Supplementary information of

Solvatochromic Multi-colour Fluorescence Driven by Thiol-type ESIPT in a 1-Mercapto-Naphthaldiimide Compound

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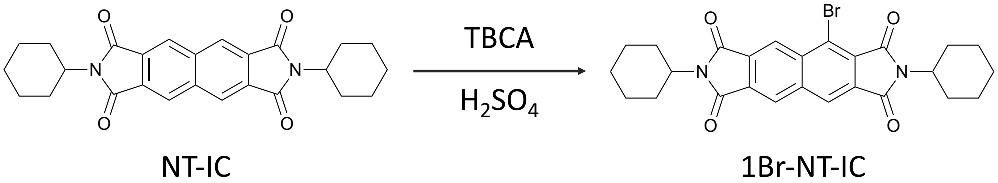
1. Materials

NT-IC[1] and TBCA[2] were synthesized according to previous reports. 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), sulfuric acid (H_2SO_4), methanol (MeOH), *N*,*N*-dimethylformamide (DMF), hydrochloric acid (HCl), chloroform ($CHCl_3$), acetonitrile (MeCN), cyclohexane (Cychex), and dichloromethane (CH_2Cl_2) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), while trifluoroacetic acid (TFA), sodium mono hydrogen sulfide n-hydrate ($NaSH \cdot nH_2O$) and *N,N*-dimethylacetamide (DMAc) were purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan), with all chemicals used without further purification. Polymethyl methacrylate (PMMA, Sumipex-LG, M_w ~100,000) was obtained from Sumitomo Chemical Co. Ltd., Japan. Cyclo olefin polymer (COP, Zeonex 480R, average M_w ~480,000) was obtained from Zeon Corp., Japan. All commercially available materials other than those mentioned above were used as received without any further purification.

