Supporting Information
**S1:** Raman spectra of the thin amorphous nifedipine films which were produced by evaporation of the solvent from solutions in different solvents as indicated above each spectra. Characteristic Raman signals of g-nifedipine are indicated in the spectra for the film produced from acetone. In the spectra for acetone and ethyl acetate only the signals of g-nifedipine were detected. For the other solvents the Raman spectra show contributions of the respective solvent as indicated in the spectra.

**S2:** Time resolved Raman spectra of a thin nifedipine film produced from a solution in ethyl acetate recorded during the growth of the first crystallites starting with the amorphous film (bottom, 8 s) to the crystalline product after 30 min. The spectra show the rapid crystallization of an up to now unknown modification of nifedipine (16 s). This polymorph is at least stable for 30 minutes (top).
S3: Time resolved Raman spectra of a thin nifedipine film produced from a solution in ethyl acetate recorded during the slower growth of the second crystallites starting with the amorphous film (bottom, 30 s) to the crystalline product after 30 min. The spectra show the crystallization of a mixture of β-nifedipine and a new modification of nifedipine (150 s). This polymorph-mixture is at least stable for 30 minutes (top).

S4: Time resolved Raman spectra of a thin nifedipine film produced from a solution in acetonitrile recorded during the growth of crystallites starting with the amorphous film (bottom, 15 s) to the thermodynamically stable crystalline material (top). The spectra show the rapid direct crystallization of the thermodynamically stable α-modification from the amorphous precursor at 60 s.
S5: Raman spectra of a thin nifedipine film produced from a solution in chloroform recorded on the amorphous film, the crystallizing spherulites and the nucleus of the crystallites as indicated above each spectra. The signals were assigned to g-nifedipine in the amorphous film, to a mixture of g-nifedipine, a-nifedipine and a new polymorph at the nucleus and the new polymorph at the spherulites.

S6: Time resolved Raman spectra of a thin nifedipine film produced from a solution in tetrahydrofuran recorded during the growth of crystallites from the thin film starting with the amorphous film (bottom, 8 s) to the crystalline product after 30 min. The spectra show the crystallization of a new modification of nifedipine (82 to 90 s). This polymorph is at least stable for 30 minutes (top).