Supporting Information for:

Thionated Naphthalene Diimides: Tuneable Chromophores for Materials Applications

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Supporting Information Table of Contents

Experimental Details including Synthesis	Page 1
Details of Crystallographic Experiments and X-ray structures	Page 4
Details of Electrochemistry Experiments	Page 6
Additional UV-vis Spectra and Spectroelectrochemistry and Data	Page 9
Additional EPR Spectra and Data	Page 24
DFT Calculations	Page 26
Additional Time Resolved Spectroscopy	Page 31
References	Page 33

Further Experimental Details

Materials

All chemical reagents were used as-purchased from Alfa Aesar, Fisher Scientific, Sigma-Aldrich, or VWR International, unless stated otherwise. Anhydrous toluene was dried by passing through a column packed with 4 Å molecular sieves, degassed and stored over a potassium mirror in a nitrogen atmosphere. Anhydrous dichloromethane was purchased from Sigma-Aldrich (Fluka) and stored over 4 Å molecular sieves. Ferrocene was purchased from Aldrich and used as received. [ⁿBu₄N][BF₄] was prepared using literature methods^{S1}. Column chromatography was performed on Merck silica gel 60 (0.2-0.5 mm, 50 - 130 mesh). Compounds NMI and PTZ-NH₂ were synthesized according to literature procedures.^{S2,S3}

Methods

¹H and ¹³C NMR spectra were recorded using Bruker spectrometers. EI M/S spectra were taken using a Bruker Apex IV 4.7 T mass spectrometer. MALDI-TOF M/S spectra were recorded with a Bruker Ultraflex III mass spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. ESI M/S spectra were recorded with a Bruker MicroTOF. Elemental analysis was performed using an automated CE-440 Elemental Analyser.

Density Functional Theory calculations were performed using Gaussian 09 software with the B3LYP and CAM-B3LYP exchange-correlation functionals and 6-311g(d,p) basis set.^{54,55,56} Geometry optimizations were performed for all molecules in a dichloromethane solvent field using the polarizable continuum model, with geometry optimizations recognized as local minima by frequency calculations. Subsequently, time-dependent calculations were performed in order to identify the lowest-energy electronic absorptions. Triplet state calculations were performed with the B3LYP

functional. The structures of NDIS₀-PTZ, NDIS₂-PTZ and NDIS₃-PTZ were approximated by analogues possessing methyl units on the NDI core rather than long alkyl chains. Plots of the molecular orbitals were generated using Molekel 4.2 software.^{57,58} All calculations were carried out on the High Performance Computer at the University of Nottingham.

Synthesis

Synthesis of NDIS₀-**PTZ.** A mixture of *N*-(octyl)-1,4,5,8-naphthalenetetracarboxylic monoimide monoanhydride (379 mg, 1 mmol), 10-(4-aminophenyl)-10H-phenothiazine (290 mg, 1 mmol) and imidazole (5 g) were heated to 130 °C for 16 h. The reaction mixture was cooled to 100 °C and hydrochloric acid (50 mL, 2 M) was added and the mixture stirred for 15 min. The product was extracted into chloroform (100 mL) and washed once with each of hydrochloric acid (2 M), water and brine, then dried (MgSO₄), filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica, chloroform) to give the title product as a blue solid (330 mg, 67.6 %). λ_{max} (abs) = 381 nm. ¹H NMR (400 MHz, CDCl₃): δ ppm 8.84 (s, 4 H), 7.45 - 7.61 (m, 4 H), 7.13 (dd, *J* = 7.53, 1.38 Hz, 2 H), 7.01 (td, *J* = 7.90, 1.40 Hz, 2 H), 6.92 (td, *J* = 7.40, 1.00 Hz, 2 H), 6.56 (d, *J* = 8.16 Hz, 2 H), 4.12 - 4.33 (m, 2 H), 1.78 (quin, *J* = 7.53 Hz, 2 H), 1.27 - 1.50 (m, 10 H), 0.89 (t, *J* = 6.40 Hz, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 163.02, 162.71, 143.56, 142.44, 132.95, 131.46, 131.08, 130.74, 129.25, 127.16, 127.12, 127.09, 127.06, 126.88, 126.57, 123.30, 122.75, 118.12, 41.11, 31.80, 29.28, 29.19, 28.09, 27.09, 22.63, 14.08. MS (MALDI)⁻ m/z: [M⁻] 651.1 calculated for C₄₀H₃₃N₃O₄S₁: 651.22. Elemental Analysis: 73.44 %C, 5.83 %H, 6.29 %N C₄₀H₃₃N₃O₄S₁ requires 73.71 %C, 5.10 %H, 6.45 %N.