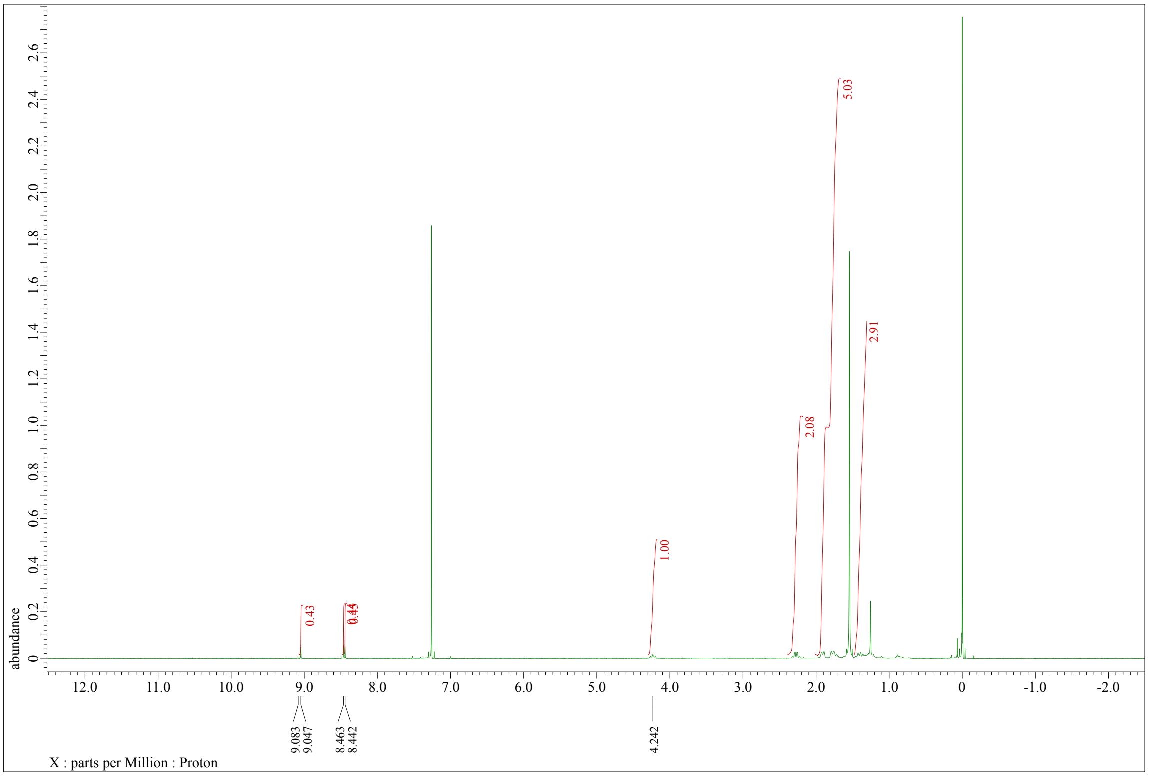
2. Synthesis

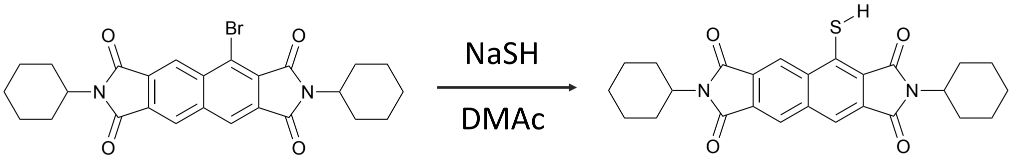


1-Bromo-*N,N'*-dicyclohexyl-2,3,6,7-naphthalenetetracarboxylic dianhydride (1BrNT-IC)

The solution of TBCA (210 mg, 0.58 mmol) in H_2SO_4 (98%, 5 mL) was dropwise added into the solution of NT-IC (500 mg, 1.2 mmol) in H_2SO_4 (98%, 2 mL) at 0 °C and stirred at 25 °C for 8 h. The resulting solution was poured into ice, and the precipitated solids were filtered, then washed with water and MeOH. The resulting solid was recrystallized by DMF and purified by column chromatography (CH_2Cl_2) to give a yellow powder (41 mg, 6.9%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 1.25-1.39 (3H, br *m,* CH_2), 1.72-1.73 (3H, br *m*, CH_2), 1.86-1.87 (2H, br *m*, CH_2), 2.15-2.25 (2H, br *m*, CH_2), 4.24 (1H, *m*, NCH), 8.44 (1H, *s*, aryl), 8.46 (1H, *s*, aryl), 9.04 (1H, *s*, aryl)



