

## Supplementary Material

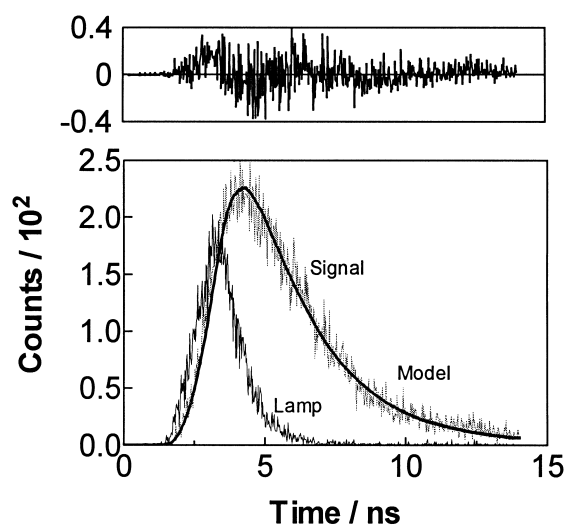


Fig. 1. Fluorescence decay kinetics in air-saturated toluene.  $\lambda_{\text{exc}} = 300 \text{ nm}$ ;  $\lambda_{\text{obs}} = 680 \text{ nm}$

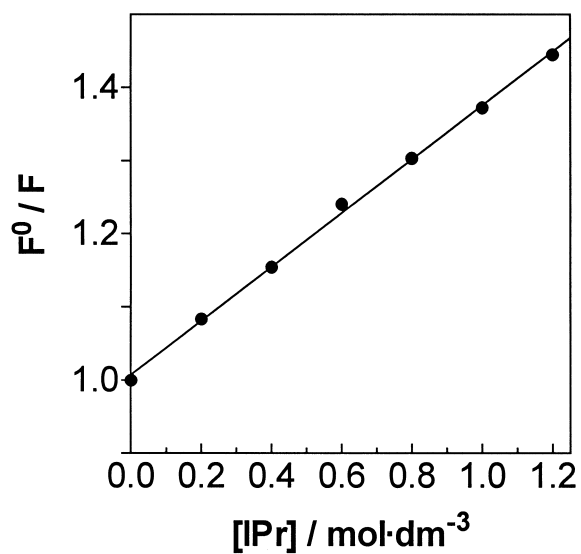


Fig.2. Stern-Volmer plot for the SubNc fluorescence quenching by 1-iodopropane in toluene, where  $F$  is the area under the fluorescence spectrum. From the slope  $K_{SV} = 0.373$  and the singlet lifetime  $\tau_s = 2.5$  ns, a quenching rate constant of  $k_q^{\text{Ipr}} = 1.47 \cdot 10^8$   $\text{M}^{-1}\text{s}^{-1}$  is calculated. The singlet-triplet energy gap is then calculated as  $\Delta E_{\text{ST}_n} = 250.5 - 25.51 \cdot \log k_q^{\text{Ipr}}$  according to Dreeskamp et al.<sup>12</sup>

