Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Selective thionation of naphtho[2,3-*b*]thiophene diimide: Tuning of the optoelectronic properties and packing structure

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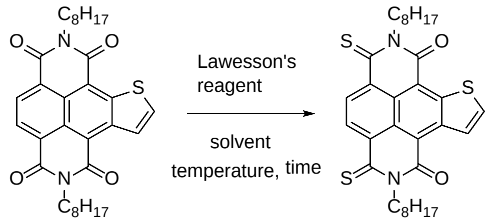
Contents

1. Optimization of conditions in the reaction of NTI and Lawesson's reagent

Table S1. Reactions of NTI with Lawesson's reagent.



run	solvent	temperature (°C), time (h)	result	remarks
1	toluene	reflux (110 °C), 5h	no reaction	LR[a]: 4.0 eq.
2	xylene	reflux (110 °C), 5h	NTI-2S: trace	LR[a]: 4.0 eq.
3	xylene	180 °C, 5h	NTI-2S: 20%	LR[a]: 4.0 eq., Microwave irradiation in a sealed tube
4	xylene	180 °C, 2h	NTI-2S: 41%	LR[a]: 4.0 eq., Microwave irradiation in a sealed tube
5	*o*-DCB	180 °C, 2h	NTI-2S: 6%	LR[a]: 4.0 eq.
6	*o*-DCB	160 °C, 1h	NTI-2S: 45%	LR[a]: 4.0 eq.
6	*o*-DCB	160 °C, 1h	NTI-2S: 59%	LR[a]: 3.0 eq.
7	*o*-DCB	160 °C, 1h	NTI-2S: 69%	LR[a]:2.2 eq.

[a] LR: Lawesson's reagent.

2. ^{13}C NMR spectrum of NTI

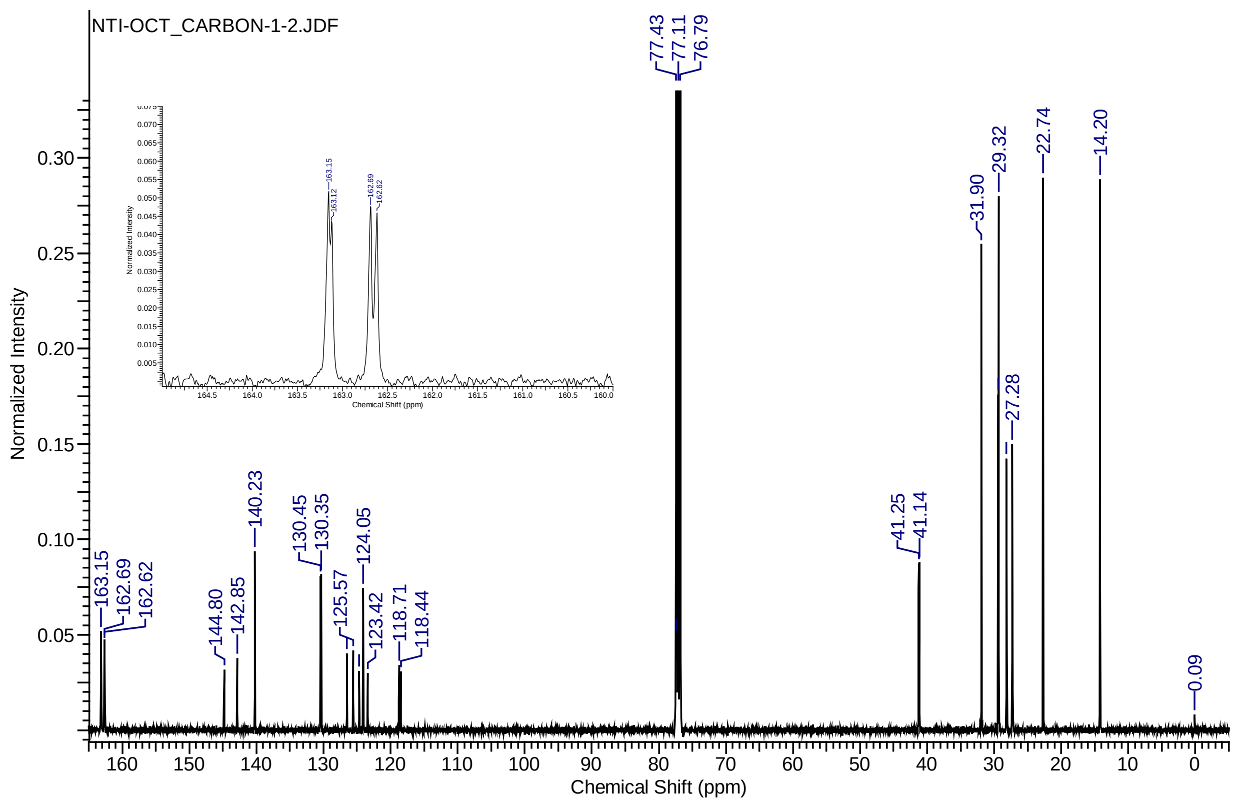


Figure S1. ^{13}C NMR spectrum of NTI.