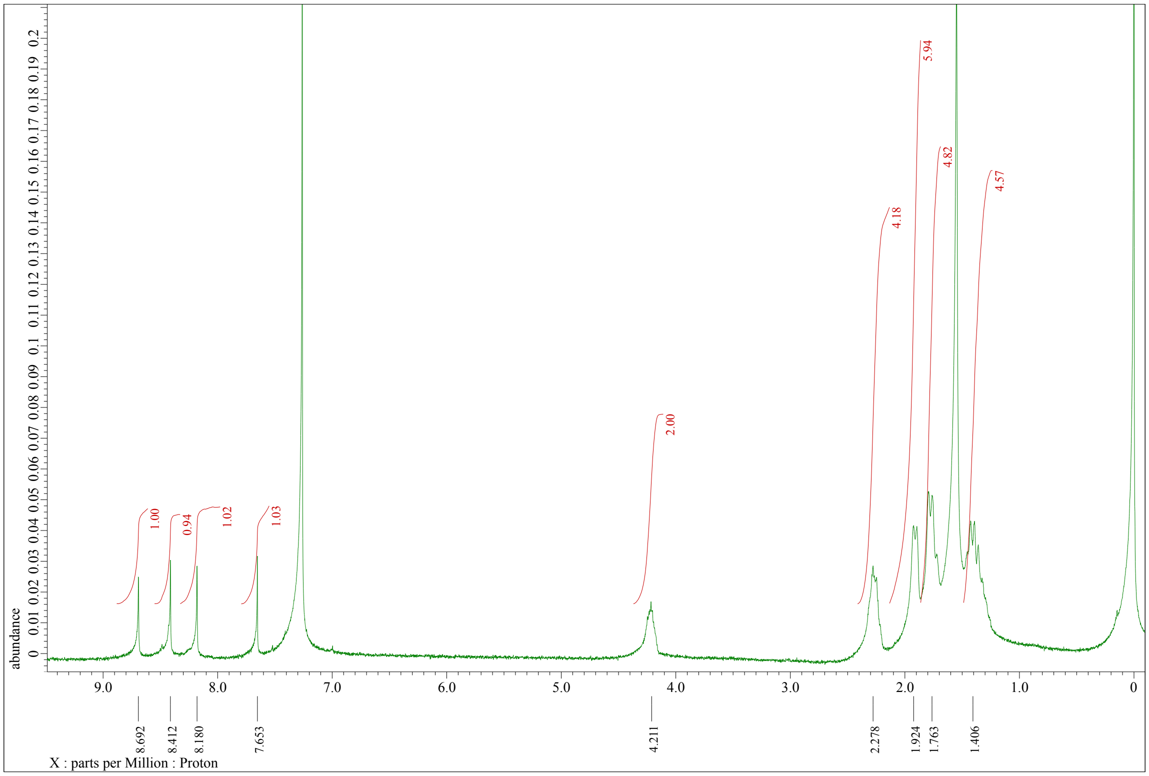


1SNT-IC

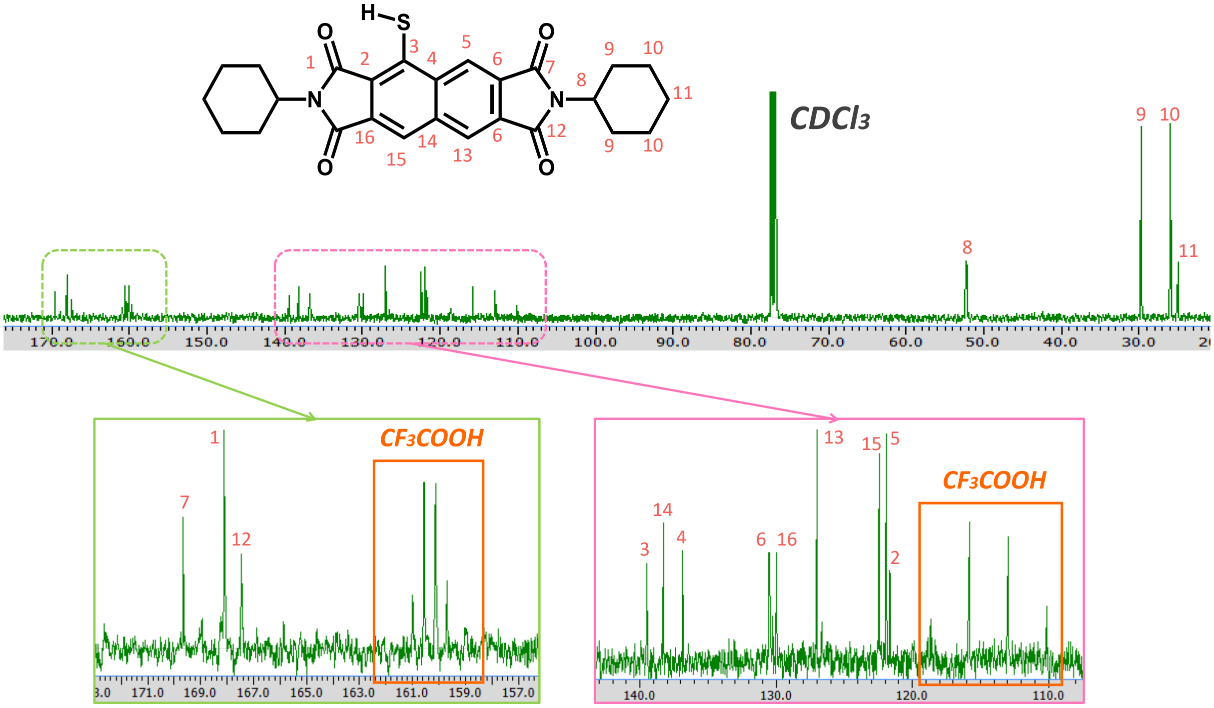
_N,N'_-Dicyclohexyl-1-mercapto-2,3,6,7-naphthalenetetracarboxylic dianhydride (1SNT-IC)

Under a nitrogen atmosphere, DMAc (1 mL) was added into NaSH · nH_2O (14 mg, 0.24 mmol) and stirred at 60 °C for 2 h. The solution of 1BrNT-IC (41 mg, 0.081 mmol) in DMAc (1 mL) was dropwise added into the solution and stirred at 120 °C for 2 h. After cooling to 25 °C, the resulting solution was poured into ice and added 5% HCl solution until pH = 1. The precipitated solid was filtered and purified by column chromatography ($CHCl_3$) to give a pale-yellow powder (74 mg, 85%).

