

Supplementary Information

Colorimetric and fluorescent sensor for water in acetonitrile based on intramolecular charge transfer: D-(π -A)₂-type pyridine-boron trifluoride complex

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Experimental Section:

General:

IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using ATR method. ^1H and ^{11}B NMR spectra were recorded on a Varian-500 FT NMR spectrometer. High-resolution mass spectral data by ESI were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. Thermogravimetry-differential thermal analysis (TG-DTA) was performed by SII EXSTRA TG/DTA6200. Photoabsorption spectra were observed with a SHIMADZU UV-3150 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields were determined by a HORIBA FluoroMax-4 spectrofluorometer by using a calibrated integrating sphere system. The addition of water to organic solvents containing **YNI-2-BF₃** was made by weight percent (wt%). The determination of water in acetonitrile was done with a MKC-610 and MKA-610 Karl Fischer moisture titrator (Kyoto Electronics manufacturing Co., Ltd.) based on Karl Fischer coulometric titration for below 1.0 wt% and volumetric titration for 1.0-40 wt%, respectively.

Preparation of 9-butyl-3,6-bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazole-boron trifluoride complex (**YNI-2-BF₃**)

To a solution of **YNI-2** (0.1 g, 0.185 mmol) in THF (40 ml) under a nitrogen atmosphere was added dropwise 47% $\text{BF}_3\text{-OEt}_2$ (0.51 mmol) diluted with THF (5 ml) for 15 min, and then the solution was stirred for 2.5 h at room temperature. The resulting precipitate was filtered and was washed by THF to give **YNI-2-BF₃** (0.05 g, yield 43 %) as a red solid; FT-IR (ATR): $\nu = 1627$ (C=N str. for pyridyl group coordinated to BF_3), 1422 (B-N str. for pyridine- BF_3 complex), 1023 (B-F str. for BF_3) cm^{-1} ; ^1H NMR (500 MHz, acetonitrile- d_3) $\delta = 0.95$ (t, $J = 7.4$ Hz, 3H), 1.37-1.42 (m, 2H), 1.87-1.88 (m, 2H), 4.43 (t, $J = 7.2$ Hz, 2H), 7.65-7.68 (m, 4H), 7.92 (dd, $J = 1.9$ and 8.6 Hz, 2H), 8.02-8.04 (m, 6H), 8.52 (d, $J = 7.0$ Hz, 4H), 8.65 (d, $J = 1.7$ Hz, 2H) ppm; ^{11}B -NMR (160 MHz, acetonitrile- d_3) $\delta = -0.975$ ppm; HRMS (ESI): m/z (%): $[\text{M}+\text{H}^+]$ calcd for $\text{C}_{34}\text{H}_{28}\text{N}_3\text{S}_2$, 542.17192; found 542.17200.