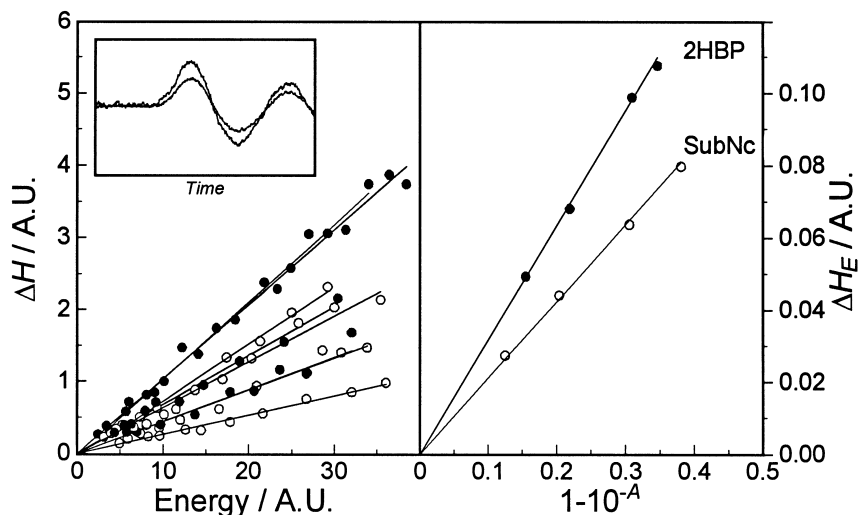


Fig.3. Determination of the product of the triplet quantum yield times the triplet energy ( $\Phi_T E_T$ ) by laser-induced optoacoustic calorimetry. **Left:** Laser-energy dependence of the optoacoustic signal (difference of amplitudes between the first maximum and the first minimum) observed upon 355 nm laser flash photolysis of argon-saturated solutions of SubNc and the calorimetric reference 2-hydroxybenzophenone. Each data set corresponds to a solution of different absorbance. **Inset:** Typical optoacoustic signals for SubNc and 2HBP in toluene. **Right:** The energy-normalized amplitudes are plotted vs. the absorption factor ( $1-10^{-A}$ ). The ratio of the slopes of the new lines,  $\alpha$ , is the fraction of absorbed energy released as heat by SubNc in the submicrosecond time scale, which is related to its photophysical properties as  $\alpha = \frac{E_1 - \Phi_F E_F - \Phi_T E_T}{E_1}$ ,

where  $E_\lambda$  is the molar energy of the laser photons (355 nm), and  $\Phi_F$  and  $E_F$  the quantum yield and average energy of fluorescence, respectively.  $\Phi_T E_T$  is readily calculated from this equation and is combined with the  $E_T$  value to yield  $\Phi_T$ .

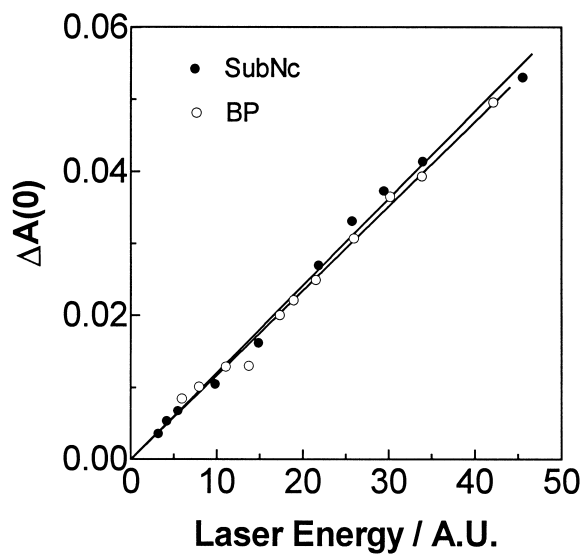


Fig.4. Laser-energy dependence of the zero-time absorbance change for optically-matched solutions of SubNc (in toluene,  $\lambda_{\text{obs}} = 436$  nm) and benzophenone (BP, in benzene,  $\lambda_{\text{obs}} = 506$  nm). The slopes of the straight lines are in the same ratio as the product of the triplet quantum yield times the triplet-minus-singlet absorption coefficient ( $\Phi_{\text{T}}\Delta\varepsilon_{\text{T-S}}$ ). Using the value of  $\Phi_{\text{T}}\Delta\varepsilon_{\text{T-S}} = 6300 \text{ M}^{-1}\text{cm}^{-1}$  at 506 nm for BP and the  $\Phi_{\text{T}}$  value for SubNc obtained above, the value of  $\Delta\varepsilon_{\text{T-S}}$  for SubNc at 436 is readily calculated.

