Electronic Supplementary Information (ESI)

Deciphering the photophysical properties of naphthalimide derivative using ultrafast spectroscopy

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S1. Discussion on Theoretical Calculations

The optimization of S_1 state when varying the twist angle was not successful with selected long-range separated functional CAM-B3LYP[1] and PCM solvent model, i.e., no significant twist was obtained in acetonitrile. On the other hand, we employed the semi-empirical evaluation with PM7[2] Hamiltonian of MOPAC[3] (with solvent model COSMO) allowed to reproduce the twisted geometries of HP-NAP in polar environment, as showed in Figure S1. The results here are similar to previous reports.[4,5]
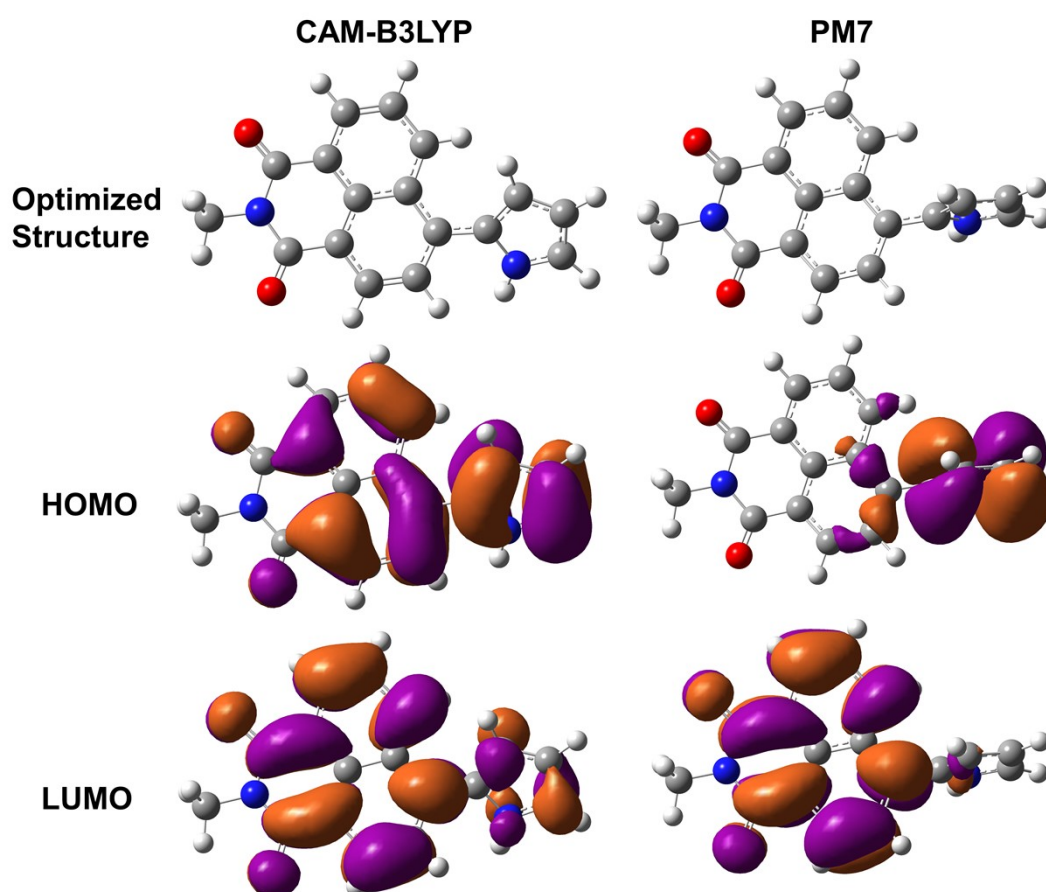

Fig. S1 The theoretical S_1 results of HP-NAP at CAM-B3LYP and semi-empirical method (PM7 Hamiltonian of MOPAC, solvent model COSMO): the optimized geometries and FMOs.

S2. Supplementary Results

Table S1. Stokes shift and solvent orientation polarizability comparison

solvent[a]	n	ε	Δf	Abs /nm	Ems /nm	Stokes Shift /cm^{-1}
Hex	1.372	1.9	0	395	460	3577
MX1	1.388	4.75	0.167	416	511	4469
CH_2Cl_2	1.4211	9.1	0.22	409	520	5219
THF	1.404	7.6	0.21	419	528	4927
MX2	1.373	22.55	0.28	417	544	5598
ACN	1.342	37.5	0.31	412	550	6090

