Study of Two-Photon Absorption and Excited-State Dynamics of Coumarin Derivatives: Effect of Monomeric and Dimeric Structures

Supporting Information

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1. Transient Dynamics

Transient dynamics of coumarins C1 and C2 in DMSO, DMF and TCM at 650 nm are

shown in **Figure S1**. It can be observed that there is no significant change in the transient kinetic process of coumarin C1 in the three solvents (See Figure S1 (a)-(c)). The slight changes in curve characteristics are caused by different solvation effects. At zero time, a large number of electrons in the ground state are excited to the high excited state energy level S_n, and then relax to the excited state energy level S_1. Within a few tens of picoseconds, the number of electrons in excited state S_1 gradually approaches equilibrium, and the curve exhibits long-lived excited state absorption signals. As time delays, the electrons in the excited state S1 gradually relax to the ground state through radiative transitions.
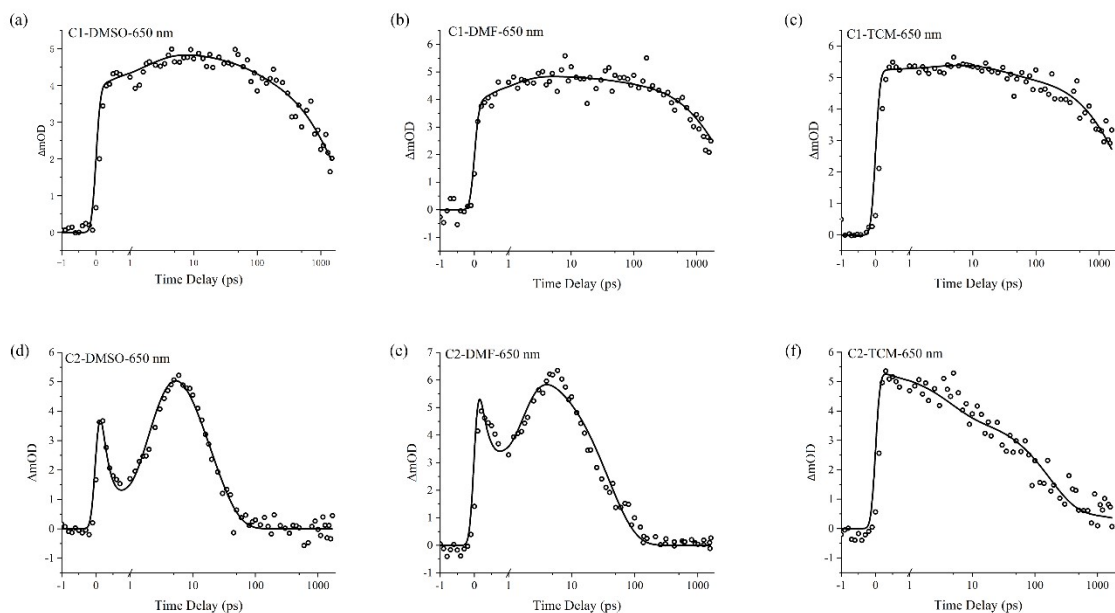

Figure S1. Transient dynamics of coumarins C1 and C2 in DMSO, DMF and TCM at 650 nm

Compared with coumarin C1, the transient dynamics of coumarin C2 show completely different curve characteristics (See Figure S1 (d)-(f)). Meanwhile, it can be observed that the transient kinetics of coumarin C2 at 650nm in TCM are different from those in

DMSO and DMF. The electronic transition and relaxation processes of coumarin C2 in low polarity (TCM) is the same as coumarin C1. With the enhancement of solvent polarity, coumarin C2 exhibits extremely significant intramolecular charge transfer characteristics, which leads to big changes in the excited state dynamics of coumarin C2 in DMSO and DMF. In **Figure S1** (d) and (e), the peak within 0-1 ps represents the excited state absorption signal based on the localized excited states. The deep valley at 1 ps represents a sharp attenuation of excited state absorption based on the localized excited states, which is caused by intramolecular charge transfer. The peak appearing at approximately 10ps indicates strong excited state absorption based on the charge transfer state. In the following tens of picoseconds, the electrons in the charge transfer state gradually relax to the ground state through radiative transitions.

