Supporting Information

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SI Methods

Spectroscopy. UV/Vis-spectra: Hitachi U3000 spectrophotometer. Luminescence spectra: Varian Cary Eclipse fluorescence spectrometer. ^{1}H- and ^{13}C- NMR (NMR) spectroscopy: Bruker UltraShield 600 MHz or Varian Unity Inova 500 MHz spectrometers.

HPLC Analyses of Luminescent Rings, Brown Spots and Yellow Areas of Peels of Bananas (*Musa acuminata*, cavendish cultivar). Extracts were produced by cutting out separately the luminescent areas of banana peels around the brown spots and the still yellow areas of the same bananas with a scalpel under UV-light. Five independent samples of each source were obtained and analyzed quantitatively. In a second set with three samples each, these were prepared by cutting out brown spots and, separately, the luminescent areas around them under the same conditions. The samples were first weighed (sample size ≈10 mg) and then transferred into an Eppendorf reaction vessel, mixed with 300 μL of methanol and 1 mL of water. The mixture was centrifuged and the supernatant was directly applied to analytical HPLC (Dionex Summit) connected to an FP920 fluorescence detector; Hypersil ODS 5 μm 250 × 4.6 mm i.d. column at r.t. protected with a Phenomenex ODS 4 mm × 3 mm i.d. precolumn, for solvent composition, see reference 8 and Figs. S1 and S3.

HPLC Analyses of Yellow (Senescent) Leaf of *Spathiphyllum Wallisii*. A piece (≈10 cm^2) of a yellow (senescent) leaf of *Spathiphyllum wallisii* was ground in a mortar and extracted two times with 2 mL of methanol. The mixture was filtered with suctcion (Buchner funnel) and diluted with 4 mL of water. The turbid solution was filtered again and 118 μL of it were subjected to analytical HPLC (Dionex Summit connected to an FP920 fluorescence detector; Hypersil ODS 5 μm 250 × 4.6 mm i.d. column at r.t. protected with a Phenomenex ODS 4 mm × 3 mm i.d. precolumn, for solvent composition, see reference 8 and Fig. S6).

Preparative HPLC for Isolation of *Mc*-FCC-49 for Structure Elucidation. (Gynkotek HPLC System with manual sampler, M300 pump, UVD 340 diode array detector and Jasco FP-920 fluorescence detector. The sample was applied directly via the pump onto the column. Data were collected with Gynkosoft 5.50 and processed with Chromeleon V6.50. Hypersil ODS 5 μm 250 mm × 21.2 mm i.d. column was used with a flow rate of 5 mL min^{-1}. Isocratic mixtures [55/45 (vol/vol)] of MeOH and potassium phosphate buffer pH 7 100 mM; solvents were degassed by sonication.