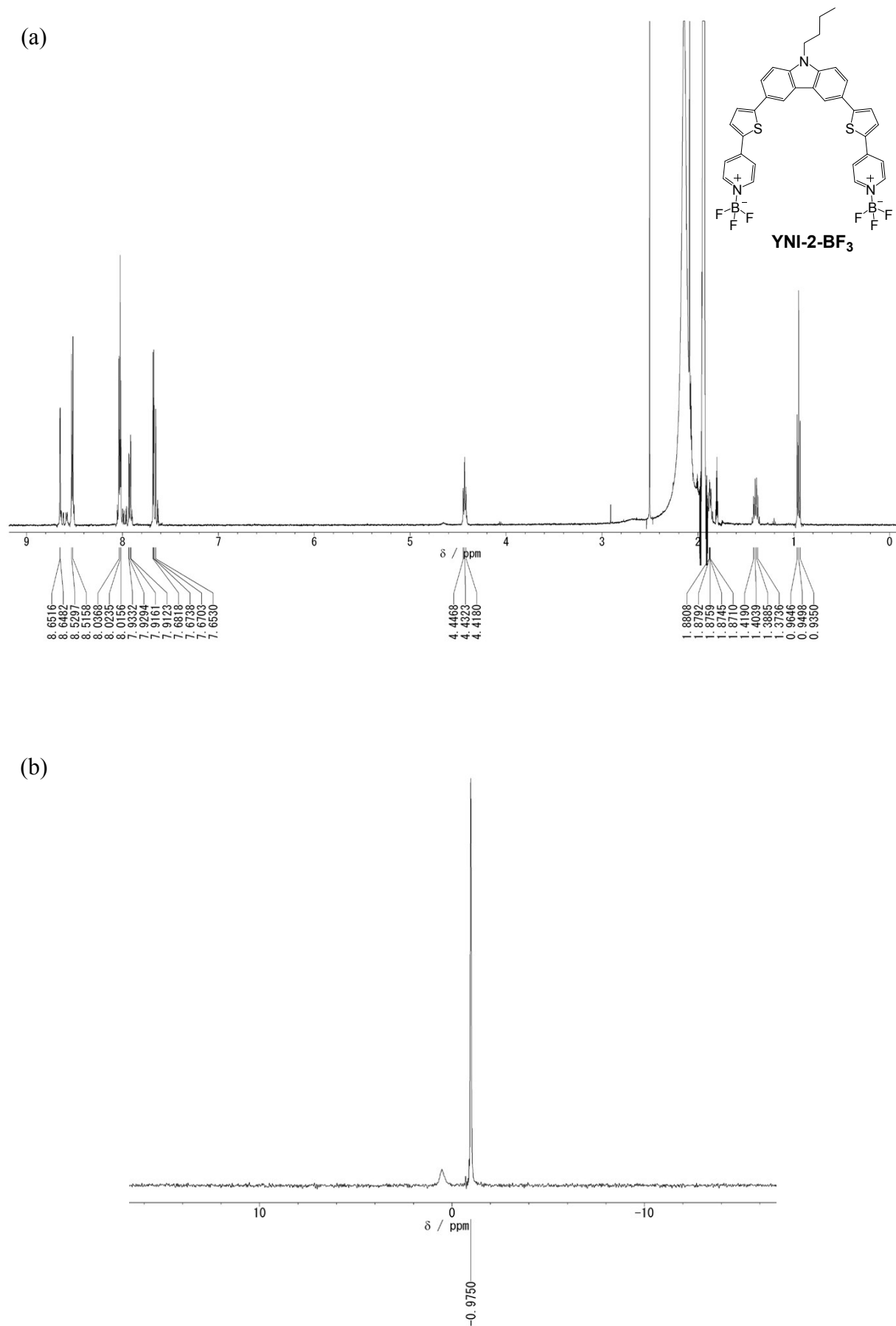


Fig. S1 (a) ¹H NMR (500 MHz) and (b) ¹¹B NMR (160 MHz) spectra of **YNI-2-BF₃** in acetonitrile-d₃.

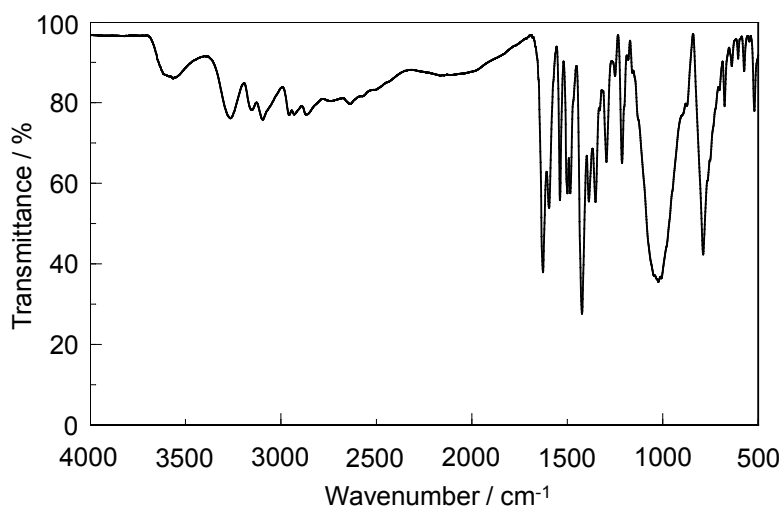


Fig. S2 FTIR spectrum of **YNI-2-BF₃**.

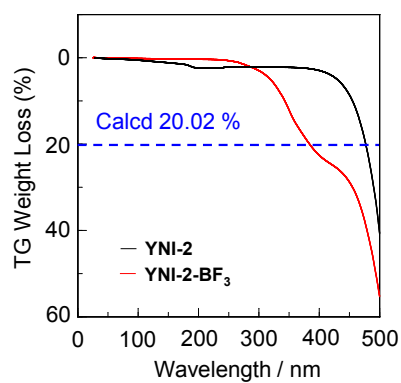


Fig. S3 TG curves for **YNI-2** and **YNI-2-BF₃** at a heating rate 10 °C min⁻¹. Calculated weight loss for the release of two BF₃ units from **YNI-2-BF** to form **YNI-2** is 20.02 %.