3. Calculated electron density of NDI, NTI and NDTI[S1]

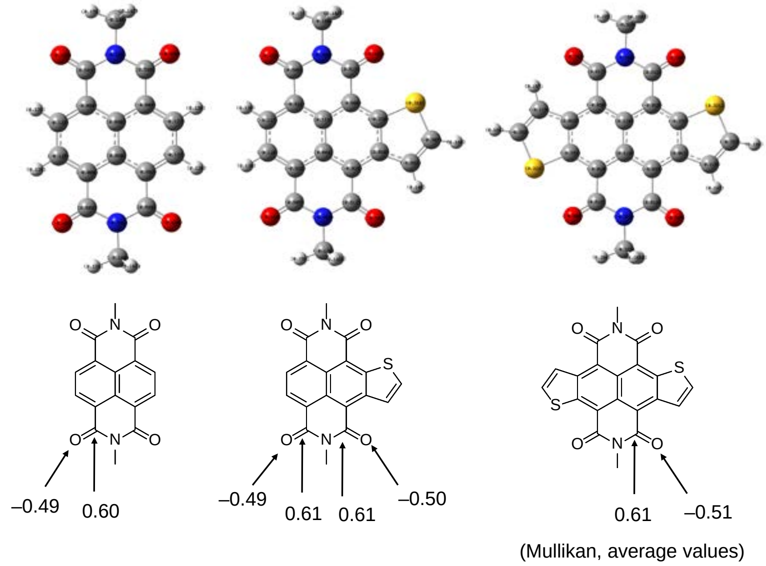


Figure S2. Calculated electron density of NDI, NTI and NDTI (DFT B3LYP 6-31g(d)).