Spectroscopic Structural Characterization of *Mc*-FCC-49. (r_t = 49 min); UV-Vis (MeOH, c = 2.8*10^{-5}M) λ_{max} (log ε) = 363 (4.0), 318 (4.3), 242 (4.32)(see Fig. S1). CD (MeOH, c = 3.1*10^{-5}M) λ_{max}/nm ($\Delta\varepsilon$) = 244 (−10.2), 289 (8.8), 325 (sh, −0.6), 350 (−5.3). ^{1}H-NMR (500 MHz, D_2O): δ = 1.06 [d, J = 7.3 Hz, $H_3C(18^1)$], 1.66 [m, $H_AC(17^1)$], 1.90 [m, $H_BC(17^1)$], 1.93 [s, $H_3C(2^1)$], 2.14 [s, $H_3C(12^1)$, $H_3C(7^1)$], 2.39 [m, $H_2C(17^2)$, HC (17)], 2.52 [m, H_AC (20)], 2.62 [m, $H_2C(8^1)$, HC (18)], 2.98 [dd, J = 4.7/20.1, H_BC (20)], 3.05 {m, HC(2″)}, 3.18 {m, HC(5″), HC(4″)}, 3.33 {m, HC(3″), $H_AC(8^2)$}, 3.55 {dd, J = 5.1/12.0 Hz, $H_AC(6')$}, 3.64 [m, $H_BC(8^2)$], 3.73 {d, J = 11.6 Hz, $H_BC(6')$}, 3.77 [s, $H_3C(13^5)$], 3.98/4.08 [AB-system, J = 17.1 Hz, H_2C (10)], 4.15 {d, J = 8.0 Hz, HC(1′)}, 4.31 [m, HC (1)], 4.41 {m, HC(6′), HC(4′)}, 5.44 [m, $H_AC(3^2)$], 5.45 {m, HC(3′)}, 5.58 {m, HC(5′)}, 5.90 [d, J = 17.9 Hz, $H_BC(3^2)$], 6.43 [dd, J = 11.7/17.7 Hz, HC(3^1)], 9.11 [s, HC (5)]. ^{1}H-NMR (600 MHz, CD_3OD): δ = 1.13 [d, J = 7.3 Hz, $H_3C(18^1)$], 1.88 [m, $H_AC(17^1)$], 1.93 [m, $H_BC(17^1)$], 2.04 [s, $H_3C(2^1)$], 2.15 [s, $H_3C(12^1)$], 2.21 [s, $H_3C(7^1)$], 2.34 [m, $H_2C(17^2)$], 2.45 [m, HC (17)], 2.49 [dd, J = 8.8/18.6, H_AC (20)], 2.67 [m, $H_AC(8^1)$, HC (18)], 2.79 [m, $H_BC(8^1)$], 3.03 [dd, J = 4.3/18.7, H_BC (20)], 3.10 {m, HC(2″)}, 3.21 {m, HC(5″)}, 3.29 {HC(3″)}, 3.34 {HC(4″)} 3.57 {m, $H_AC(8^2)$, $H_AC(6'')$}, 3.75 [s, $H_3C(13^5)$], 3.82 {m, $H_BC(8^2)$, $H_BC(6'')$}, 4.03/4.19 [AB-system, J = 16.8 Hz, H_2C (10)], 4.23 {d, J = 7.9 Hz, HC(1″)}, 4.37 {b, HC(6′)}, 4.41 [m, HC (1)], 5.40[dd, J ≈2/12 Hz, $H_AC(3^2)$], 5.46 {m, HC(5′)}, 5.56 {m, HC(3′)}, 6.19 [dd, J ≈2/18 Hz, $H_BC(3^2)$], 6.51 [dd, J = 11.7/17.8 Hz, HC(3^1)], 9.34 [s, HC (5)]. ^{13}C-NMR: (150 MHz, CD_3OD, signal assignment from HSQC experiment): δ = 8.1 (12^1), 8.2 (7^1), 11.5 (2^1), 17.3 (18^1), 23.4 (10), 27.5 (8^1), 27.8 (17^1), 30.7 (17^2), 38.0 (20), 47.4 (17), 51.7 (18), 52.5 (13^5), 62.4 (6″), 62.5 (8^2), 70.4 (5′), 74.4 (2″), 75.3 (3″), 77.5 (5″), 77.9 (4″), 80.3 (6′), 103.9 (3′), 104.2 (1″), 119.8 (3^2), 127.2 (3^1). LSIMS-MS: m/z (%) = 1033.57 (42), 1032.54 (58), 1031.58 (71, $[M+K]^+$), 1015.58 (47, $[M+Na]^+$), 993.57 (30, $[M+H]^+$), 846.69 (54), 845.73 (100, $[M-C_7H_6O_6+K]^+$), 807.96 (93, $[M-C_7H_6O_6+H]^+$). HR-LSIMS-MS: m/z = 993.369 ($[M+H]^+$), m/z_{calc} ($C_{48}H_{49}N_4O_{19}$) = 993.361.