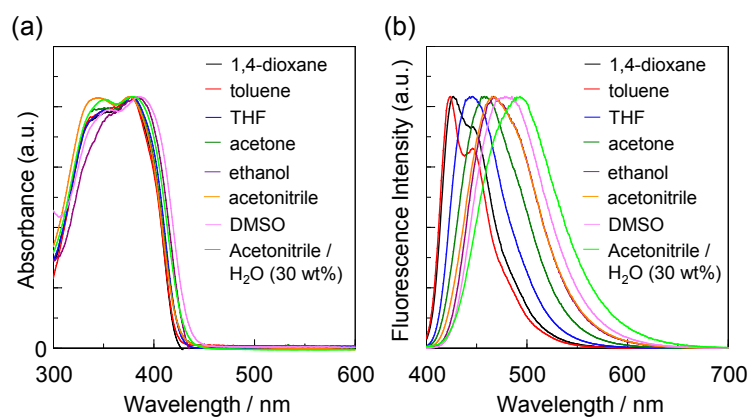


Fig. S4 (a) photoabsorption and (b) fluorescence ($\lambda_{\text{ex}} = 375\text{-}385$ nm) spectra of **YNI-2** in various solvents.

Table S1 Optical data of **YNI-2** in various solvents

Solvent	ϵ_r	$\lambda_{\text{max}}^{\text{abs}} / \text{nm}$	$\lambda_{\text{max}}^{\text{fl}} / \text{nm}$	Φ_{fl}
1,4-dioxane	2.21	376	427	0.52
toluene	2.38	378	424	0.41
THF	7.58	378	448	0.67
acetone	20.6	377	458	0.63
ethanol	24.6	384	467	0.46
acetonitrile	35.9	375	465	0.60
DMSO	46.5	385	478	0.87
acetonitrile / H ₂ O (30 wt%)	46.8	379	493	0.16

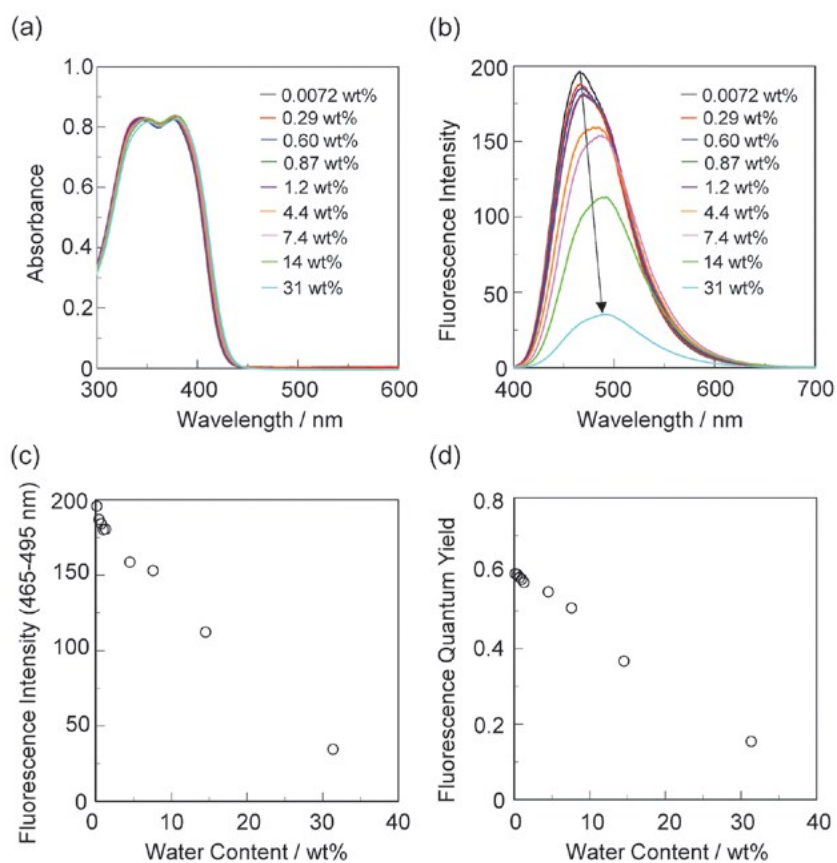


Fig. S5 (a) Photoabsorption and (b) fluorescence spectra of **YNI-2** ($c = 2.0 \times 10^{-5}$ M) by photoexcitation at 375–380 nm in acetonitrile containing water content of 0.0072–31 wt%. (c) Fluorescence peak intensity at 465–495 nm by photoexcitation at 375–380 nm and (d) fluorescence quantum yield of **YNI-2** by photoexcitation at 376 nm as a function of water content (0.0072–31 wt%) in acetonitrile.