4. Calculated structures of plausible intermediates in the reaction of NTI and Lawesson's reagent [S2]

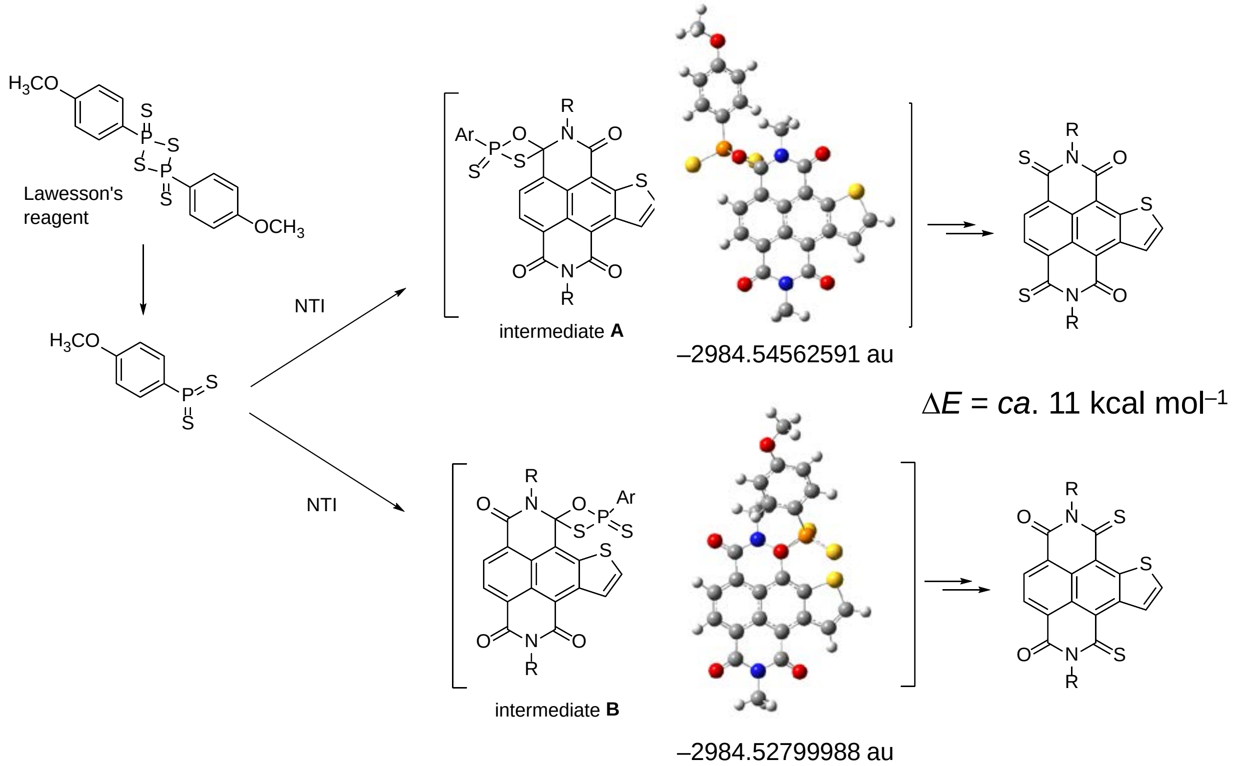


Figure S3. Plausible reaction paths of thionation and intermediates: the intermediate **A** is calculated to be energetically stable compared to the intermediate **B** by ca. 11 kcal mol^{-1} (DFT B3LYP/6-31G(d)).

5. ^{1}H NMR spectra of NTI-2S under different conditions

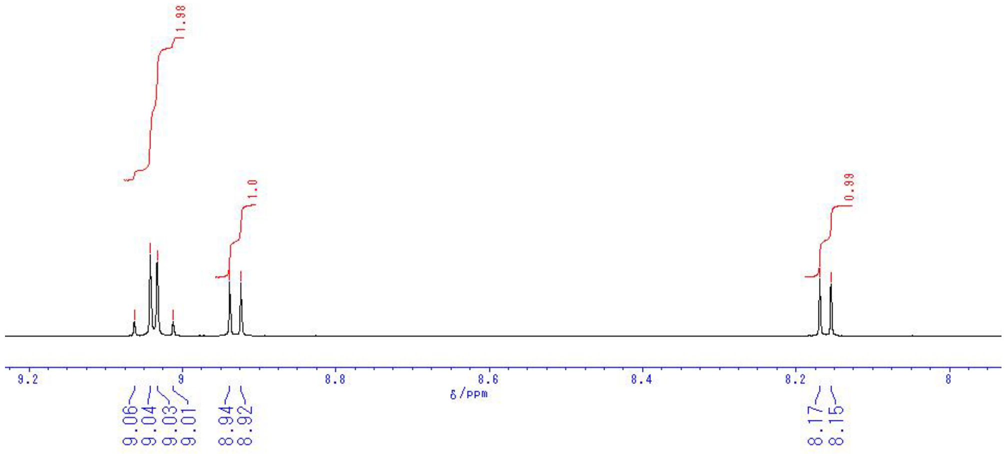


Figure S4. Pristine sample of NTI-2S.

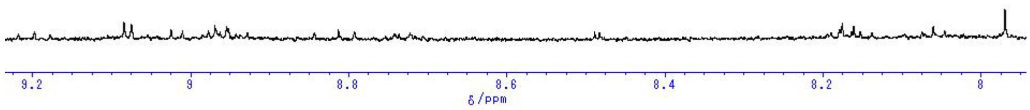


Figure S5. ^{1}H NMR spectra of NTI-2S under fluorescent light (room light) in air (1h).

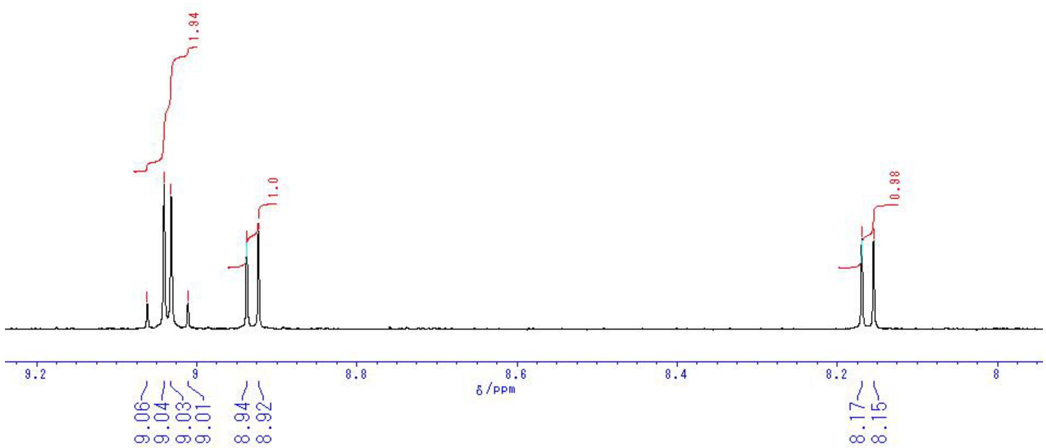


Figure S6. ^{1}H NMR spectra of NTI-2S under fluorescent light (room light) under argon atmosphere (1 day).