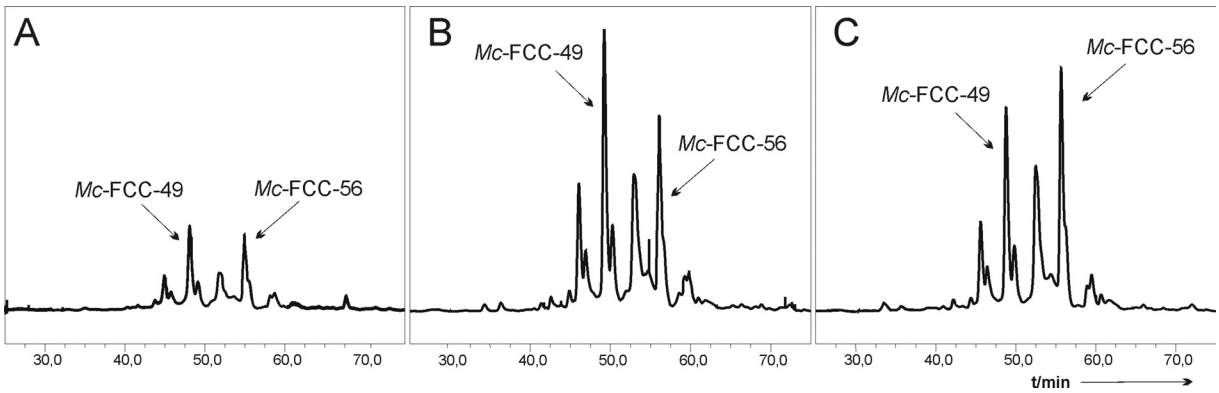

Fig. S1. Analysis by HPLC of extracts obtained from dark spots (*A*), of luminescent rings (*B*) and of the surrounding dull yellow areas (*C*) on a banana peel. Samples were prepared by cutting out the specified areas with a scalpel, under UV light (see *Materials and Methods* and Fig. S3). Trace from detection of luminescence at 450 nm (excitation at 350 nm).

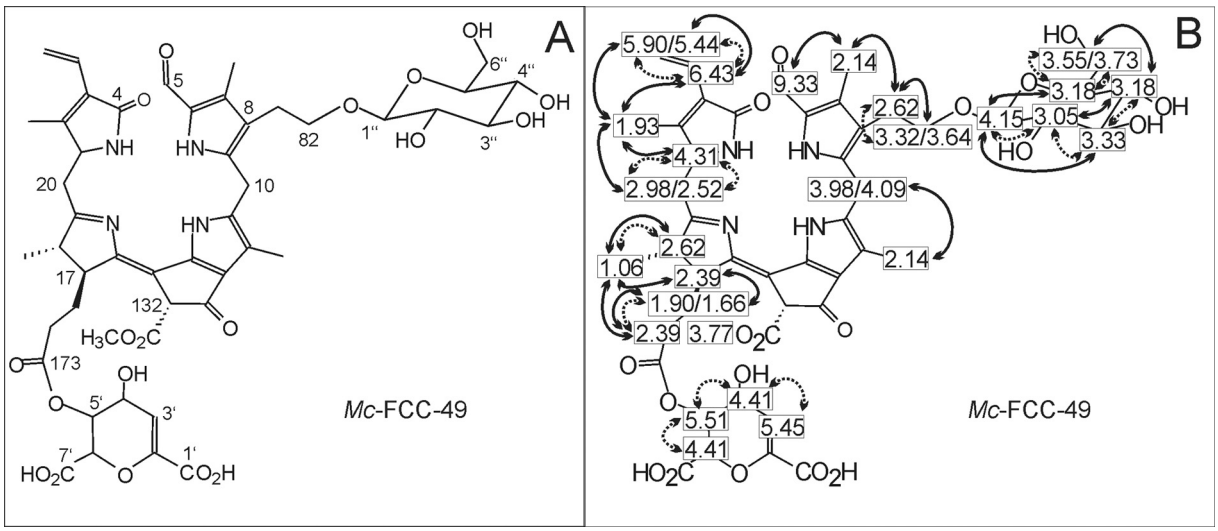

Fig. S2. (*A*) Constitutional formula of *Mc*-FCC-49; (*B*) ^{1}H chemical shift data and homonuclear correlations (dashed arrows indicate COSY couplings, bold arrows show NOEs from a ROESY spectrum) from 500 MHz NMR spectra in D_2O.

