Supplementary Information for

Spin-observation revealing mechanism of low but stable device performance in a perovskite solar cell with a novel high-local-mobility hole-transport material

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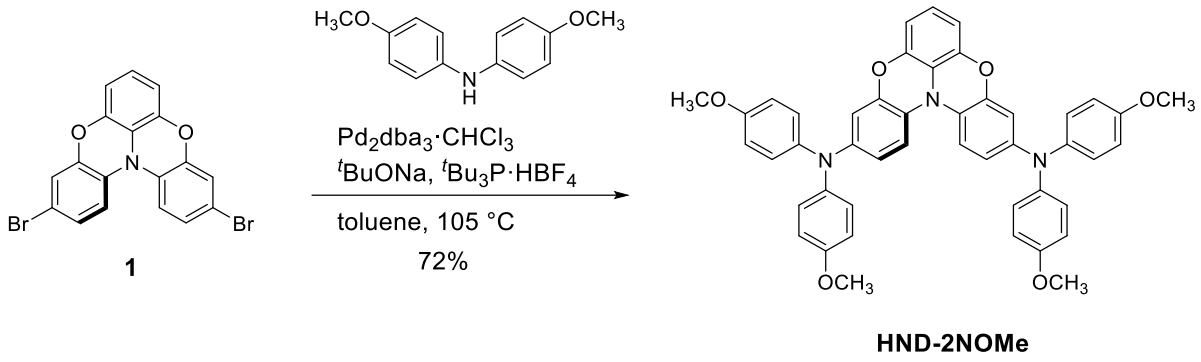
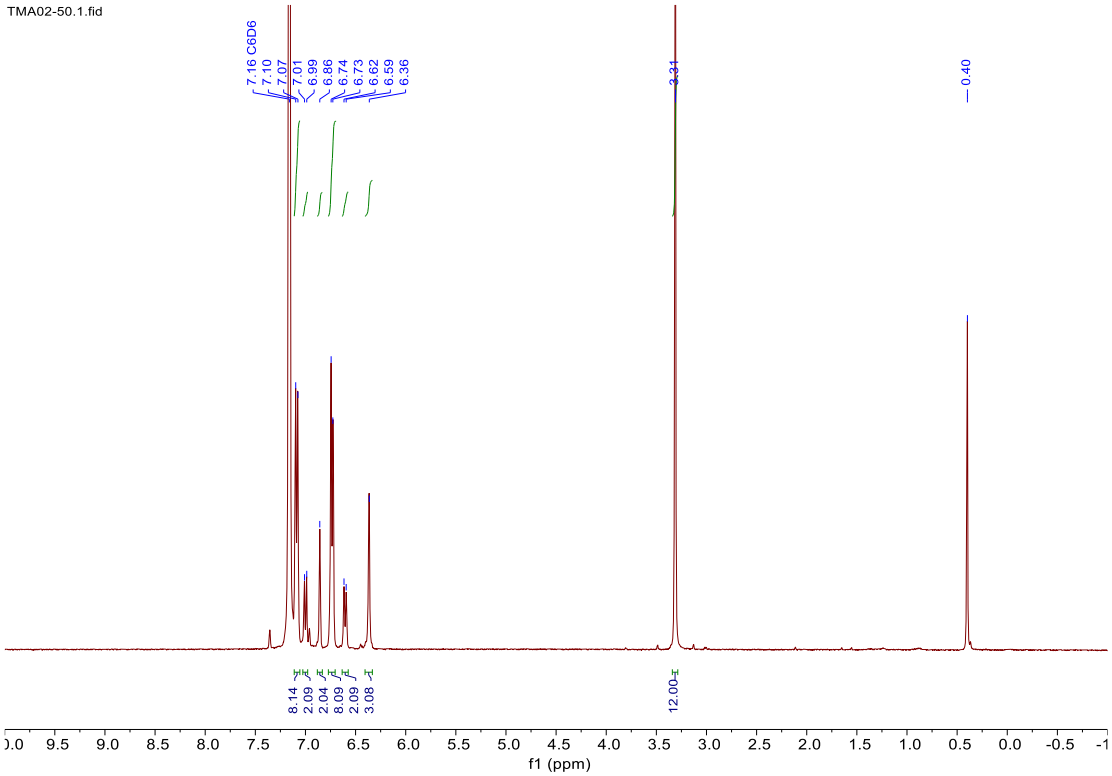
S1. Synthesis of HND-2NOMe

