

1P28 Huge fluorescence lifetime elongation of catechol by complexation with 18-Crown-6 ether

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[Introduction] Although catechol belongs to benzenediol, it shows some difference from other benzenediols (resorcinol, hydroquinone) in terms of photochemistry. Among them, only catechol has intramolecular hydrogen (H-) bond between two adjacent OH groups. This H-bond reduce the energy gap between S_1 ($\pi\pi^*$) and S_2 ($\pi\sigma^*$), resulting in short S_1 lifetime (7.0ps). In present study, we found huge S_1 lifetime elongation by complexation with 18-Crown-6 ether (18C6) leading dissociation of the intramolecular H-bond and formation the intermolecular H-bond.

[Experimental and computational] To investigate the structure and S_1 lifetime of catechol \cdots 18C6 complex, we applied several laser spectroscopic methods combined with supersonic jet expansion. From the experimental results and with the aid of theoretical calculations, we determined the stable structure and obtained S_1 lifetime of the complex. We also measured S_1 lifetime and fluorescence spectra of catechol and catechol \cdots 18C6 complex in cyclohexane solutions.

[Results] <Gas phase> From the measurement electronic spectra, we found that 1:1 catechol \cdots 18C6 complex has two stable isomers. In this complex, two O-H groups of catechol are directed to out of plane to form two H-bonds with oxygen atoms of 18C6. We obtained the S_1 lifetime of these complexes from the fluorescence decay curves to be 10 ns for both isomers. In comparison with bare catechol, this value is 1,430 times longer (Left of Fig.1). This dramatic lifetime elongation arose from not only by catechol forming the intermolecular H-bond with 18C6 but also dissociation of the intramolecular H-bond of catechol to fit 18C6.

<Liquid phase> The right panel of Fig.1 shows fluorescence spectra obtained by changing mixing ratio of catechol and 18C6 from 1:0 to 1:0.7 in cyclohexane at catechol concentration of 5.3×10^{-5} mol/L. With increase of 18C6 ratio, fluorescence intensity increases monotonically. These results show that, in cyclohexane, catechol emit very weak fluorescence but once they are complexed with 18C6, fluorescence quantum yield greatly increases as in the case of gas phase.

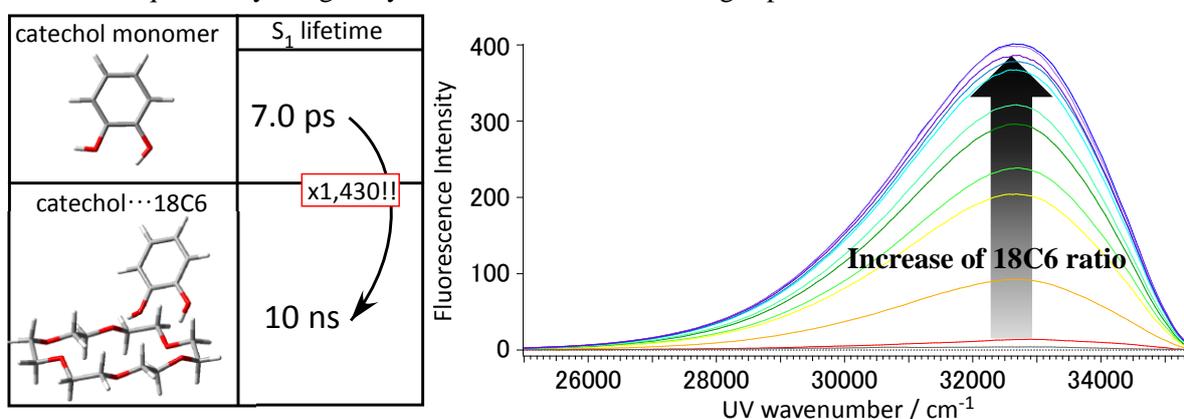


Fig.1 **Left:** bare catechol and one of the stable structure of catechol \cdots 18C6 complex and each S_1 lifetime. **Right:** 18C6 concentration dependence of the fluorescence spectra in cyclohexane solution.