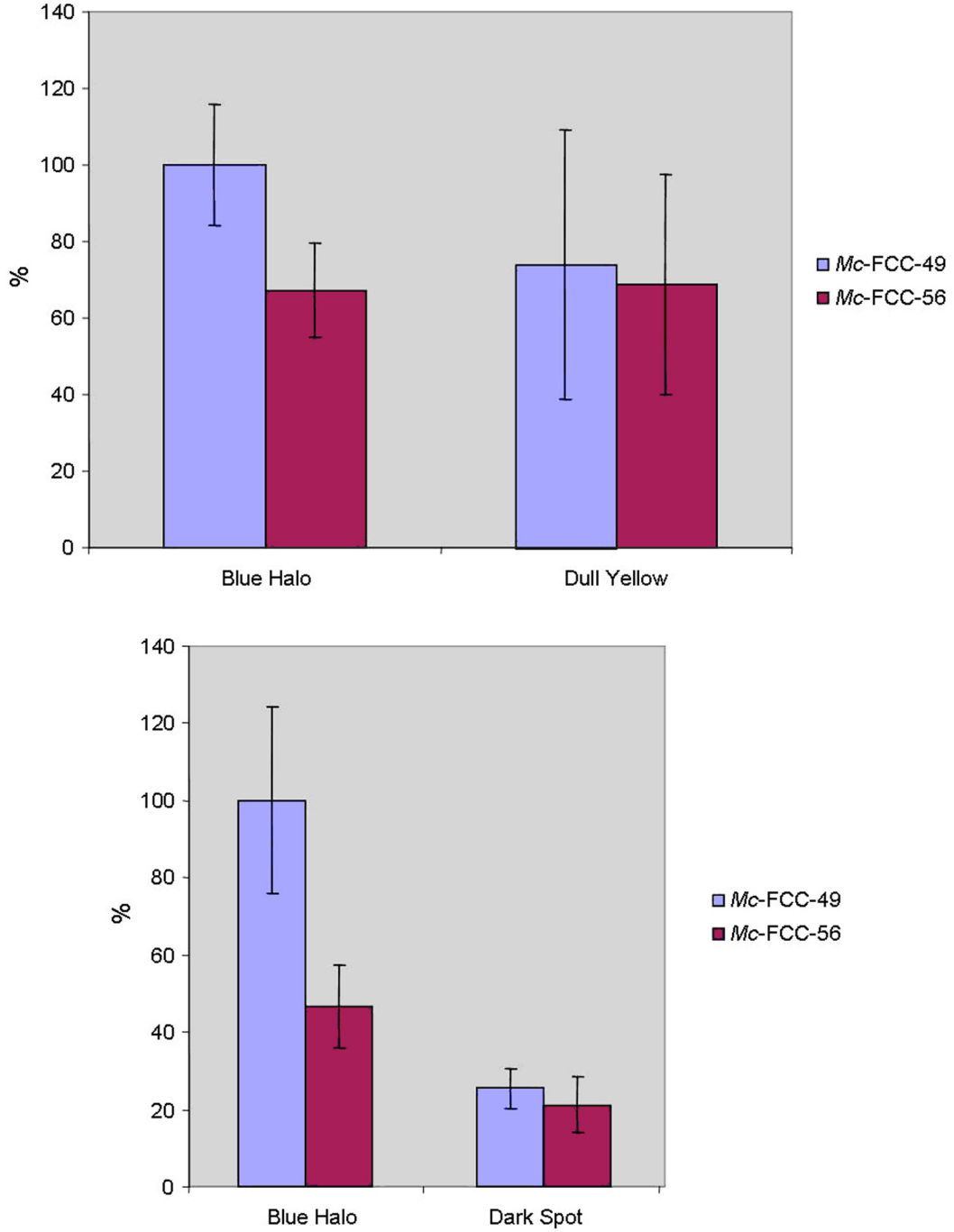

Fig. S3. HPLC-analysis of FCCs *Mc*-FCC-49 and *Mc*-FCC56 in the areas of the blue luminescent rings and the plain (dull) yellow parts of the peels of bananas (five samples each) (*Top*) and of the blue luminescent rings and of the dark spots (three samples each) (*Bottom*). Normalized peak areas and standard deviations are given.