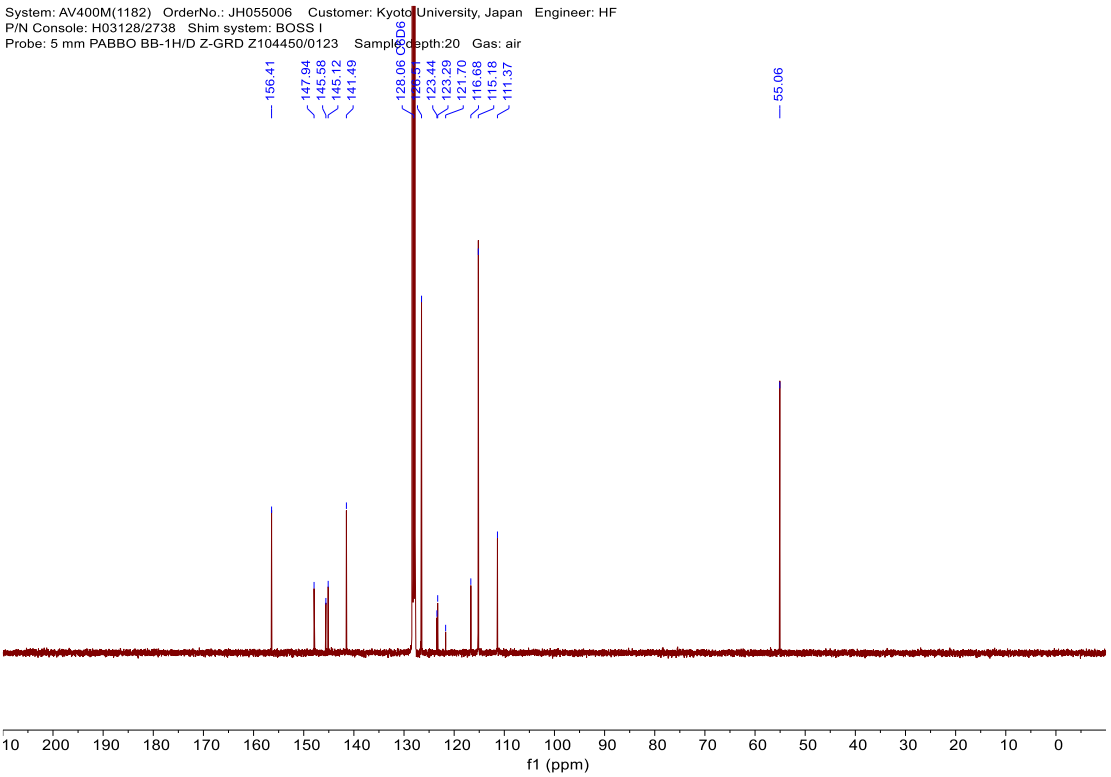


Supplementary Scheme 1 | Synthesis route of HND-2NOMe.

Dibromo intermediate **1** (1.15 g, 2.67 mmol), bis(4-methoxyphenyl)amine (1.35 g, 5.89 mmol), ^{t}BuONa (0.65 g, 6.75 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (118 mg, 0.11 mmol), and $^t Bu_3P{\cdot}HBF_4$ (233 mg, 0.81 mmol) in toluene (40 mL) were added to a Schlenk tube. After flushing with argon three times, the mixture was stirred at 105 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with toluene. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product, which was then purified using silica gel column chromatography (toluene, R_f = 0.41) to give 1.40 g of N^3,N^3,N^{11},N^{11}-tetrakis(4-methoxyphenyl)[1,4]benzoxazino[2,3,4-*kl*]phenoxazine-3,11-diamine (HND-2NOMe) (1.92 mmol, 72% yield) as a yellowish green powder: mp 149 °C; ^{1}H NMR (400 MHz, C_6D_6): δ 7.10–7.07 (d, J = 12.0 Hz, 8H), 7.01–6.99 (d, J = 8.0 Hz, 2H), 6.86 (s, 2H), 6.74–6.72 (d, J = 8.0 Hz, 8H), 6.62–6.59 (d, J = 12.0 Hz, 2H), 6.36 (s, 3H), 3.31 (s, 12H); ^{13}C NMR (101 MHz, C_6D_6): δ 156.41, 147.94, 145.58, 145.12, 141.49, 126.51, 123.44, 123.29, 121.70, 116.68, 115.18, 111.37, 55.06; HRMS (APCI) (*m/z*): $[M+H]^+$ calcd. for $C_{46}H_{38}N_3O_6$, 728.2761; found, 728.2725.