2. Quantum Chemical Calculation

To demonstrate the reliability of the quantum chemical calculations, we further compared the calculated results of the first excited state absorption peaks of coumarins C1 and C2 in DMSO, DMF and TCM with experimental results, see **Table S1**. It can be found that the error between the calculated results and the experimental results is less than 15 nm, which fully proves the reliability of our calculated results.

Table S1. Calculated and experimental results of the first excited state absorption peaks of coumarins C1 and C2 in DMSO, DMF and TCM

Coumarin	Solvent	Calculated	Experiment
C1	DMSO	367 nm	380 nm
	DMF	367 nm	376 nm
	TCM	364 nm	378 nm
C2	DMSO	450 nm	465 nm
	DMF	450 nm	461 nm
	TCM	450 nm	460 nm

The frontier molecular orbitals and natural transition orbitals of C1 and C2 in DMF and TCM are shown in Figure S2 and S3, respectively. There is a significant difference in the HOMO→LUMO transition of coumarin C2 in DMF and TCM. Compared with in DMF, coumarin C2 exhibits significantly smaller π-electron delocalization on the right-side branch in TCM, which leads to the attenuation of the localized excitation. Similar phenomena can also be observed in natural transition orbits of coumarin C2 in DMF and TCM.
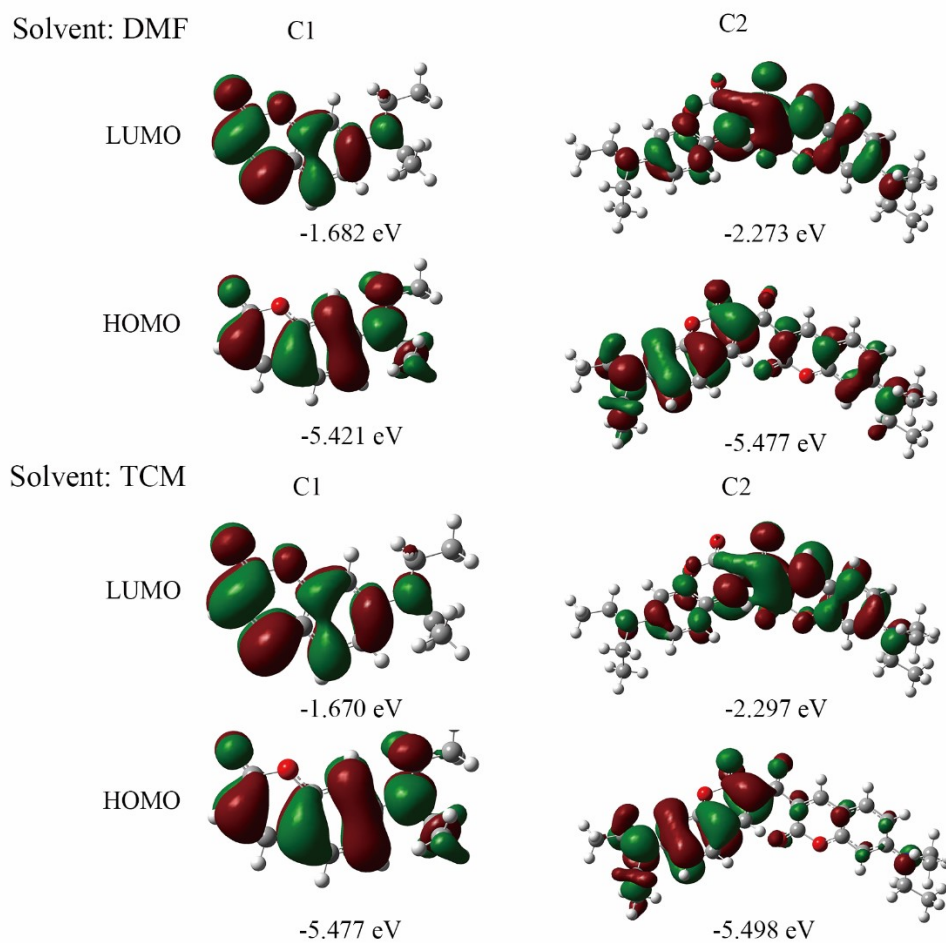