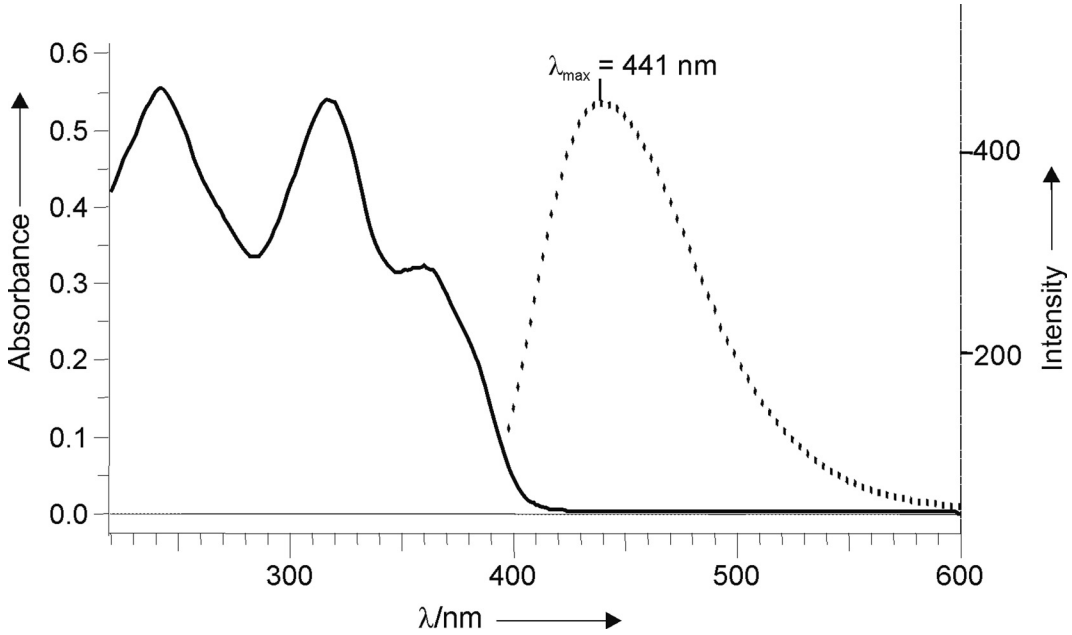

Fig. S4. UV/Vis-spectrum of *Mc*-FCC-49 (bold line, 28 μM) and fluorescence emission spectrum (dashed line, 15 μM, excitation at 350 nm) in methanol.

