	1.5	1741	743	143.3	9.5

1321, 1309, 1286, 1227, 1210, 1193, 1184, 1159, 1143, 1128, 1108, 1081, 1042, 1010, 1000, 977, 954, 914, 867, 819, 793, 772, 751, 730, 688, 657, 643, 617, 587, 563, 551, 496, 432.

### Chemical wood modification procedure

In general, the standard amount of 7 mmol of the appropriate wood modifying reagent was applied per gram of veneer chips of Scots pine (*Pinus sylvestris*) wood (approx. 25 mm × 15 mm × 0.6 mm, approx. 0.100 g). Thus, all reactions were performed in 12 ml of anhydrous DMF with two equivalents of triethylamine and 10 mol% of 4-dimethylaminopyridine under nitrogen atmosphere. Prior to modification, the wood was extracted for 1 day in a Soxhlet apparatus with a solvent mixture comprising toluene/acetone/MeOH 4:1:1. The pre-treated wood was subsequently oven-dried at 105°C for 1 day and then stored in a laboratory desiccator. All wood modification reactions were conducted for 16 h at 120°C (compound 6–9) or 70°C (compound 10), respectively. After this reaction time, the mixture was allowed to cool down to room temperature and the modified wood was transferred to a filter. The wood was then washed successively with THF (50 ml), CHCl<sub>3</sub> (50 ml) and diethyl ether (50 ml). Afterwards, the wood sample was extracted again for 1 day in the Soxhlet apparatus with the same solvent mixture as stated above. Finally, the modified wood was dried at 105°C for 1 day and then cooled to room temperature in a desiccator.

## Results and discussion

### Chemical syntheses of wood modification reagents

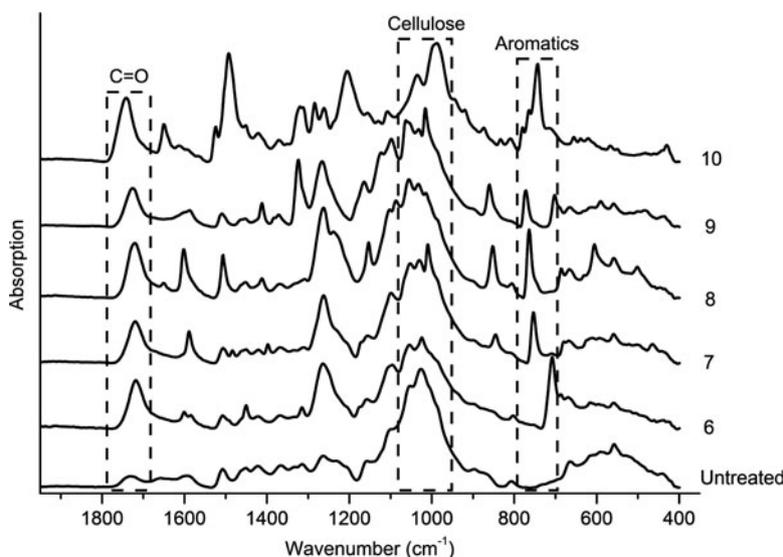
Following our procedure for the synthesis of the wood modifying precursors (Namyslo and Kaufmann 2009), the activated acids 6–10 (6, 7, Katritzky et al. 1999, 2002; 8: Shao et al. 2009; 9, 10: Kreutzberger and van der Goot 1975) were obtained from the corresponding commercially available free acids 1–5 and 1*H*-benzotriazole in the presence of thionyl chloride and anhydrous CH<sub>2</sub>Cl<sub>2</sub> (Figure 1a).

During wood modification, benzotriazole-activated benzoic acid derivatives esterified with accessible hydroxyl groups of the sample (Figure 1b).

### WPG and covalently bonded organomaterial (QCO)

After solvent extraction and drying of the modified wood, WPG was determined (Table 1).

In consideration of the fact that the veneer pieces had been chemically modified with different functional organo-substituents with different molecular weights, we suggest a novel analytic parameter—the quantity of covalently bonded

**Figure 2** ATR-IR spectra with modification reagents given.

organomaterial (QCO) in millimole per gram of wood. Such QCO values, also given in Table 1, allow for comparability of the extent of not only identical, but similar wood modifications.