Synthesis of NIS₀-PTZ. 1,8-Naphthalic anhydride (200 mg, 1.01 mmol), 10-(4-aminophenyl)-10Hphenothiazine (322 mg, 1.11 mmol) and imidazole (3 g) were heated to 130 °C under a N₂ atmosphere for 7 h. The mixture was cooled to 100 °C, hydrochloric acid (50 mL, 2 M) was added and the suspension stirred for 10 min. After cooling to room temperature, the mixture was extracted with chloroform (100 mL) and washed with hydrochloric acid (2 x 100 mL, 2 M), water (1 x 100 mL) and brine (1 x 100 mL). The solution was concentrated using a rotary evaporator and purified by column chromatography (silica, chloroform) to afford the title compound as a bright yellow powder (438 mg, 92 %). λ_{max} (abs) = 337 nm. ¹H NMR (400 MHz, CDCl₃): δ ppm 8.70 (d, J = 7.28 Hz, 2 H), 8.33 (d, J = 7.65 Hz, 2 H), 7.85 (t, J = 7.78 Hz, 2 H), 7.55 (s, 4 H), 7.08 (dd, J = 7.53, 1.38 Hz, 2 H), 6.96 (td, J = 7.91, 1.63 Hz, 2 H), 6.88 (td, J = 7.40, 1.00 Hz, 2 H), 6.47 (dd, J = 8.03, 1.00 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 164.33, 143.84, 141.51, 134.49, 131.80, 131.73, 131.10, 130.41, 128.57, 127.15, 127.03, 126.89, 122.89, 122.70, 121.36, 117.23. HRMS (EI)⁺ m/z: $[M^+]$ 470.1102 calculated for $C_{30}H_{18}N_2O_2S_1$: 470.1089. Synthesis of NDIS₀. A mixture of naphthalene-1,4,5,8-tetracarboxylic dianhydride (3.00 g, 11.2 mmol) and 3-aminopentane (4.5 mL, 38.6 mmol) in N,N-dimethylformamide (30 mL) was stirred at 120 °C for 16 h. After 16 h, the solution was allowed to cool and the solvent removed under reduced pressure to give a brown solid which was dissolved in chloroform (100 mL) and washed with H_2O (2 x 250 mL) and sat. aq. NaCl (1 x 250 mL), dried over MgSO₄, filtered and concentrated. The brown solid was purified by column chromatography (silica, chloroform) to afford the title compound as a pale orange-pink solid (2.213 g, 46%). λ_{max} (abs) = 382 nm. ¹H NMR (500 MHz, CDCl₃) δ ppm 8.73 (s, 4 H), 4.98 - 5.11 (m, 2 H), 2.23 (ddd, J = 14.03, 9.38, 7.49 Hz, 4 H), 1.93 (dt, J = 13.87, 6.78 Hz, 4 H), 0.90 (t, J = 7.49 Hz, 12 H). ¹³C NMR (500 MHz, CDCl₃) δ ppm 163.72, 130.94, 126.79, 126.60, 77.00, 58.09, 24.92, 11.23. FT-IR (neat, cm⁻¹) 1698 (v C=O), 1653 (v C=O). HRMS (EI)⁺ m/z 406.1893 (C₂₄H₂₆N₂O₄ [M]⁺ requires 406.1891). General procedure for thionation of dyads, NDI and NI compounds. The desired compound for thionation (200 mg) and Lawesson's reagent (1.5 eq. per carbonyl) were dissolved in anhydrous toluene (50 mL) and heated to reflux for 16 h. The reaction mixture was cooled and washed with NaOH (100 mM, 250 mL), water (250 mL) and brine (250 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography (silica gel, hexane:dichloromethane 50 % to 100% dichloromethane gradient elution).

cis-**NDIS**₂-**PTZ** as a brown powder (8 mg, 8 %). λ_{max} (abs) = 473 nm. ¹H NMR (400 MHz, CDCl₃): δ ppm 9.02 (m, *J* = 8.30 Hz, 2 H), 8.76 - 8.83 (m, 2 H), 7.50 - 7.57 (m, 2 H), 7.39 - 7.45 (m, 2 H), 7.13 (dd, *J* = 7.53, 1.53 Hz, 2 H), 7.00 - 7.05 (m, 2 H), 6.93 (td, *J* = 7.45, 1.17 Hz, 2 H), 6.58 (dd, *J* = 8.18, 1.17 Hz, 2 H), 4.70 - 4.78 (m, 2 H), 1.85 (quin, *J* = 7.60 Hz, 2 H), 1.37 - 1.29 (m, 10 H)), 0.91 (t, *J* = 6.90 Hz, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 194.23, 192.80, 160.88, 160.32, 143.54, 142.18, 138.21, 135.51, 135.36, 131.55, 131.49, 130.58, 129.43, 129.19, 128.98, 127.16, 127.08, 126.87, 126.62, 125.61, 125.33, 123.29, 122.75, 118.12, 47.78, 31.81, 29.22, 29.21, 27.01, 26.62, 22.65, 14.10. MS (MALDI)⁻ m/z: [M⁻] 683 calculated for C₄₀H₃₃N₃O₂S₃: 683.17.