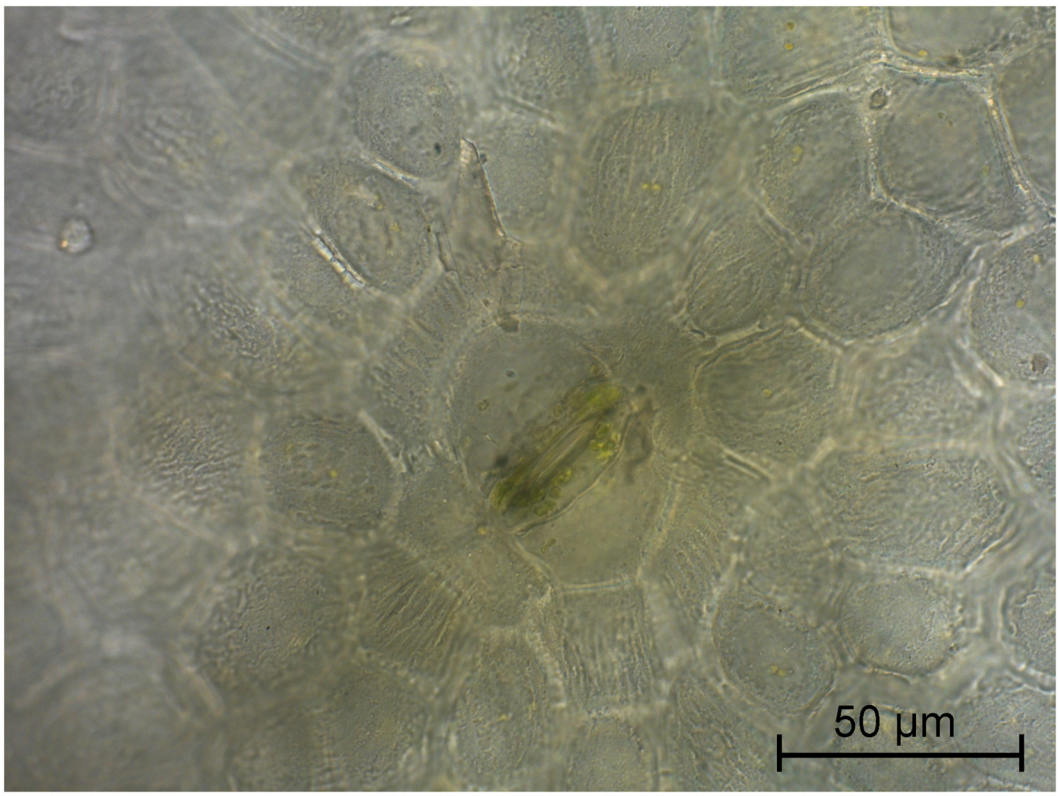

Fig. S5. Microscopic image of a pair of guard cells (of a stoma) and their surroundings on the surface of a smooth yellow banana peel.

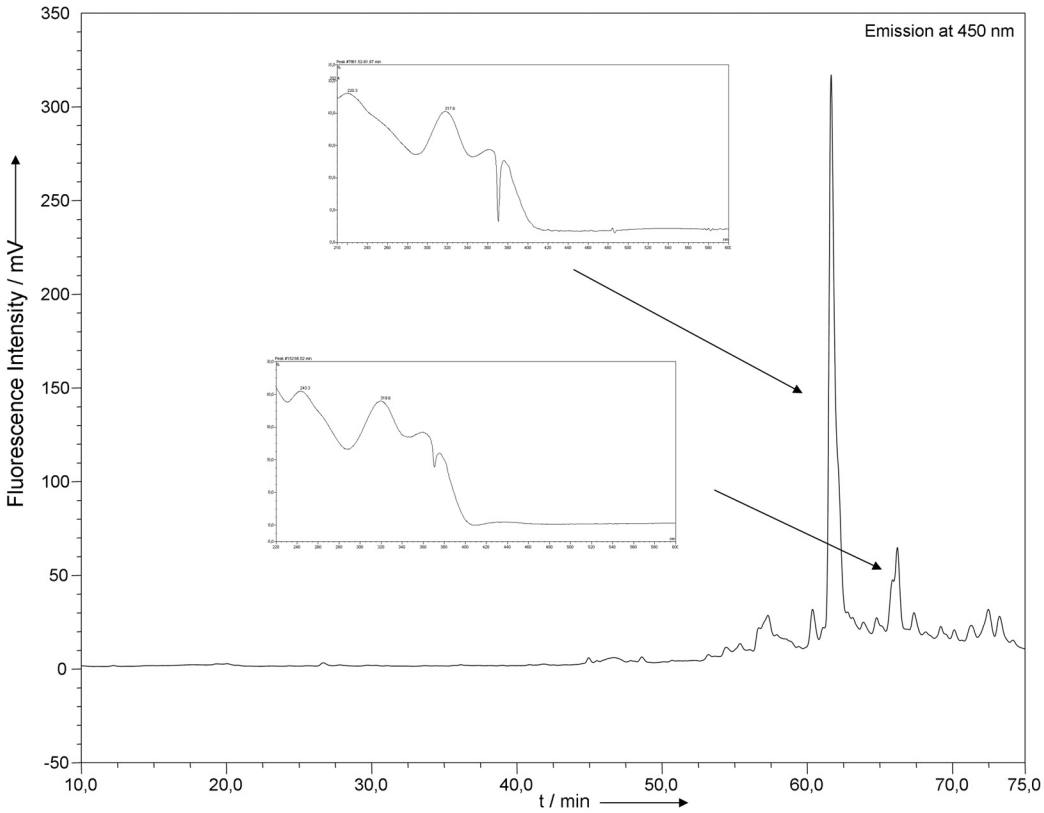

Fig. S6. Analysis by HPLC of an extract from a yellow (senescent) leaf of *Spathiphyllum wallisii*, trace from detection of luminescence at 450 nm (excitation at 350 nm, for details see *Materials and Methods*). (*Insets*) Absorbance spectra indicated two major fractions of FCCs and were registered on-line (at 360 nm an artifact is generated).