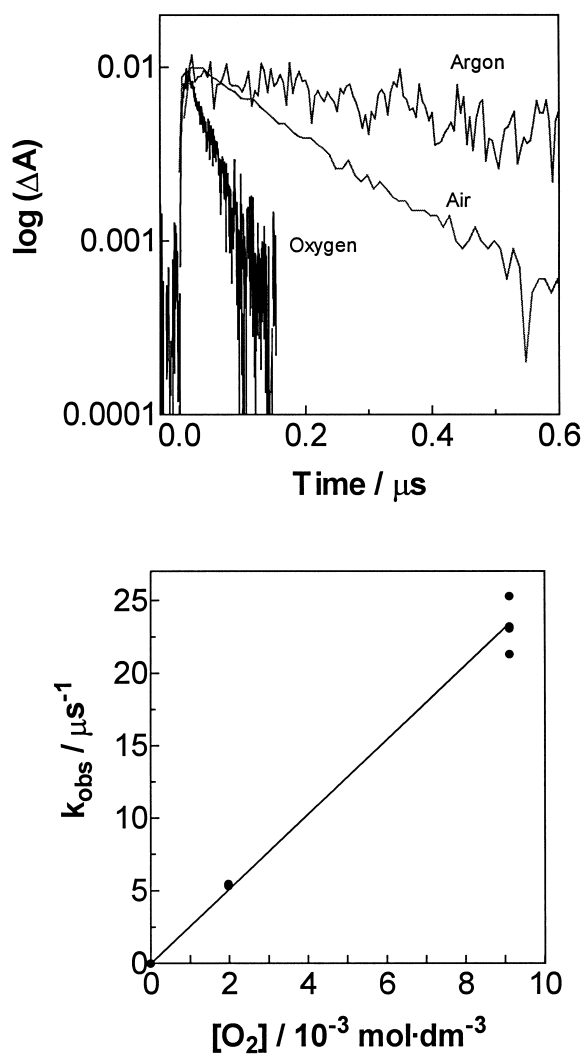


Fig.5. **(Top)** Triplet decay traces in argon, air- and oxygen-saturated toluene solutions of SubNc.  $\lambda_{\text{exc}} = 355 \text{ nm}$ ;  $\lambda_{\text{obs}} = 436 \text{ nm}$ . **(Bottom)** Stern-Volmer plot for the triplet quenching by oxygen in toluene. The rate constant  $k_q^{\text{O}_2}$  was determined from the equation

$$k_{\text{obs}} = k_{\text{T}}(0) + k_q^{\text{O}_2}[\text{O}_2],$$

where  $k_{\text{T}}(0)$  is the triplet decay rate constant observed in argon-saturated solutions.

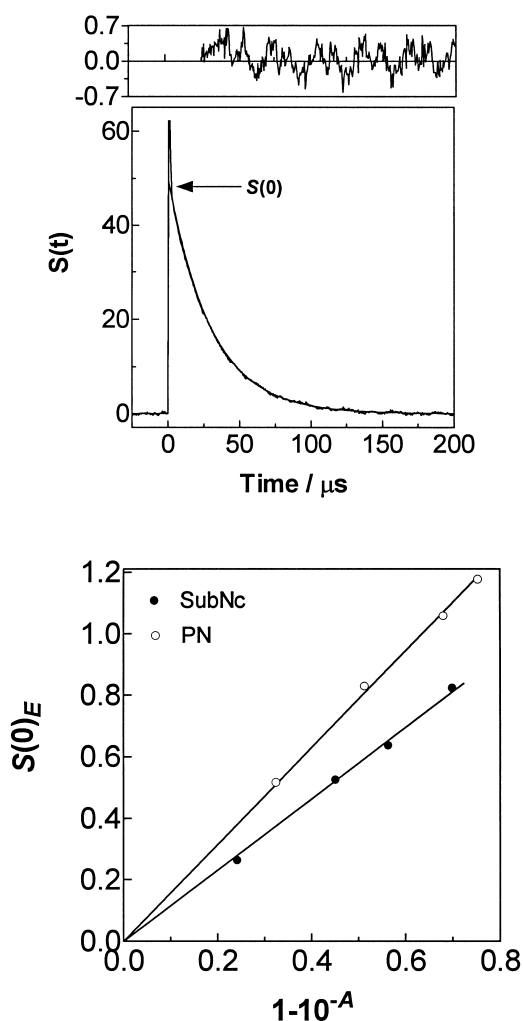


Fig.6. Determination of the singlet oxygen  $\text{O}_2(^1\Delta_g)$  quantum yield,  $\Phi_\Delta$ , by time-resolved near-IR emission spectroscopy (TRNIR). **(Top)** Typical  $\text{O}_2(^1\Delta_g)$  phosphorescence signal observed ( $\lambda_{\text{obs}} = 1270 \text{ nm}$ ) upon 355 nm laser photolysis of SubNc in air-saturated toluene. The decay is monoexponential with lifetime 29  $\mu\text{s}$ . **(Bottom)** The laser energy-normalized signal amplitude for SubNc and for the reference phenalenone (PN) is plotted as a function of the absorption factor ( $1-10^{-A}$ ) for a series of solutions with different absorbance. The slopes of this lines are in the same ratio as the  $\Phi_\Delta$  values for the two compounds.