^{1}H-NMR (400 MHz, CDCl$_3$): δ [ppm] 1.41 (5H, br *m*, CH$_2$), 1.76 (5H, br *m*, CH$_2$), 1.92 (6H, br *m*, CH$_2$), 2.28 (4H, br *m*, CH$_2$), 4.20 (2H, *m*, NCH), 7.65 (1H, *s*, SH), 8.18 (1H, *s*, aryl), 8.41 (1H, *s*, aryl), 8.69 (1H, *s*, aryl)



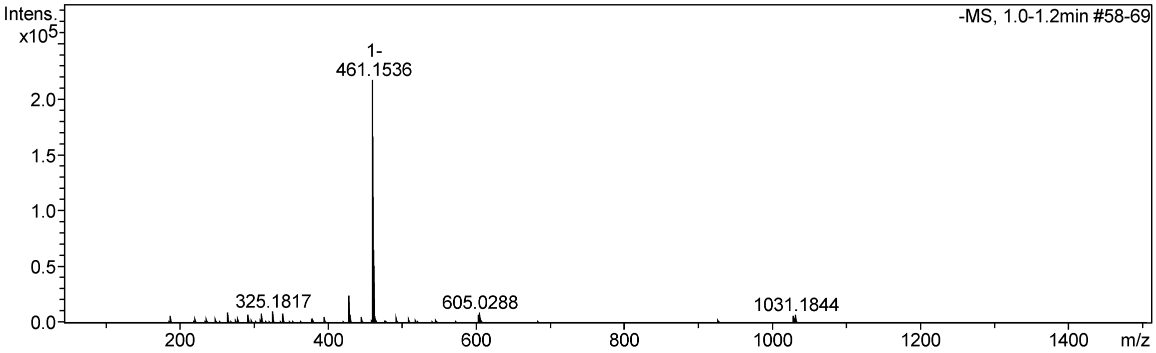
^{13}C NMR (400 MHz, $CDCl_3$ with a trace amount of trifluoroacetic acid to enhance solubility): δ [ppm] = 25, 26, 29.5, 52.5, 121.7, 121.9, 122.4, 127.0, 130.0, 130.5, 136.9, 138.3, 139.5, 167.5, 168.1, 169.7



Elemental analysis calcd. for $C_{26}H_{26}N_2O_4S$ (%): C 67.51, H 5.67, N 6.06, O 13.84, S 6.93; found: C 63.65, H 5.41, N 5.71 (J-Science JM-10), O 13.59 (Elementar Vario micro cube), S 11.54 (Thermo ICS-1100).

Note: This deviation may originate from the intrinsic difficulty in achieving complete combustion of the highly stable polycyclic imide structure, resulting in slightly lower carbon, hydrogen, and nitrogen values. In addition, the sulphur content was measured using ion chromatography, which can detect trace amounts of residual inorganic sulphur species (*e.g.*, Na_2SO_4 formed by oxidation of NaSH used during synthesis), potentially leading to an overestimation of the sulphur content. The structure and purity of the sample were fully confirmed by NMR and high-resolution mass spectrometry (HRMS).

HRMS (ESI-TOF, Bruker micrOTOF II): m/z 461.1536 $[M–H]^-$, calcd. for $C_{26}H_{26}N_2O_4S$: 461.1541, error: 0.5 mDa (1.0 ppm).



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
461.153589	1	C26H25N2O4S	100.00	461.154052	0.5	1.0	1.4	15.5	even		ok	M-H

3. Preparation of 1SNT-IC/PMMA, COP Films

PMMA (110 mg) was stirred in $CHCl_3$ (1 mL) for 3 h. 1SNT-IC (1.14 mg, 0.00246 mmol, 1 wt% of PMMA) was then added to the solution, followed by stirring for 24 h. The resulting colourless and transparent solution was spin-coated (800 rpm for 60 s and 1500 rpm for 3 s) onto a fused silica substrate (dimensions: 13 mm × 10 mm × 1 mm) and dried at 65 °C for 3 h under a nitrogen atmosphere. The film of 1SNT-IC dispersed in COP were prepared in a similar manner.

4. Optical Measurements

For solution sample, the concentration 1SNT-IC was set to 2.5×10^{-4} mol L^{-1}. The UV-Vis absorption spectrum was measured using a V-670 spectrophotometer (JASCO Corp., Japan). Photoluminescence excitation/emission spectra were measured at 25 °C using a F-7100 fluorescence spectrometer (Hitachi High-Tech Corp., Japan) equipped with an R928 photomultiplier tube (Hamamatsu Photonics K.K., Japan). The absolute photoluminescence quantum yield was measured using a C9920-02 spectrometer (Hamamatsu Photonics K.K., Japan) connected to a C7473 photonic multichannel analyser (Hamamatsu Photonics K.K., Japan). Fluorescence lifetime measurement was measured using a Quantaurus-Tau C11367 fluorescence lifetime spectrometer (Hamamatsu Photonics K.K., Japan).