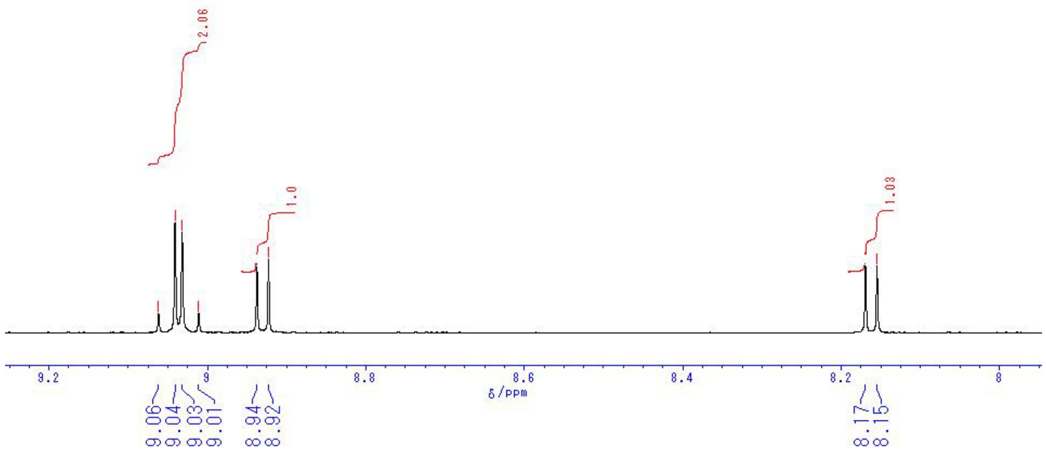


Figure S7. [1]H NMR spectra of NTI-2S in air in dark (1 day).

6. Preliminary data obtained from solution processed field-effect transistors based on NTI-2S

OFET devices based on NTI-2S were fabricated in a top-contact-bottom-gate (TCBG) configuration on a heavily doped n+-Si (100) wafer with a 200 nm thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}). The substrate surfaces were treated with octadecyltrichlorosilane (ODTS) as reported previously. Thin films as the active layer were spin-coated from chloroform. On top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (L) and width (W) are 40 μm and 1.5 mm, respectively.

Characteristics of the OFET devices were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility (μ_{FET}) was calculated in the saturation ($V_d = V_g = \pm 60$) of the I_d using the following equation,

$$I_d = C_i\ \mu_{FET}\ (W/2L)\ (V_g - V_{th})^2$$

where C_i is the capacitance of the SiO_2 dielectric layer, and V_g and V_{th} are the gate and threshold voltages, respectively.

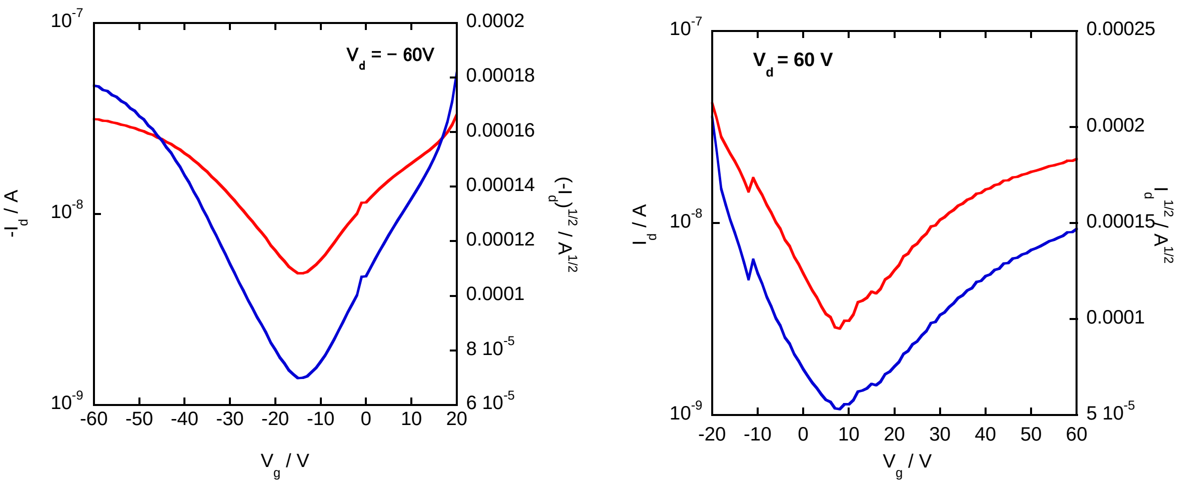


Figure S8. Transfer characteristics of NTI-2S-based transistor: p-channel operation (left) and n-channel operation (right).

7. References

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