Supporting Information

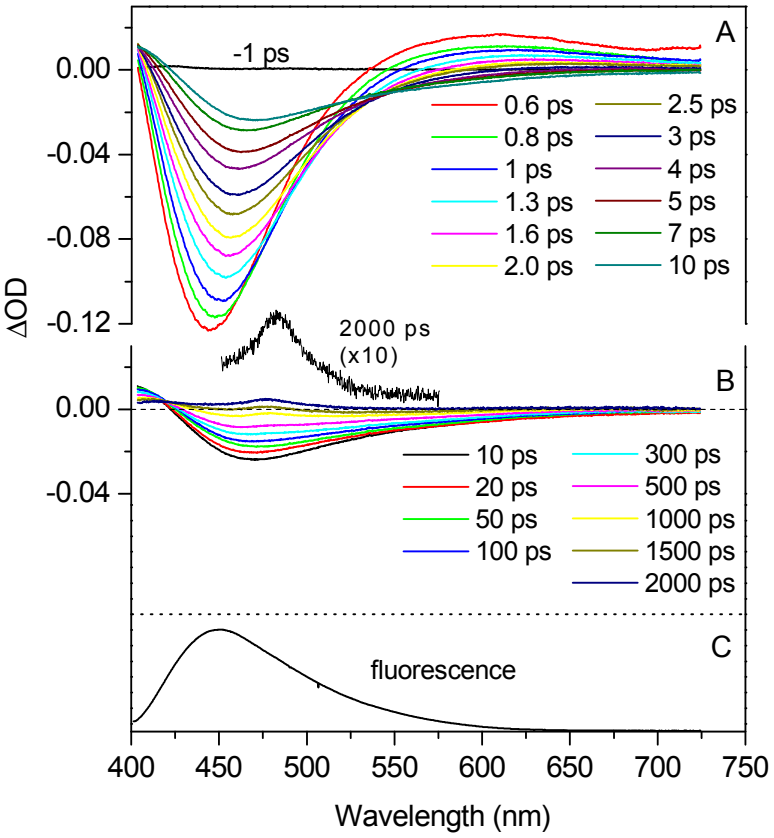

Fig. S1. PPA spectra of HOPPy-1 in MeCN after pump excitation at 383 nm. For clarity, the spectral evolution is separated in 2 time domains 0-10 ps (A) and 10-2000 ps (B). An enhancement of the 450-575 nm region of the spectrum recorded at 2000 ps is also shown. The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. A reference steady-state fluorescence spectrum of HOPPy-1 in MeCN is given (C).