5. Density Functional Theory Calculation

Density functional theory (DFT) calculations were conducted using the Gaussian-16 software (Rev.C.01). Geometry optimisation was independently performed with the M06-2X functional with the 6-311G(d) basis set for the ground (S_0) and excited (S_1) states, respectively. The 6-311++G(d,p) basis set was used to calculate the vertical excitation wavelengths and oscillator strengths (f) for each of the S_0 and S_1 geometries. The S_0 - S_1 transition at the optimised S_0 geometry corresponds to the optical absorption of the ground state. Contrarily, that at the optimised S_1 geometry corresponds to the fluorescent emission according to Kasha's rule. Each calculated transition was replaced by a Gaussian broadening function with a width of 0.10 eV, producing the shapes of the calculated spectra. The solvent effects in the ground and excited states were incorporated based on the polarisable continuum model (PCM) implemented in the Gaussian software.

6. Supplementary Figures

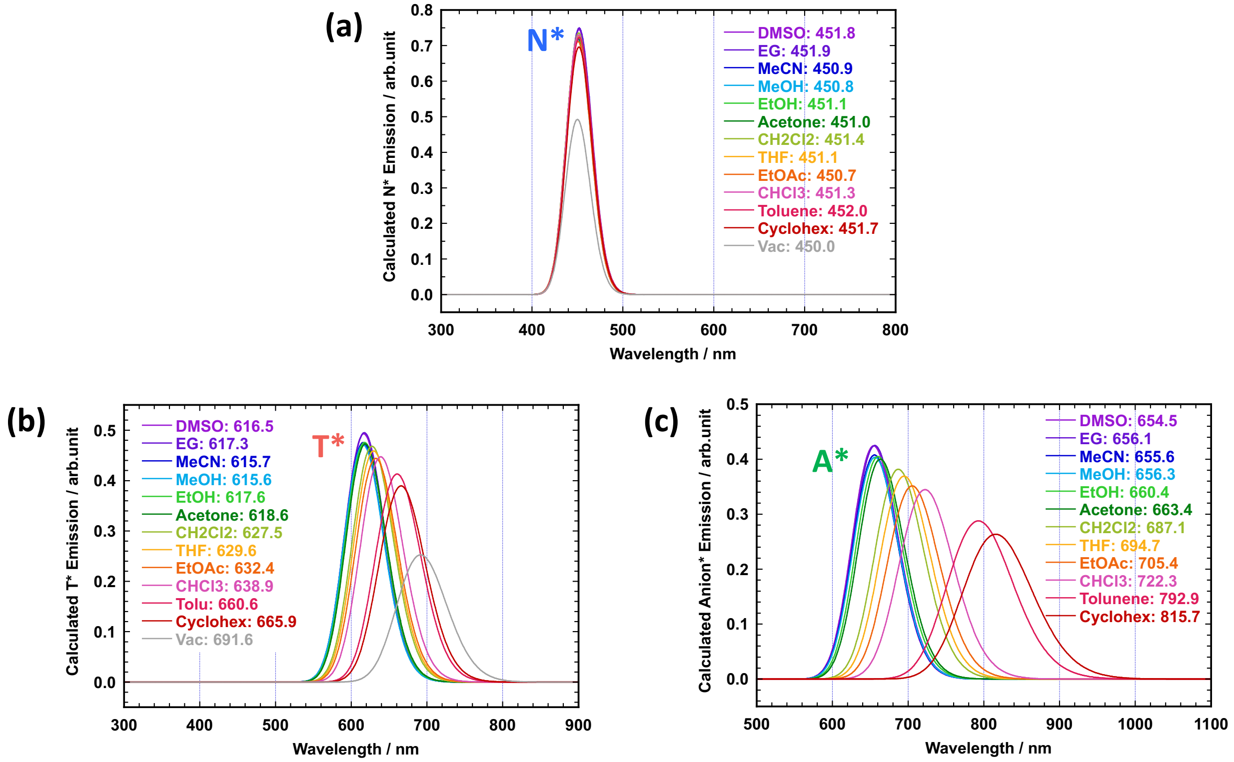


Figure S1. (a) N*, (b) T*, and (c) A* emission spectra of 1SNT-IC calculated using the TD-DFT theory.