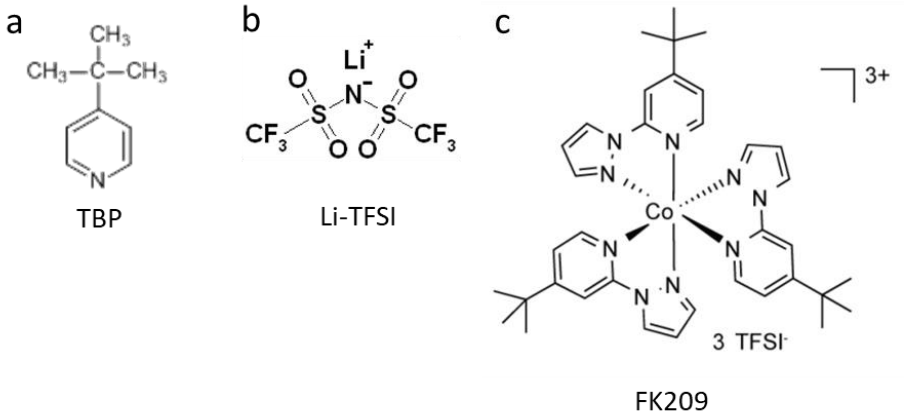


Supplementary Figure 1 | ^{1}H NMR (400 MHz, C_6D_6) spectrum of HND-2NOMe.



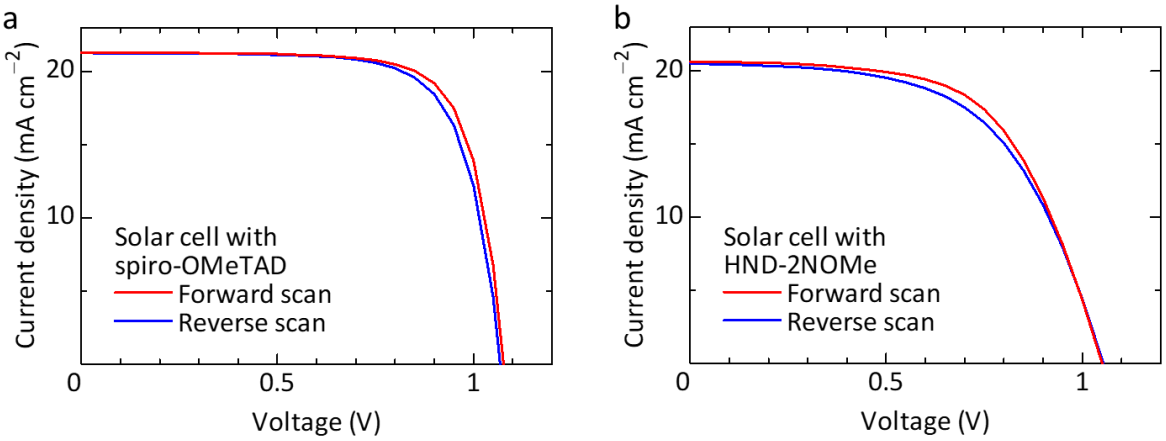
Supplementary Figure 2 | ^{13}C NMR (101 MHz, C_6D_6) spectrum of HND-2NOMe.

S2. Dopants for HTMs



Supplementary Figure 3 | Dopants for HTMs. a–c, Chemical structures of 4-*tert*-butylpyridine (TBP) (a), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) (b), and cobalt complex (FK209) (c).