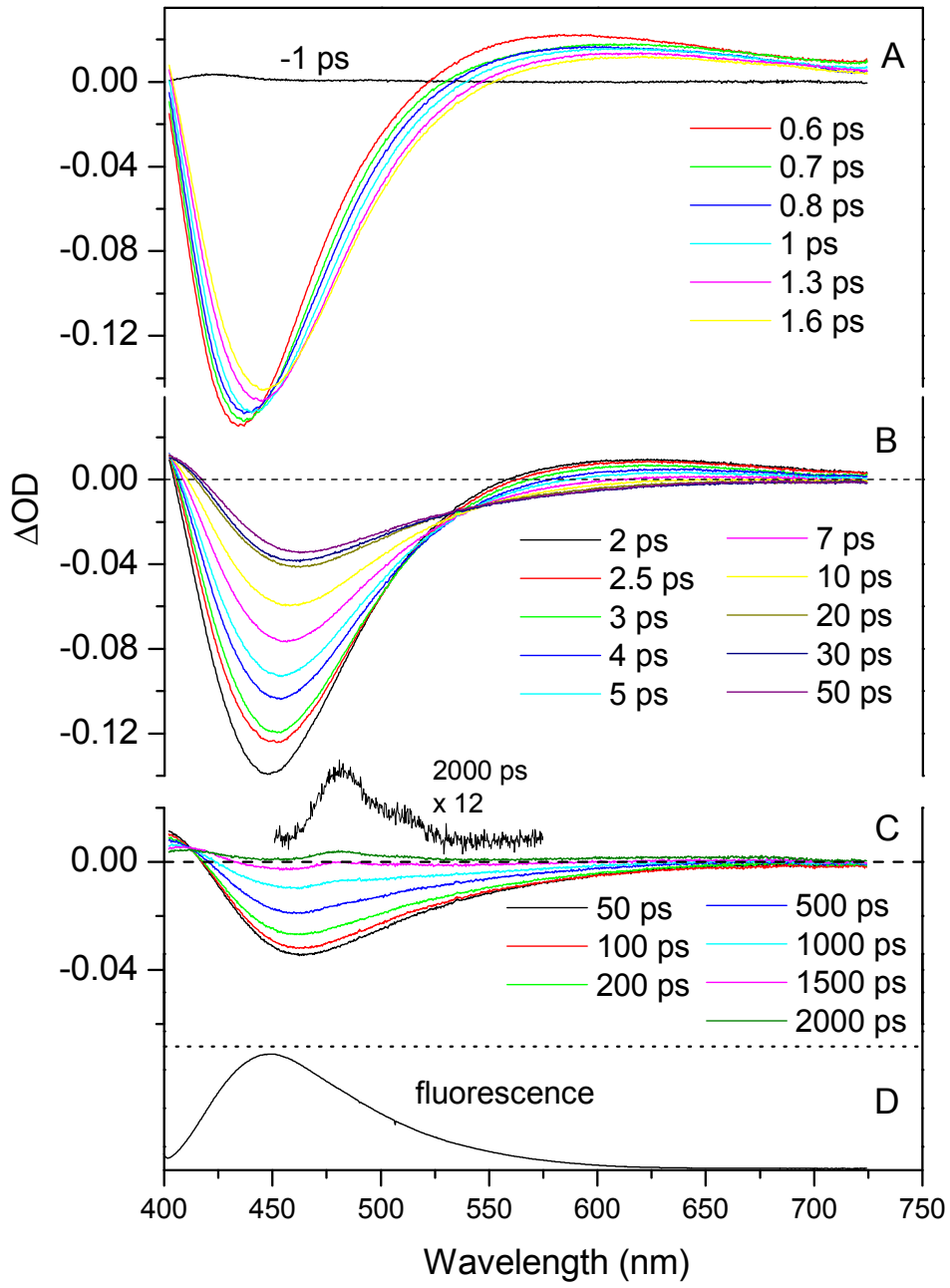

Fig. S2. PPA spectra of HOPPy-1 in BuCN after pump excitation at 383 nm. For clarity, the spectral evolution is separated in 3 time domains 0-1.6 ps (A), 2-50 ps (B), and 50-2000 ps (C). An enhancement of the 450-575 nm region of the spectrum recorded at 2000 ps is also shown. The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. A reference steady-state fluorescence spectrum of HOPPy-1 in BuCN is given (D).

