Fluorescent Solvatochromic Behaviors and Nonfluorescence Processes of Charge-Transfer-Type Compounds with A 4-Nitrophenyl Moiety

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Owing to its strong electron-withdrawing ability, an introduction of a nitro group(s) can extend charge-transfer character in an electronic transition. Most compounds with a nitro group(s) are, however, nonemissive[1] and, therefore, effects of the presence of a nitro group(s) on the excited-state properties are not necessarily clear. In this work, we synthesized a series of compounds with a 4-nitropheny moiety (**1**–**3**, Figure) and evaluated their spectroscopic/photophysical properties.

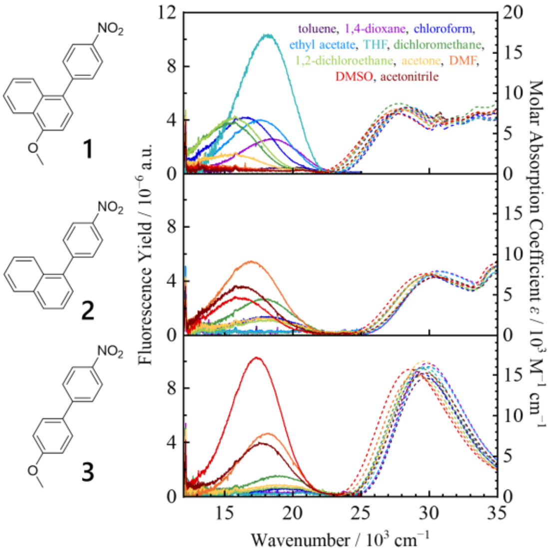

Figure. Chemical structures and absorption/ fluorescence spectra of **1**–**3** in various solvents.

1–**3** showed large fluorescent solvatochromism and, especially, fluorescence maximum energy ($\tilde{\nu}_\mathrm{f}$) of **1** drastically decreased from 20000 cm^{-1} to 16000 cm^{-1} with increasing the solvent polarity (Figure). Large fluorescent solvatochromism of **1**–**3** is explainable by large excited-state electric dipole moments being 9.7 (**1**), 7.0 (**2**) and 8.7 D (**3**) determined by the solvent dependences on the absorption/fluorescence maxima. Furthermore, nonfluorescence rate constants (k_d) of the compounds exhibited an identical trend, irrespective of the compound and solvent. In the region being $\tilde{\nu}_\mathrm{f} < 17500$ cm^{-1}, k_d decreased with increasing $\tilde{\nu}_\mathrm{f}$, as expressed by the energy gap law. On the other hand, in the >17500-cm^{-1} region, k_d increased with the fluorescence energy. The latter reverse energy gap dependence of k_d originates from intersystem crossing to a triplet excited state as evaluated by transient absorption measurements and TD-DFT calculations.

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