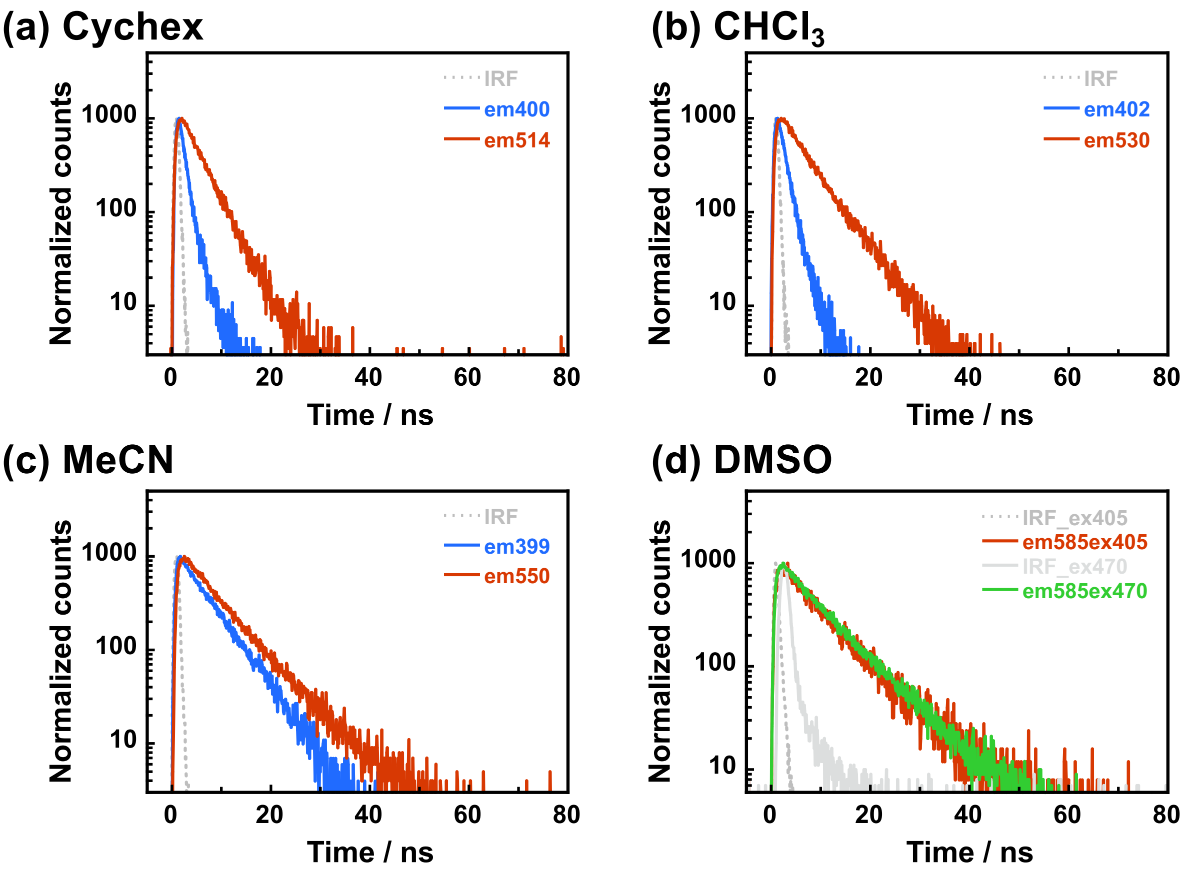


Figure S2. Fluorescence decay curves of 1SNT-IC in (a) Cychex, (b) $CHCl_3$, (c) MeCN, and (d) DMSO. IRF is the instrument response function.

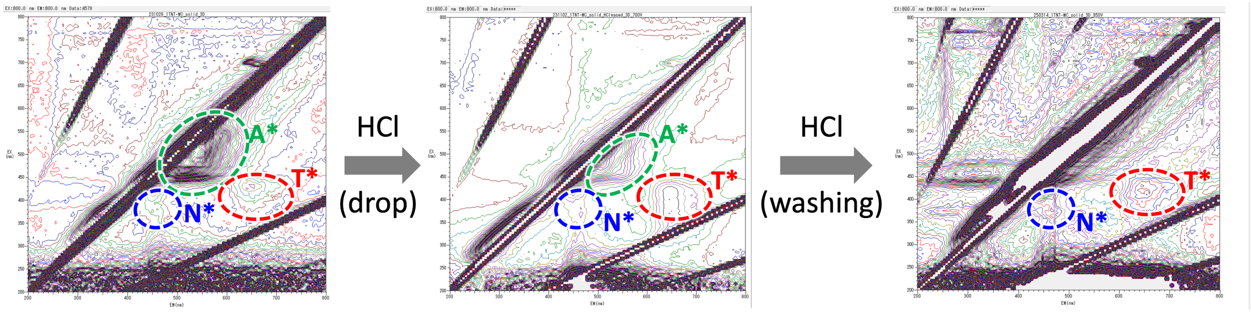


Figure S3. Contour plot of the 3D fluorescence excitation/emission spectra of 1SNT-IC in the solid state. The formation of anionic species after drying is attributed to proton loss. Upon the dropwise addition of hydrochloric acid, the emission intensity of A* decreased, and after washing with dilute hydrochloric acid, the peak completely disappeared.