### IR spectroscopic characterization

Attenuated total reflection (ATR)–IR spectra of the modified wood are presented in Figure 2. Compared with untreated material, all modified samples show strongly increased carbonyl stretching bands, which appear at significantly shifted wavenumbers (Table 1). Aside from the chemical modification with the electronically unique perfluorophenyl compound **10**, carbonyl bands of all modified samples show a shift to lower wavenumbers.

Additionally, at about  $1250\text{ cm}^{-1}$ , some C–O stretching bands arise, which also originate from the individual modification reagents. Furthermore, in each IR spectrum of a treated wood a relatively sharp band around  $750\text{ cm}^{-1}$  is characteristic. It is caused by the deformation vibrations of the aromatic ring introduced by the modifying reagent. For example, treatment with **10** leads to a signal at  $743\text{ cm}^{-1}$  (see Table 1).

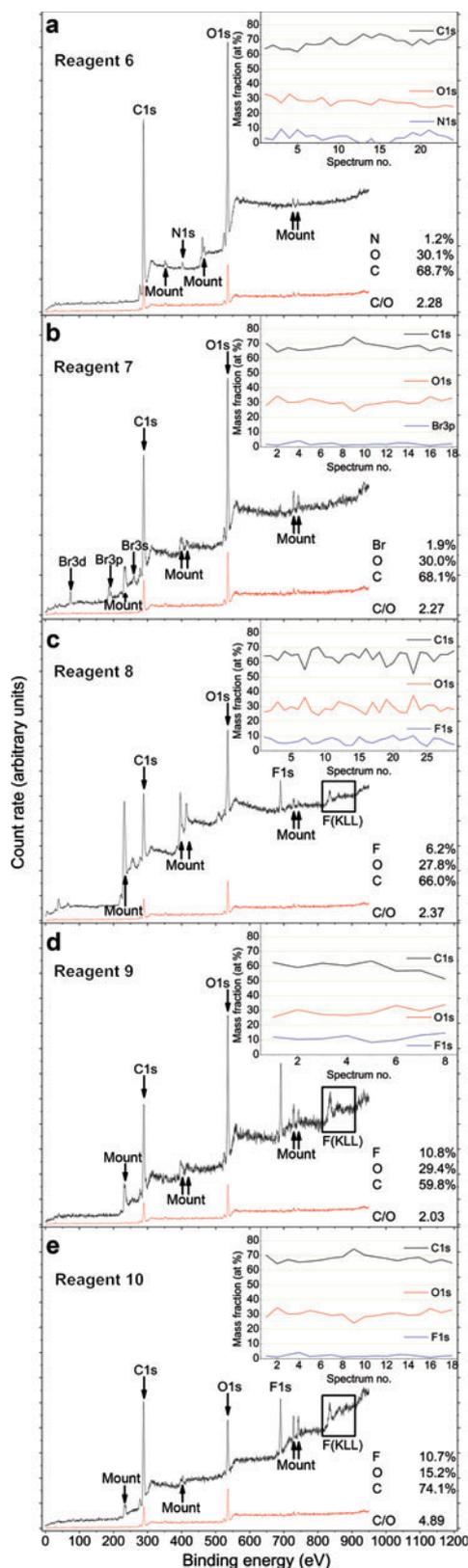
### Semi-quantitative IR analysis

The quantities of attached materials have been estimated based on the intensities of the normalized carbonyl bands. The normalization was done based on the most intense band of the spectrum, which is localized at approximately  $1050\text{ cm}^{-1}$  (cellulose). The accuracy of such estimations is always limited, especially in the case of the ATR technique (pressure and surface quality influences the results). The obtained normalized intensities are 1.9 (**6**), 2.8 (**7**), 2.1 (**8**), 3.1 (**9**) and 2.0 (**10**), with the modification reagents given in parentheses. The first three values correspond roughly with the obtained WPG values, i.e., to the quantities of covalently attached reagents. However, such a comparison appears to be quite problematic in case of fluorine-containing samples, maybe because of different absorption coefficients.

### XPS

XPS afforded the stoichiometric surface compositions. During XPS measurement, the pressure inside the UHV chamber increased to about  $3 \times 10^{-9}$  hPa. Because every chemical element (apart from hydrogen) gives characteristic XPS signals, it was possible to proof the efficiency of the extraction processes that followed each wood modification reaction. Whenever molybdenum was used as mount, the N 1s peak was superimposed by the Mo 3p structure. Thus, structures are visible around the characteristic binding energy of 400 eV, even though detailed analysis by fitting Mo  $3p_{3/2}$ , N 1s and Mo  $3p_{1/2}$  yielded no nitrogen content.