S3. Device performance

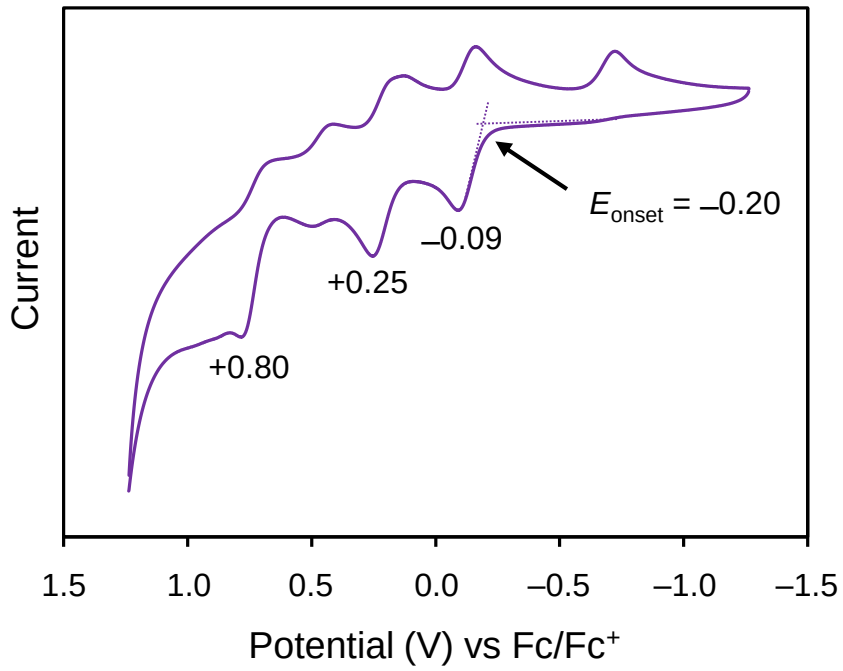


Supplementary Figure 4 | Device performance of perovskite solar cells. a, **b**, Current density – voltage (*J*-*V*) characteristics of a perovskite solar cell with spiro-OMeTAD (a) and with HND-2NOMe (b). These solar cells, which have an active area of 0.1 cm^2, were fabricated on an indium-tin-oxide (ITO) substrate.

Supplementary Table 1 | Device parameters of the perovskite solar cells with HTMs shown in Supplementary Figure 2

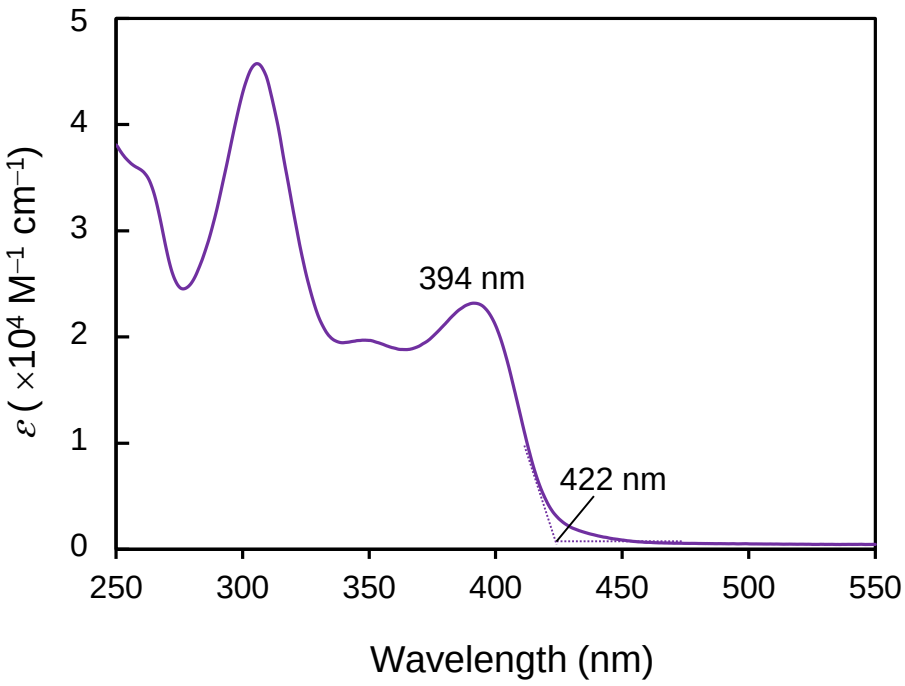
HTM	Scan direction	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)
Spiro-OMeTAD	forward	21.27	1.08	0.75	17.27
	reverse	21.26	1.07	0.73	16.64
HND-2NOMe	forward	20.66	1.05	0.60	13.04
	reverse	20.54	1.05	0.57	12.37