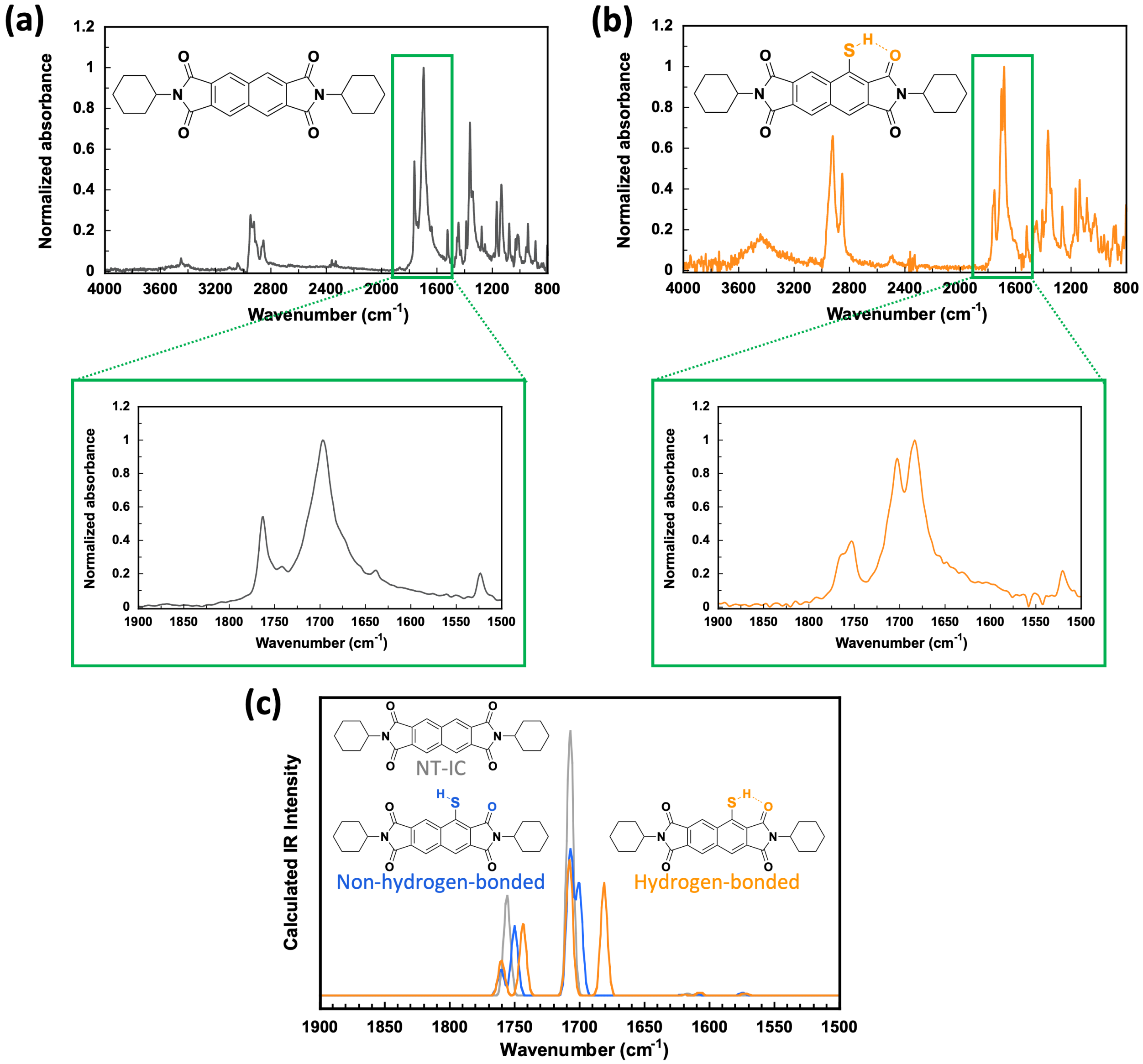
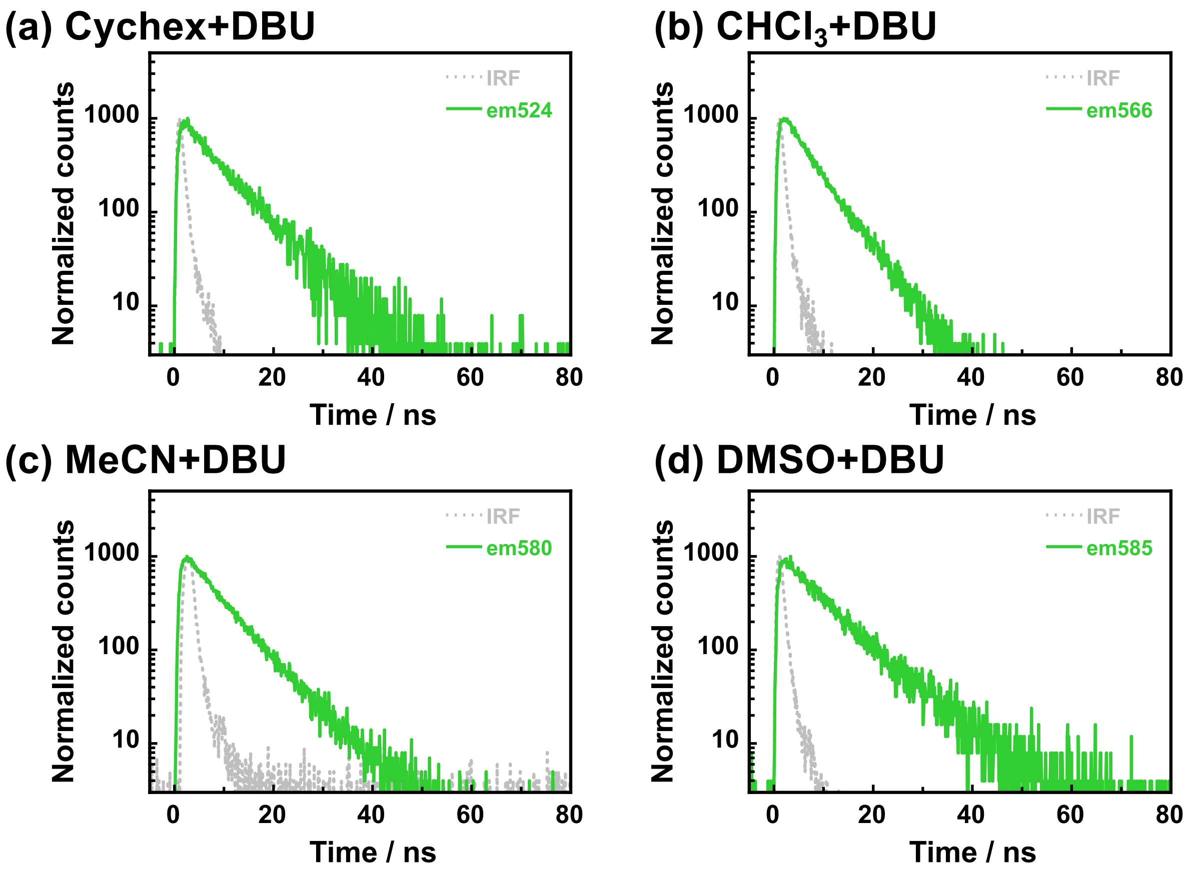


Figure S4. FT-IR spectra of (a) NT-IC and (b) 1SNT-IC highlighting differences in the C=O stretching vibrations around 1700 and 1750 cm^{-1}. The peak splitting observed for 1SNT-IC is attributed to the asymmetric naphthalimide structure induced by –SH moiety. (c) Calculated IR spectra of 1SNT-IC with and without intra-HB. The peak splitting is more pronounced in the former (orange line), which reproduced well the experimental spectrum.


(a) Cychex+DBU

(b) $CHCl_3$+DBU

(c) MeCN+DBU

(d) DMSO+DBU

Figure S5. Fluorescence decay curves of 1SNT-IC in (a) Cychex, (b) $CHCl_3$, (c) MeCN, and (d) DMSO after adding DBU. IRF is the instrument response function.

6. Supplementary References

1. M. Doi, R. Ishige and S. Ando, *ChemPhotoChem*, 2023, **7**, e202200310.
2. Y. V. Suseela, M. Sasikumar and T. Govindaraju, *Tetrahedron Lett.*, 2013, **54**, 6314–6318.