

Experimental

Hexa-(p-tert-butylphenyl)subphthalocyaninato boron chloride: 1 g (2.55 mmol) of bis-4,5-(*p*-*tert*-butylphenyl)phthalonitrile [16b] and 6 ml of 1M solution of BCl₃ in *p*-xylene were mixed together under argon atmosphere. The mixture was continuously stirred and gradually brought into strong reflux for about 1 hour. After further addition of 3-4 ml of BCl₃ solution, reflux was kept for another hour, the flask was flushed with a strong argon stream, and the solvent was removed under vacuum. The residue was dissolved in dichloromethane for the successive separation by column chromatography on silica-gel. The first purple fraction was taken, the eluent was evaporated and about 50 - 100 ml methanol were added to the dried fraction. The precipitate was filtered off and washed with a small portion of methanol. 1.2 g of violet powder resulted after drying in vacuo. Reaction was run approximately for 5 hours. Yield 0.32 g (31 %). EA percentages calculated for C₈₄H₈₄N₆BCl (%): C (82.44), H (6.92), N (6.87); found: C (82.37), H (7.02), N (6.21). ¹H-NMR (in CDCl₃), δ, ppm: 8.90 (s, 6H, *α*-H), 7.22-7.31 (m {dd}, 24H, *aryl*-H 6,7). ¹³C-NMR (in CDCl₃), δ, ppm: 31.3 (s, 10), 34.5 (s, 9), 124.2 (s, 3), 124.9 (s, 7), 129.8 (s, 6), 129.9 (s, 2), 138.2 (s, 5), 143.4 (s, 4), 150.1 (s, 8), 150.2 (s, 1). MALDI-TOF: m/z = 1179 (MH⁺ - B - Cl), 1189 (MH⁺ - Cl), 1224 (MH⁺, 100%), 1398 (MH⁺ + matrix) and other peaks of low intensity. UV-Vis [λ_{\max} (nm) /relative intensity in chloroform]: 589 /1.00; 544(shoulder)/0.334; 355/0.388; 289 /0.919.

Subphthalocyaninato boron chlorides 2: 10 ml of 1M BCl₃ in *p*-xylene were slowly syringed into a flask containing 2.5 g (6 mmol) of 4,5-bis-(*m*-trifluoromethylphenyl)phthalonitrile (**1**) [16b]. Addition of BCl₃ was carried out under argon atmosphere. The mixture was continuously stirred and gradually brought into strong reflux for about 1 hour. After further addition of 3-4 ml of BCl₃ solution, reflux was kept for another hour, the flask was flushed with a strong argon stream, and the solvent was removed under vacuum. The residue was dissolved in dichloromethane for the successive separation by column chromatography on silica-gel. The first purple fraction was taken, the eluent was evaporated and about 50 - 100 ml methanol were added to the dried fraction. The precipitate was filtered off and washed with a small portion of methanol. 1.2 g of violet powder resulted after drying in vacuo. Yield: 45% (calculated for the average formula C₆₆H₃₀N₆BCl₃F₁₆). EA percentages calculated for C₆₆H₃₀N₆BCl₃F₁₆ (%): C (59.69), H (2.28), N (6.33); found: C (59.64), H (2.18), N (6.25). ¹H-NMR (in CDCl₃), δ, ppm: 8.86 (s, 6H, *α*-H), 7.37-7.83 (m, 24H, *aryl*-H 6,8,9,10). ¹³C-NMR (in CDCl₃), δ, ppm: 123.7 (q, ¹J ≈ 272 Hz, 11), 124.3 (s, 8+3), 126.9 (q, pure resolved, 6), 129.0 (s, 9), 130.3 (s, 2), 130.8 (q, ²J ≈ 32.8 Hz, 7), 133.3 (s, 10), 140.8 (s, 5), 141.8 (s, 4), 150.0 (s, 1). MALDI-TOF: m/z = 1262 (MH⁺ - Cl), 1277 (MH⁺ - F), 1295 (MH⁺, 100%), 1311 (MH⁺ - F + Cl), 1326 (MH⁺ - 2F + 2Cl), 1344 (MH⁺ - 3F + 3Cl) and other peaks of lower intensity. UV-Vis [λ_{\max} (nm) /relative intensity in toluene]: 584.7 /1.00; 564 (shoulder) /0.50; 538/0.38; 350/0.30; 327 /0.30; 281/0.52. The partial exchange of F atoms in the CF₃ groups of phthalonitrile **1** with Cl atoms from BCl₃ during the preparation of **2** could be verified by MALDI-TOF spectrometry and EA. In fact, the formula of **2** resulted to be C₆₆H₃₀N₆BCl₃F₁₆, which correspond to SubPcs with Cl atoms replacing two F atoms per molecule on the average. The presence of CF₂Cl groups in mixture **2** could be furtherly verified from ¹³C-NMR spectra of **2** because the aromatic C linked to the CF₃ group appears as an intense quadruplet at 130.8 ppm with a splitting constant of ²J ≈ 32.8 Hz, whereas the aromatic C linked to CF₂Cl group appears as a triplet at 136.5 ppm with a splitting constant ²J ≈ 26.6 Hz.

NLO measurements

Nonlinear transmission measurements were carried out with 9 ns pulses of a Nd:YAG laser (Quantel YG980E) at its duplicated frequency (532 nm) at 2 Hz. Measurements of the incident and transmitted energies were recorded pulse by pulse with a pyroelectric detector (Scientech SPHD25) and a calibrated photodiode.

A half-wave plate and a cube polarizer were used for controlling the pulse energies. Glass cuvettes with 2 mm optical path length were used for the solutions in toluene. The laser beam diameter on the sample was in the order of 2.5 mm. Associated linear optical spectra were recorded with a UV-vis-NIR spectrometer (Varian Cary 5) before and after the NLO transmission measurements.

Rate equations for the five level model

Absorption cross sections σ_i , rate constants k_i and the populations N_i refer to the model reported in the inset of Figure 3.

$$\frac{dN_{S0}}{dt} = -\sigma_S(N_{S0} - N_{S1})I + k_S N_{S1} + k_{TS} N_{T1}$$

$$\frac{dN_{S1}}{dt} = -\sigma_S(N_{S1} - N_{S0})I - k_S N_{S1} - k_{ST} N_{S1}$$

$$\frac{dN_{T1}}{dt} = -\sigma_{T1}(N_{T1} - N_{T2})I + k_{ST} N_{S1} + k_{T1} N_{T2} - k_{TS} N_{T1}$$

$$\frac{dN_{T2}}{dt} = -\sigma_{T2}(N_{T2} - N_{T3})I - k_{T1} N_{T2} - \sigma_{T1}(N_{T2} - N_{T1})I + k_{T2} N_{T3}$$

$$\frac{dN_{T3}}{dt} = -\sigma_{T2}(N_{T3} - N_{T2})I - k_{T2} N_{T3}$$