S4. Determination of energy levels of HND-2NOMe



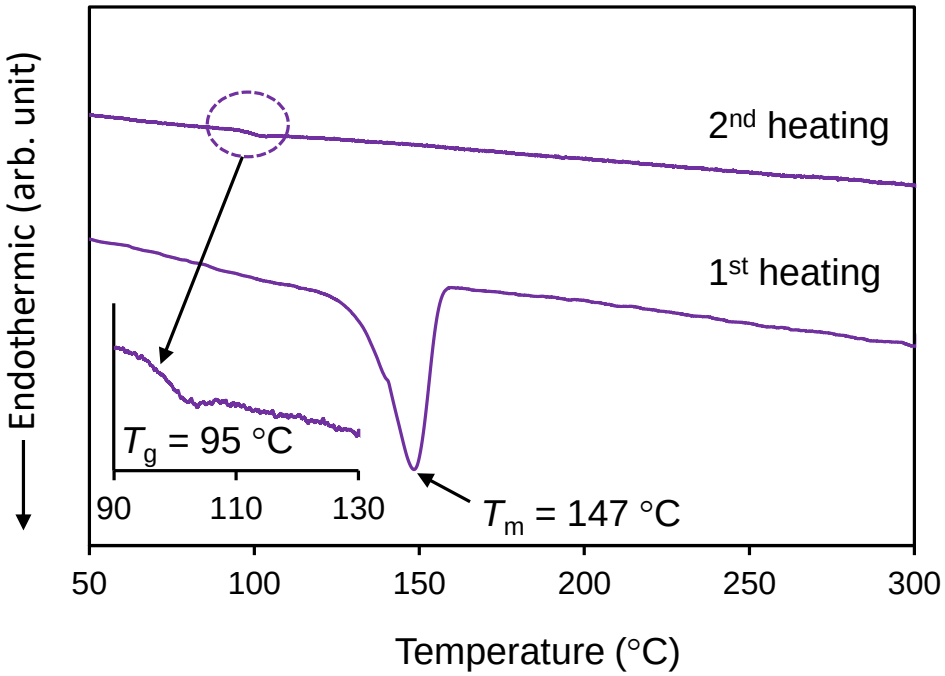
Supplementary Figure 5 | Cyclic voltammogram of HND-2NOMe. Data were measured in DMF solution.

Cyclic voltammetry (CV) was performed on an ALS/chi-620C electrochemical analyzer with the CV cell consisting of a glassy carbon working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurement was conducted under an argon atmosphere using DMF solution of HND-2NOMe (1.0 mM) with 0.1 M tetrabutylammonium hexafluorophosphate ($^nBu_4N^+PF_6^-$) as a supporting electrolyte at a scan rate of 100 mV s^{-1}. The redox potentials were calibrated with ferrocene as an internal standard. The HOMO energy level was calculated using the following equation: $E_{HOMO} = -(E_{onset} + 5.1)$ (eV).



Supplementary Figure 6 | UV–vis absorption spectrum of HND-2NOMe. Data were measured in dilute CH_3CN solution (10^{-5} M). The band gap was calculated using the following equation: $E_{bandgap} = 1240/\lambda_{edge}$ (eV).

S5. Determination of thermal properties of HND-2NOMe



Supplementary Figure 7 | Thermal property of HND-2NOMe. Differential scanning calorimetry (DSC) first and second heating curves of HND-2NOMe at a scan rate of 10 °C min^{-1} under a N_2 atmosphere. T_g and T_m respectively stand for the glass transition temperature and melting temperature.