Figure S2. Frontier molecular orbitals of coumarins C1 and C2 in DMF and TCM
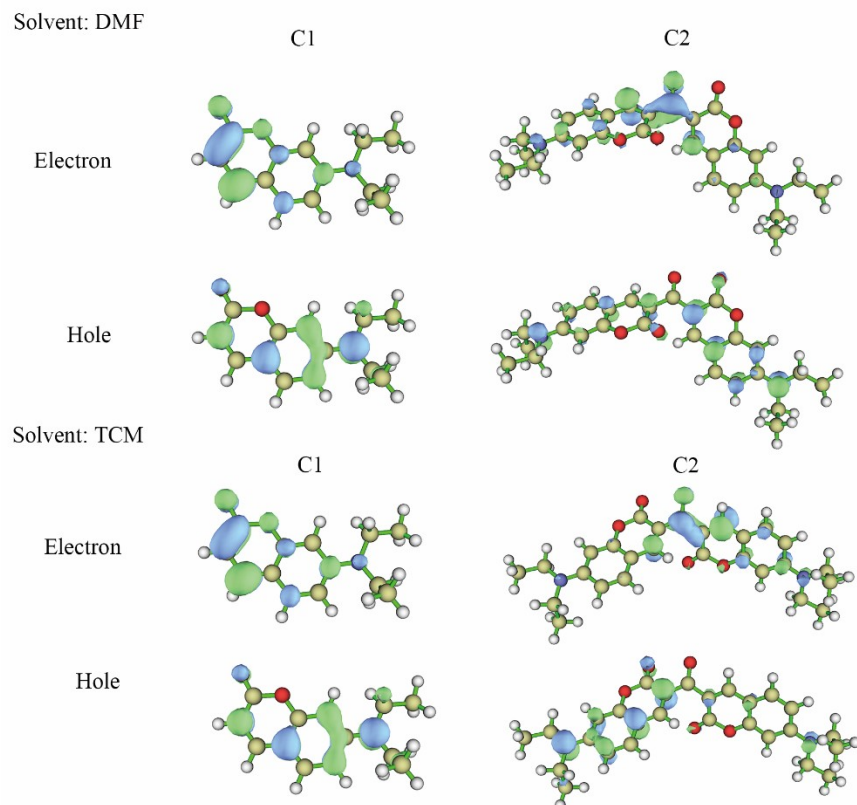
Figure S3. The NTOs of coumarins C1 and C2 in DMF and TCM in the first excited state S_1.

We further characterized the torsion angle of coumarin C2 between right-side branch and left-side branch, see **Figure S4**. We infer that the different torsion angles which leads to the different π-electron delocalization of coumarin C2 on the right-side branch. Of course, this inference needs further verification.
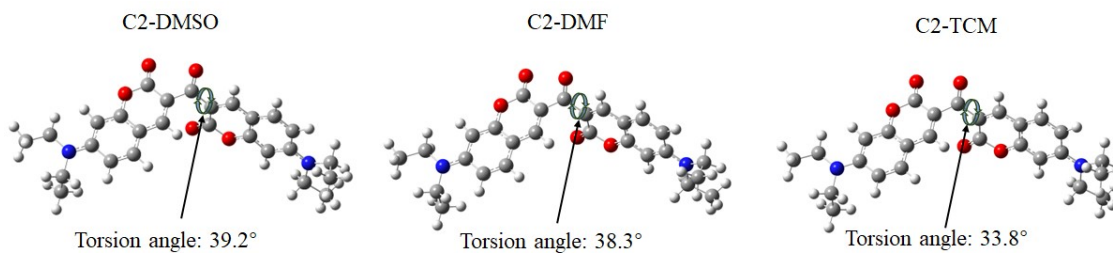

Figure S4. Torsion angle of coumarins C2 in DMSO, DMF and TCM