Figure 3a–e show the XPS spectra of the samples modified with reagent numbers **6–10** (black line) as opposed to the untreated reference sample (red line). As it is known that X-ray irradiation may degrade wood surfaces (Johansson and Campbell 2004; Johansson et al. 2005), the progress of



**Figure 3** XPS spectra with modification reagents given.

the stoichiometry of the modified wood sample during measurement is displayed over the number of measuring cycles as an inset to the XPS spectra. Only slight changes can be

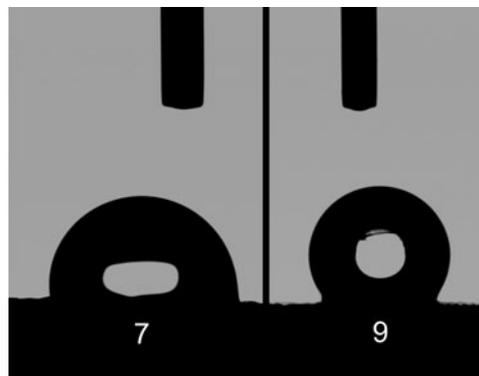
observed; thus, the C/O ratios resulting from the analysis are valid. It was found that none of the samples contained any detectable amount of nitrogen except for wood treated with modification reagent **6**. Therefore, in all wood samples that had been treated with reagents **7–10** followed by an extraction, 1*H*-benzotriazole was absent. The C/O ratio increases upon wood modification because the introduced organic material contains disproportionately more carbon than oxygen atoms. No further spectral manipulations, for example the deconvolution of the C 1s peak into oxidation states has been carried out. Thus, the short measurement time helped to avoid significant sample degradation. All XPS results are summarized in Table 2.

### Contact angles

The CA is a valuable standard measure for the degree of hydrophobization obtained by various modification reactions (Asandulesa et al. 2010; Bryne and Wälinder 2010; De Vetter et al. 2010). All measurements were carried out with distilled water. Figure 4 illustrates the shape of single water drops on veneer, which were modified by compounds **7** and **9**. In the case of the 4-fluorophenyl-, trifluoromethylphenyl- and pentafluorophenyl-derived wood samples (modified by compound **8–10**, respectively), the water did not penetrate the wood. In comparison, the water was absorbed from the wood within minutes in the case of the bromophenyl-derived wood modification with compound **7**. In contrast, the veneer, which had been reacted with the phenyl-compound **6** (bearing no fluorine or bromine at all), was lacking any hydrophobicity. Consequently, the water drop was completely soaked up immediately. Therefore, no contact angle of water on pine wood could be measured for the untreated, as well as the latter mentioned, wood that was modified by compound **6** (Table 1).

### Conclusions

Wood esterification by benzotriazolyl-activation is highly efficient for permanent wood modification. In comparison to previous experiments, milder reaction conditions have been applied, i.e., the reaction temperature was lowered from 150°C to 120°C and 70°C, respectively. Thus, thermal decomposition of wood components can be neglected. The currently presented attachment of fluoroorganyl benzoic acid derivatives



**Figure 4** Water on modified (reagent **7,9**) pine wood.

by covalent bonds led to highly hydrophobic wood surfaces with outstanding contact angles up to 143.3° (Teflon® 126°). The resulting minimized uptake of water is assumed to slow down initial biological degradation. In this context, the results of biological degradation experiments will be published soon. Another question is the outdoor stability of the modification if exposed to sunshine and rain (weathering). The effective depth of the protected (hydrophobic) layer is also a matter of ongoing investigation for our laboratory.

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**Table 2** Summarized XPS results.

Modified reagents	Stoichiometry (atomic%)					C/O ratio
	C	O	N	F	Br	
Untreated	62.8	37.2	0.0	0.0	0.0	1.69
<b>6</b>	68.7	30.1	1.2	0.0	0.0	2.28
<b>7</b>	68.1	30.0	0.0	0.0	1.9	2.27
<b>8</b>	66.0	27.8	0.0	6.2	0.0	2.37
<b>9</b>	59.8	29.4	0.0	10.8	0.0	2.03
<b>10</b>	74.1	15.2	0.0	10.7	0.0	4.89

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