Supplementary Material for New Journal of Chemistry

Supplementary data

Zirconium organophosphonates as photoactive and hydrophobic host materials for sensitized luminescence of Eu(III), Tb(III), Sm(III), and Dy(III)

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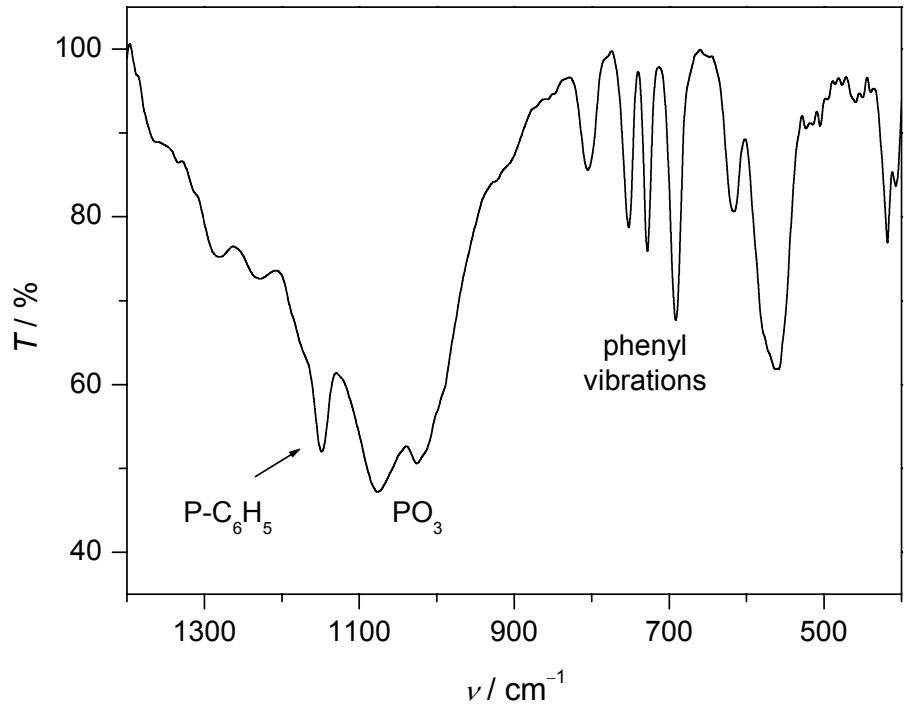
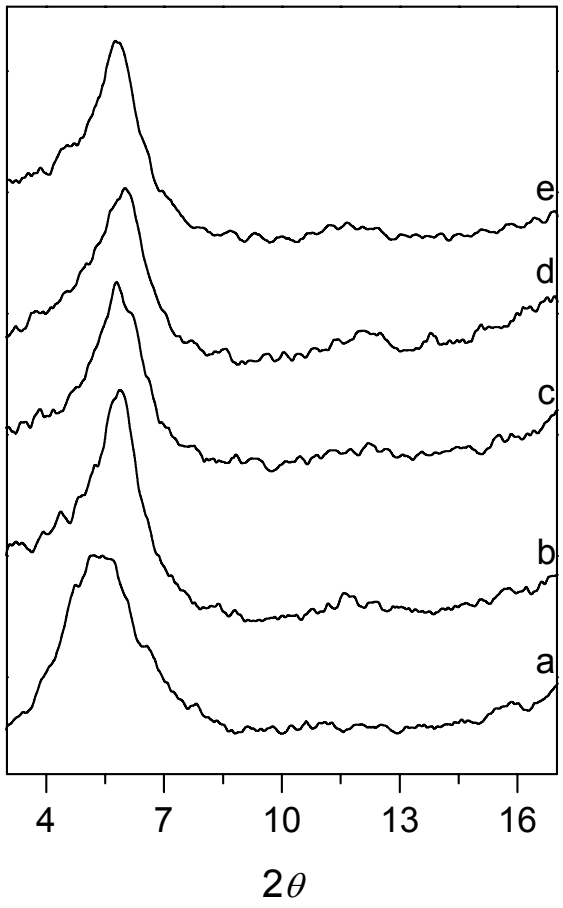
Synthesis of phenylphosphonic acid. Phenylphosphonic acid was prepared by oxidation of phenylphosphinic acid. 10.0 g (69.7 mmol) of phenylphosphinic acid were melted in a round-bottom flask equipped with a thermometer. When the temperature reached 100 ºC, 3.5 mL (54.4 mmol) concentrated nitric acid was added carefully. After cooling down to room temperature, the yellow solid was poured into 100 mL water and the product extracted with 3 × 50 mL diethylether. The combined organic phase was dried over $MgSO_4$. After removal of the solvent and re-crystallization from diethylether a colorless solid was obtained (4.2 g, 40 % yield). M.p., 160-161 ºC (lit., m.p., 158 ºC).

$C_6H_7O_3P$: calcd. C 45.54 %, H 4.43 %; found C 45.52 %, H 4.46 %. ^{1}H NMR (200 MHz, d_6-DMSO): δ 7.99 (br, 2H), 7.79-7.64 (m, 2H), 7.54-7.38 (m, 3H).

Synthesis of *m*-sulfophenylphosphonic acid. 17.0 g (105.0 mmol) Phenylphosphonic acid was added under stirring and at room temperature to 22 mL (321.0 mmol) chlorosulfonic acid. Then the solution was heated to 150 ºC for three hours. After cooling down to room temperature the excess of chlorosulfonic acid was removed with a rotary evaporator, yielding viscous oil. This oil was dissolved in 120 mL diethylether, and under ice-cooling 40 mL of water was added. After extraction with 3 × 50 mL diethylether, the combined organic phase was dried over $MgSO_4$. Upon removal of the solvent, *m*-sulfophenylphosphonic acid was obtained as crystalline solid (15.9 g, 59 % yield). The solid is very hygroscopic, such that no exact elemental analysis could be obtained. ^{1}H NMR (200 MHz, D_2O): δ 8.28-8.21 (d, 1H), 8.08-7.93 (m, 2H), 7.74-7.65 (m, 1H), 5.44 (s, 2H).



FT-IR spectrum of parent ZrSPP.



Powder X-ray diffraction patterns of (a) Na@ZrSPP, (b) Eu@ZrSPP,

(c) Tb@ZrSPP, (d) Sm@ZrSPP, and (e) Dy@ZrSPP.