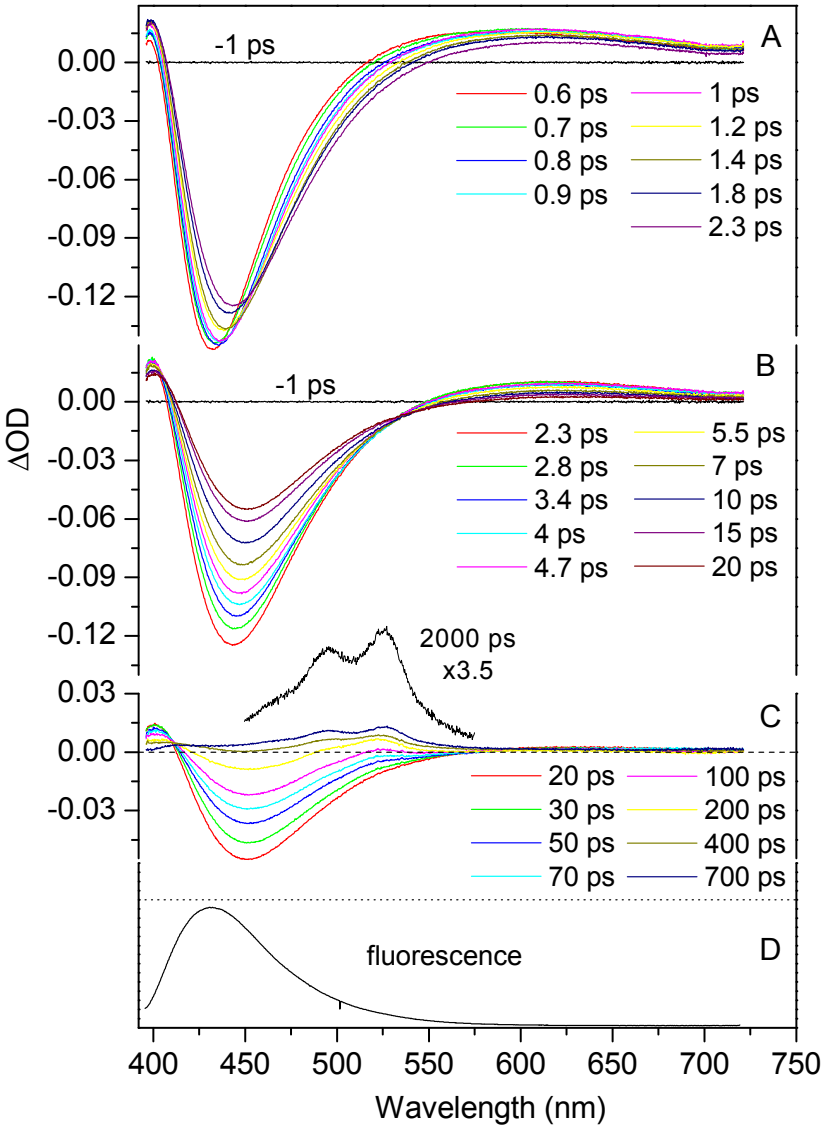

Fig. S3. PPA spectra of HOPPy-1 in THF after pump excitation at 383 nm. For clarity, the spectral evolution is separated in 3 time domains 0-2.3 ps (A), 2.3-20 ps (B), and 50-700 ps (C). An enhancement of the 450-575 nm region of the spectrum recorded at 700 ps is also shown. The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. A reference steady-state fluorescence spectrum of HOPPy-1 in THF is given (D).

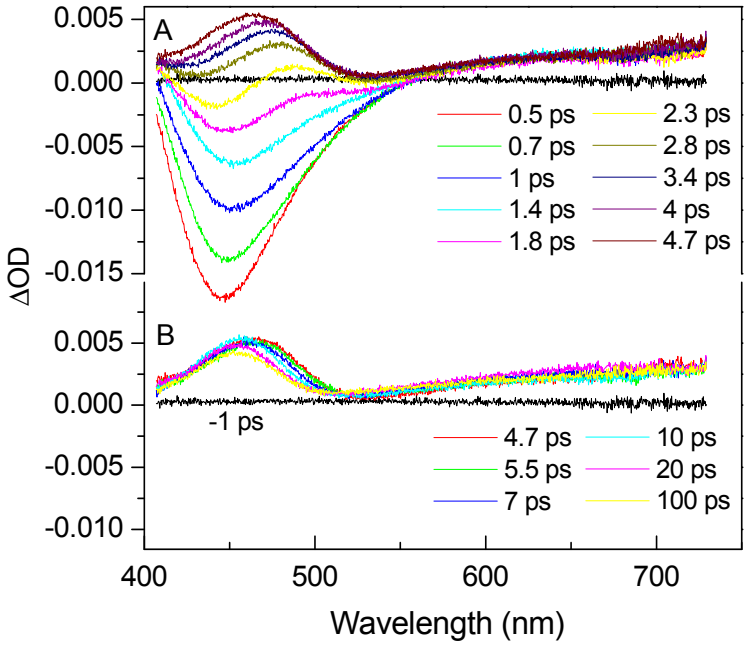

Fig. S4. PPA spectra of HOPPy-1 in water after pump excitation at 383 nm. For clarity, the spectral evolution is separated in 2 time domains 0-4.7 ps (A) and 4.7-100 ps (B). The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation.

