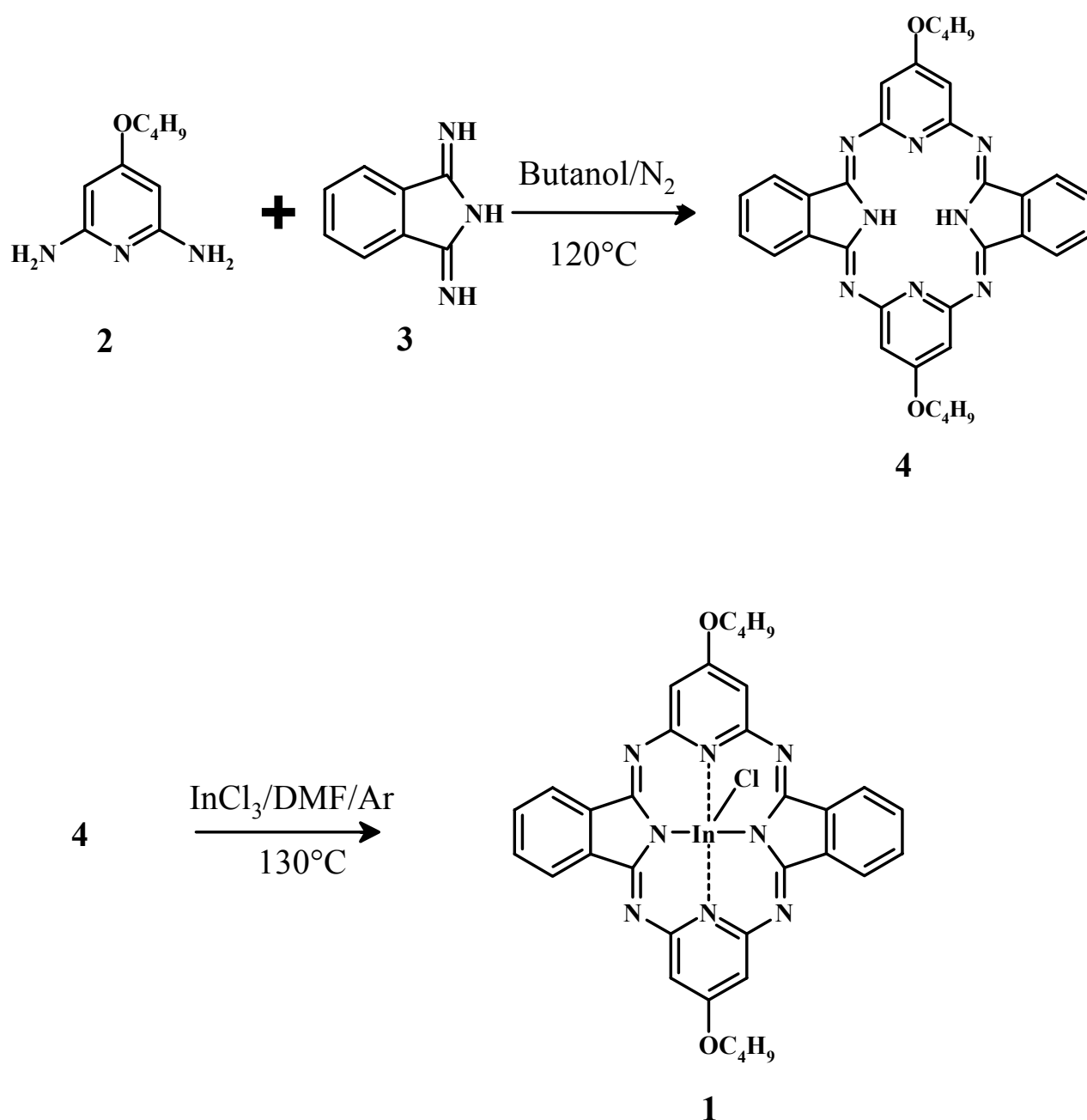


Electronic supplementary information relative to the communication titled *First demonstration of optical limiting effect for an hemiporphyrazine* (Authors: D. Dini, M.J.F. Calvete, M. Hanack, V. Amendola, M. Meneghetti)

Experimental Section

4-butoxy-2,6-diaminopyridine (2)

4-butoxy-2,6-diaminopyridine (**2**) was prepared from chelidamic acid following a modified version of the multistep procedure which was reported for the first time by Markees et al. [SI1,SI2].



Scheme 1. Synthesis of (BuO)₂HpInCl (**1**).

9,22-bis-(dibutoxy)hemiporphyrizinato chloro indium (1)

The hemiporphyrizinato indium chloride complex **1** was obtained by heating 9,22-bis-(dibutoxy)hemiporphyrizine (**4**) [SI1a] with InCl₃ in excess (Scheme 1). A suspension of 290 mg (0.5 mmol) of **4** and 220 mg (1 mmol) of InCl₃ in 3 ml dry DMF was heated at 130 °C for 6 hours. On cooling, water was added to precipitate the mixture. The solid was washed with water and cold methanol to remove DMF traces. After washing the solid was dried at 80°C in vacuum. Yield: 250 mg (0.40 mmol-80 %) yellowish solid. Mass (EI, 70 eV), m/z: 618 [M⁺], 561 [M⁺ - C₄H₉]. ¹H-NMR (CDCl₃): 0.96 (t, 6H), 1.47 (m, 4H), 1.73 (m, 4H), 3.95 (t, 4H, OCH₂), 6.30 (4H, H-6), 7.50 (br, 4H, H-1), 7.70 (br, 4H, H-2). ¹³C-NMR (CDCl₃): 13.70, 19.14, 30.83, 68.08, 107.22, 120.91, 129.39, 137.89, 157.19, 167.49.

NLO Transmission Measurements

Nonlinear optical transmission measurements were carried out with 9 ns pulses at 532 nm from a doubled Nd:YAG laser (Quantel YG980E) and at 2 Hz in an open-aperture configuration [SI4]. Transmitted energies were measured pulse by pulse with a pyroelectric detector (Scientech mod. SPHD25) and a calibrated photodiode. When incident intensity is below $1.0 \cdot 10^{25}$ photons cm⁻² s⁻¹ scattering of transmission data can take place due to the poor sensitivity of the pyroelectric detector at these values. The intensity of the incident pulses was controlled with a $\lambda/2$ wave-plate and a polarizing cube beam-splitter. The illuminated area on the sample was 0.050 cm². The measurements were carried out using 2 mm thick glass cells. Experiments were performed with $1 \cdot 10^{-4}$ M solutions of (BuO)₂HpInCl (**1**) in toluene ($\epsilon = 218$ L mol⁻¹cm⁻¹ at 532 nm for **1**). Linear optical spectra have been recorded with a Varian Cary 5 UV-Vis Spectrophotometer.

Pump and probe experiments

Pump and probe experiments have been performed on (BuO)₂HpInCl (**1**) solutions in order to examine the characteristics of the excited state of **1** which is responsible for its nonlinear optical behaviour. The lifetime and the spectral properties of complex **1** have been evaluated through pump and probe experiments with nanosecond laser pulses as pump radiation and probing the kinetics of fast absorption at different wavelengths on a microsecond timescale with nanosecond resolution. A Xenon lamp was used as a source for the probe and 1-GHz digital oscilloscope (LeCroy LC564A) to record the transient signals which were detected by

a Jobin-Yvon Horiba TRIAX 320 spectrometer equipped with an Hamamatsu phototube (R2257).

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