a. MS1 represents mixed solvent of Hex and THF (v/v=1:1); MS2 represents mixed solvent of THF and ACN (v/v=1:1). The corresponding ε_{mix} and n_{mix} were calculated according to $\varepsilon_{mix} = v_a\varepsilon_a + v_b\varepsilon_b$ and $n_{mix}^2 = v_a n_a^2 + v_b n_b^2$, respectively; v_a and v_b are the volume percentages of each solvent.
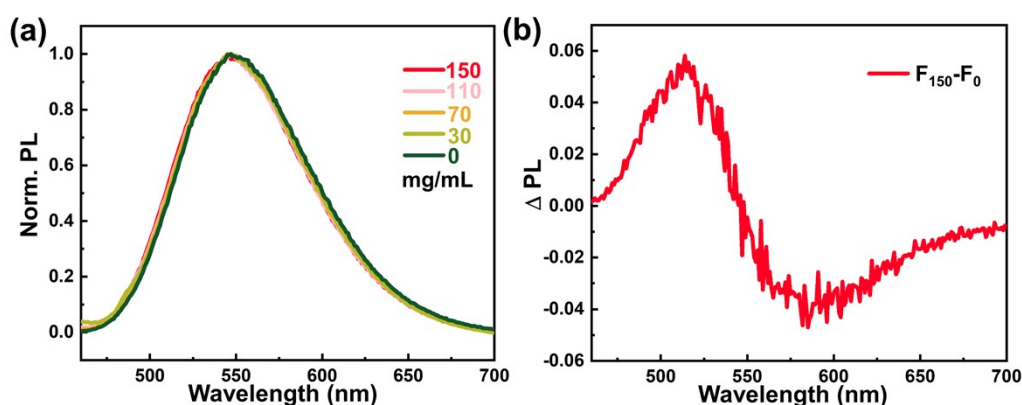

Fig. S2 (a) The normalized fluorescence spectra of HP-NAP in ACN solvent with different mass concentration of PMMA. (b) The differential spectrum between the normalized fluorescence spectra with PMMA concentration of 150 mg/mL and PMMA concentration of 0 mg/mL.

Table S2. The viscosity dependent fluorescence lifetime of HP-NAP in ACN solvent with different mass concentration

PMMA/ mg·ml^{-1}	τ/ ns
150	3.24
110	3.07
70	3.02
30	2.79
0	2.69

Table S3. The time constants of HP-NAP obtained from global analysis in different polar solvents.

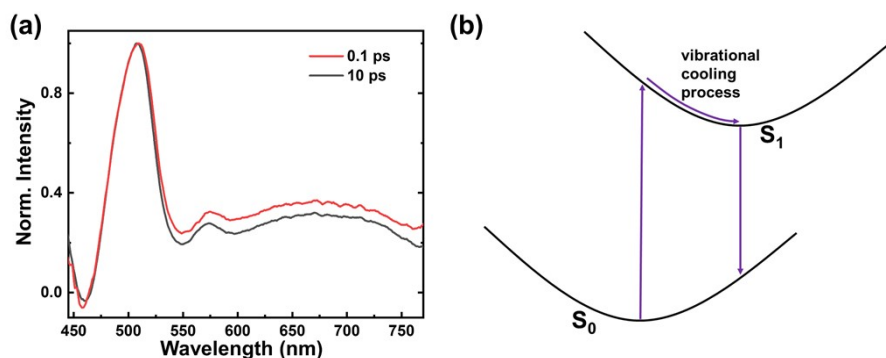|	τ_1/ps	τ_2/ns
Hex	6.72	3.02
THF	1.82	4.50
ACN	0.64	2.25

Fig. S3 (a) The normalized fs-TA spectra at different delay times of HP-NAP in Hex to demonstrate the signal change associated with the vibrational cooling. (b) The schematic diagram of vibrational cooling process of HP-NAP in Hex.

Table S4. The viscosity dependent time constants of HP-NAP obtained from global analysis in ACN solvent with different mass concentration.

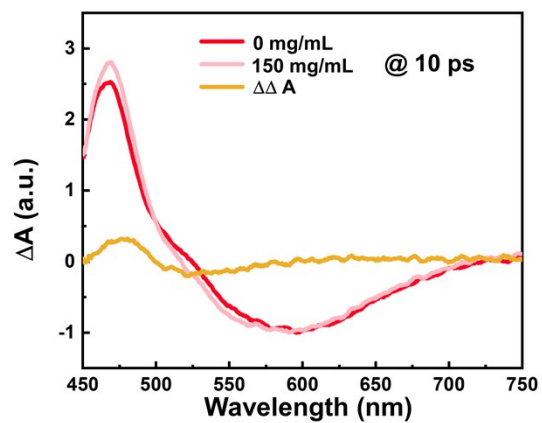| PMMA/ mg·ml^{-1}	τ_1 /ps	τ_2 /ns
0	0.64	2.25
30	0.72	2.56
70	0.77	2.78
110	0.92	3.04
150	0.95	3.13

Figure S4. The TA differential spectrum (ΔΔA) between the normalized spectra with PMMA concentration of 150 mg/mL and PMMA concentration of 0 mg/mL. Noted that the TA spectra are normalized at the SE signals for showing the SE shift.

S3. References

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3. J. J. P. Stewart. Stewart Computational Chemistry, Colorado Springs, CO, USA, HTTP://OpenMOPAC.net, **2016**.
4. J. Jovaišaitė, P. Baronas, G. Jonusauskas, D. Gudeika, A. Gruodis, J. V. Gražulevičius, S. Juršėnas. Phys. Chem. Chem. Phys., **2023**, 25, 2411-2419.
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