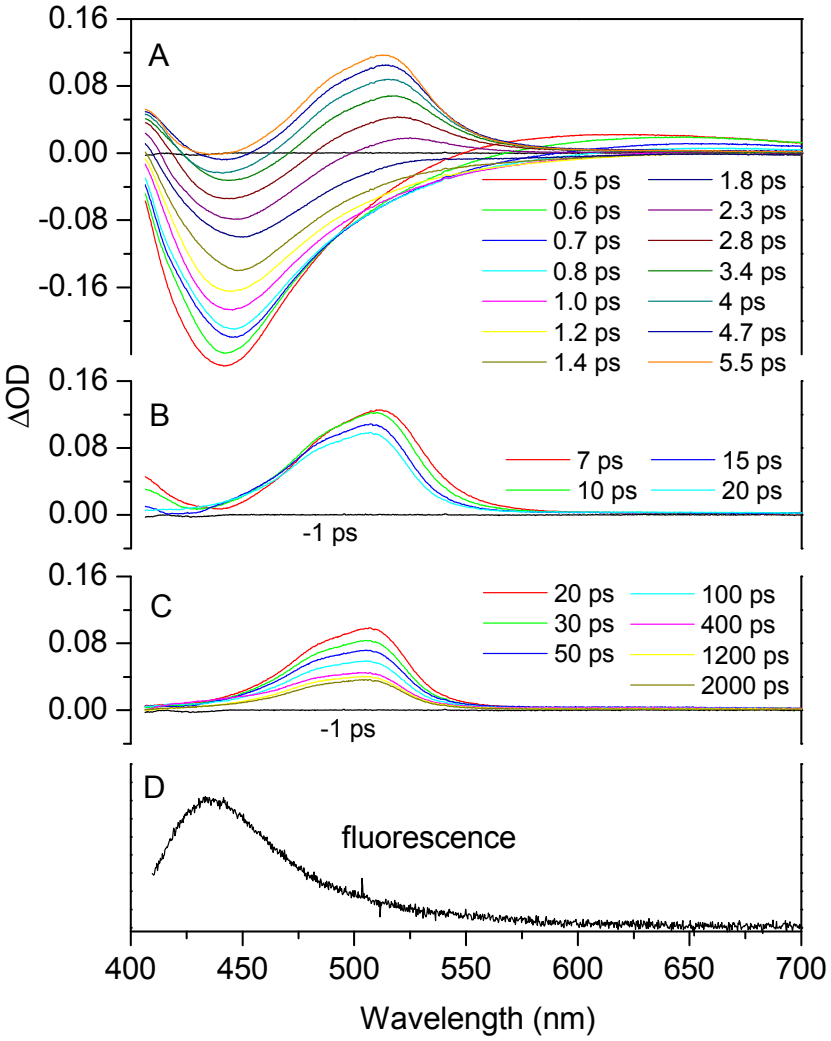

Fig. S5. PPA spectra of HOPPy-1 in EtOH after pump excitation at 383 nm. For clarity, the spectral evolution is separated in 3 time domains 0-5.5 ps (A), 7-20 ps (B), and 20-2000 ps (C). The -1 ps trace corresponds to the spectral baseline in the absence of pump excitation. A reference steady-state fluorescence spectrum of HOPPy-1 in EtOH is given (D).

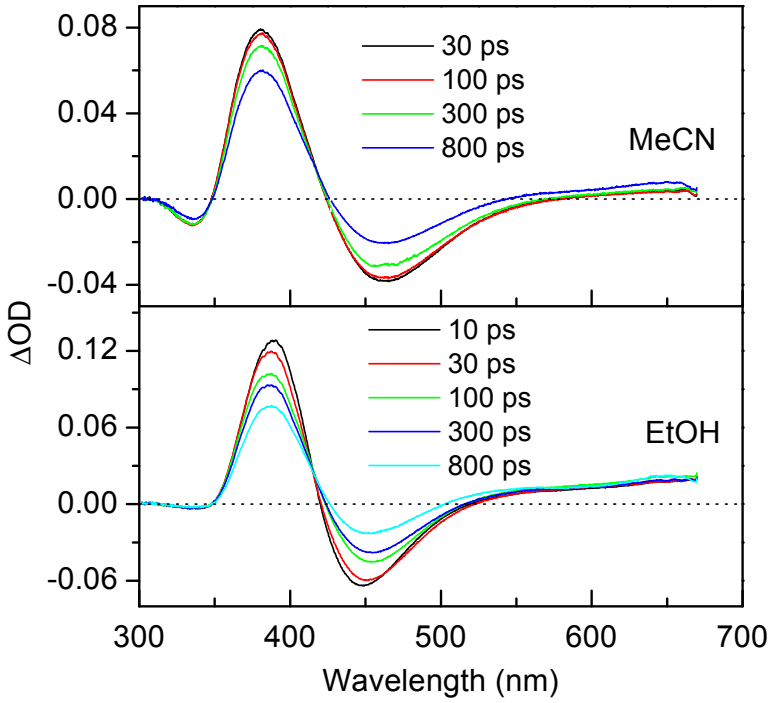

Fig. S6. PPA spectra of MOPPy-1 in MeCN (top) and EtOH (bottom) after excitation at 266 nm. The pump-probe time delays are given. The negative bands at ~340 and ~450 nm correspond to the ground state bleach (GSB) and stimulated emission (SE), respectively. The TA band at ~390 nm is due to the excited state absorption (ESA). The broad positive signal seen above 525 nm in EtOH is due to the presence of solvated electron produced by two-photon ionization of the solvent. Excited state lifetimes of ~1.3 and ~2.5 ns are estimated from the ESA and SE decay kinetics in MeCN and EtOH, respectively, in satisfactory agreement with the reported fluorescence decay times lifetimes (1.36 and 2.1 ns[28]).

