Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Electronic Supplementary Information

Laser-induced Reprecipitation of Pyrene at 77 K and Its Dynamics as Studied by Spectroscopic Technique

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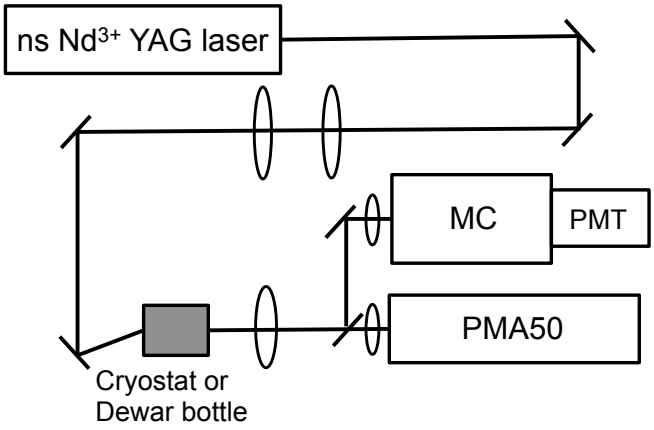

Fig. ESI1. Schematic representation of the ns-laser apparatus.

The inner-filter effect of Py excitation

To quantitatively elucidate the heat conversion due to the inner-filter effect, its contribution to the local heating was calculated on the basis of the molecular absorption coefficients as shown in main text. Fig. ESI2 shows the excitation intensity dependence of the number of the S_1 state, which was originally simulated and was confirmed with the experimental results.[1] In the case where the S_1 state of Py has no absorption at 355 nm ($\varepsilon_{355\ nm} = 0$), the number of molecules in the S_1 state linearly increases with an increase in the excitation intensity.[1] On the other hand, the strong saturation tendency was observed for the actual condition with the extinction coefficients[2] of 21100 $M^{-1}cm^{-1}$for the $S_n \leftarrow S_1$ absorption at 355 nm. With increasing excitation intensity, the difference between the former and the later value increases and this difference is converted into the heat resulting in the elevation of the temperature[1]. In actual, iterative processes of the absorption into higher excited state and subsequent rapid nonradiative deactivation to the lower excited state was pointed out for the dopant-induced laser ablation by Fukumura and Masuhara.[3] In the present case, the absorption from the S_1 state ($S_n \leftarrow S_1$ absorption) and rapid internal conversion in the singlet manifold can be repeated during a laser pulse leading to the temperature elevation of the surrounding solvent. We can adapt the concept in the Py solidification at rigid matrix.

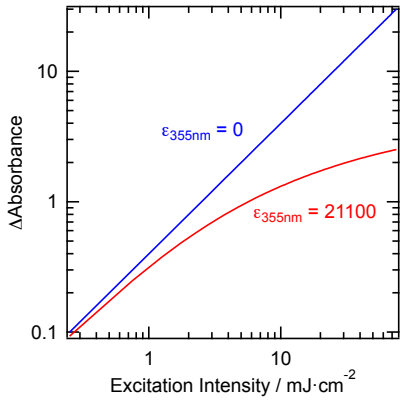

Fig. ESI2. Simulated inner filter effect on the $S_n \leftarrow S_1$ absorbance (λ = 468 nm) of pyrene, assuming extinction coefficients of $S_n \leftarrow S_1$ absorption were 0 and 21100 at λ = 355nm.

The transient temperature elevation could be estimated to be 20 K under the-355nm laser irradiation with the intensity of 25.5 mJ/cm^2. The number of Py molecules of the solution with the concentration of 8.0 mol·dm^{-3} is 4.82×10^{18}/ cm^3. The occupied volume of Py is 2.08×10^{-19} cm^3. The elevation temperature is estimated to be 5.1 K from the molar heat capacity of solvent (63.76 J·K^{-1}mol^{-1}), the quantum yield of the internal conversion and energy of the 355-nm photon (5.6×10^{-19} J), leading to transient melting of the glassy solvent by local temperature elevation.

1. H. Miyasaka, H. Masuhara and N. Mataga, *Laser Chem.*, 1983, **1**, 357.
2. M. F. M. Post, J. Langelaar and J. D. W. Van Voorst, *Chem. Phys. Lett.*, 1971, **10**, 468.
3. H. Fukumura and H. Masuhara, *Chem. Phys. Lett.*, 1994, **221**, 373-378.