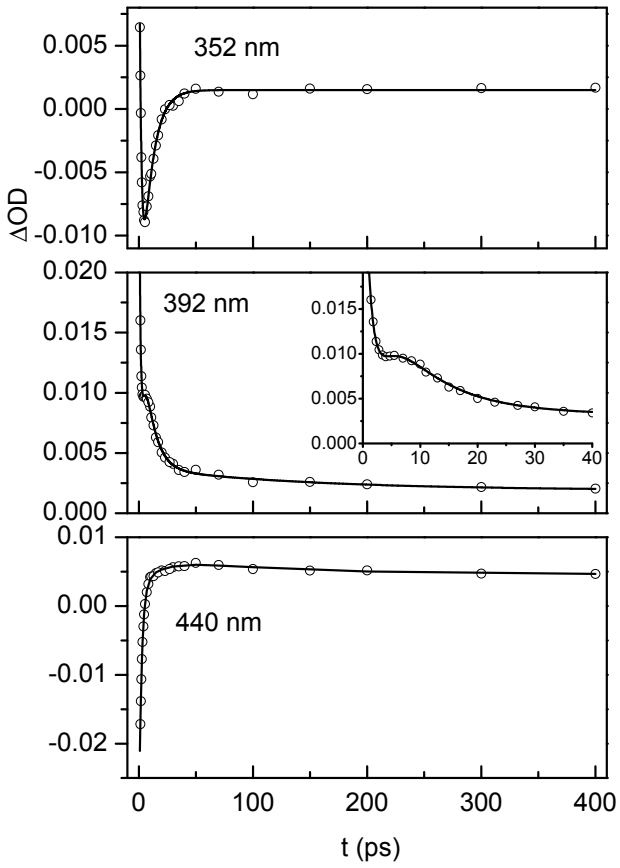

Fig. S7. Kinetic plots measured at 352 nm (GSB band), 392 nm (TA band), and 440 nm (SE band) for HOPPy-1 in EtOH (pump excitation at 266 nm).

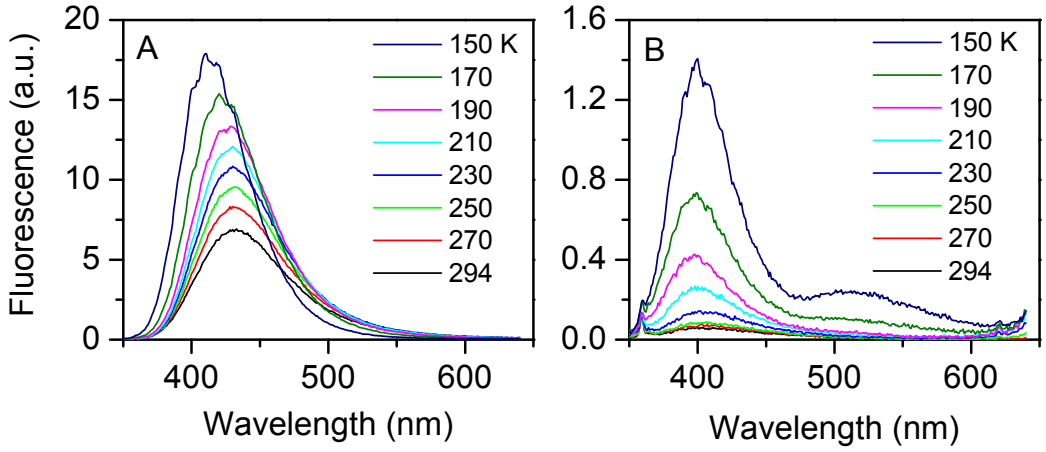

Fig. S8. Comparison of the temperature dependence of the fluorescence spectra of MOPPy-1 (A) and HOPPy-1 (B) in EtOH.