NDIS₃-PTZ as a dark red powder (15 mg, 14 %). Suitable crystals for X-ray diffraction were grown by vapour diffusion of pentane into a CHCl₃ solution of the compound). λ_{max} (abs) = 505 nm. ¹H NMR (400 MHz, CDCl₃): δ ppm 8.98 (d, J = 8.04 Hz, 1 H), 9.02 (d, J = 8.33 Hz, 1 H), 8.88 (d, J = 8.33 Hz, 1 H), 8.68 (d, J = 8.04 Hz, 1 H), 7.47 - 7.54 (m, 2 H), 7.40 - 7.70 (m, 1 H), 7.31 - 7.37 (m, 2 H), 7.13 (dd, J = 7.53, 1.53 Hz, 2 H), 7.00 - 7.06 (m, 2 H), 6.92 (td, J = 7.49, 1.24 Hz, 2 H), 6.57 (dd, J = 8.11, 1.10 Hz, 2 H), 4.69 - 4.77 (m, 2 H), 1.85 (quin, J = 7.56 Hz, 2 H), 1.28 - 1.49 (m, 10 H), 0.91 (t, J = 6.70 Hz, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 193.01, 190.27, 190.19, 160.71, 143.74, 143.56, 141.60, 136.47, 135.85, 135.55, 131.29, 131.00, 130.54, 130.46, 129.91, 128.52, 127.10, 127.07, 125.43, 123.20, 122.48, 122.39, 117.83, 47.78, 31.81, 29.21, 29.21, 27.01, 26.59, 22.65, 14.10. MS (MALDI)⁻ m/z: [M⁻] 699 calculated for C₄₀H₃₃N₃O₁S₄: 699.15. HRMS (EI)⁺ *m/z* 699.1531 (C₄₀H₃₃N₃O₁S₄ [M]⁺ requires 699.1501). **NDIS**₁ as a pale green powder (414 mg, 40 %). λ_{max} (abs) = 429 nm. ¹H NMR (400 MHz, CDCl₃) δ ppm 9.07 (d, J = 8.04 Hz, 1 H), 8.71 (s, 2 H), 8.63 (d, J = 8.04 Hz, 1 H), 6.08 - 6.31 (m, 1 H), 5.04 (tt, J = 9.61, 5.88 Hz, 1 H), 2.16 - 2.37 (m, 4 H), 1.99 - 2.11 (m, 2 H), 1.87 - 1.98 (m, 2 H), 0.88 - 0.95 (m, 12 H). ¹³C NMR (500 MHz, CDCl₃) δ ppm 196.56, 160.03, 137.15, 130.96, 130.51, 130.27, 127.29, 126.94, 126.21, 125.24, 124.84, 65.70, 58.07, 25.36, 24.93, 11.24, 11.16. FT-IR (neat, cm⁻¹) 1700 (sym. v C=O), 1682 (sym. v C=O), 1660 (antisym. v C=O), 1153 (v C=S). HRMS (EI)⁺ m/z 422.1660 (C₂₄H₂₆N₂O₃S₁ [M]⁺ requires 422.1664).

cis-**NDIS**₂ as a dark brown solid (225 mg, 21 %). λ_{max} (abs) = 474 nm. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.96 (s, 2 H), 8.69 (s, 2 H), 6.20 (t, *J* = 6.87 Hz, 2 H), 2.17 - 2.40 (m, 4 H), 2.04 (dquin, *J* = 14.11, 7.14, 7.14, 7.14, 7.14, 7.14 Hz, 4 H), 0.92 (t, *J* = 7.45 Hz, 12 H). ¹³C NMR (500 MHz, CDCl₃) δ ppm 196.60, 160.32, 136.69, 130.92, 128.87, 126.97, 124.91, 65.61, 25.35, 11.17. FT-IR (neat, cm⁻¹) 1682 (v C=O), 1152 (v C=S). HRMS (EI)⁺ *m/z* 438.1427 (C₂₄H₂₆N₂O₂S₂ [M]⁺ requires 438.1436).

trans-**NDIS**₂ as deep green crystals (178 mg, 17 %). λ_{max} (abs) = 476 nm. ¹H NMR (400 MHz, CDCl₃) δ ppm 9.06 (m, *J* = 8.03 Hz, 2 H), 8.61 (m, *J* = 8.03 Hz, 2 H), 6.04 - 6.32 (m, 2 H), 2.17 - 2.42 (m, 4 H), 2.04 (dquin, *J* = 14.12, 7.13, 7.13, 7.13, 7.13 Hz, 4 H), 0.93 (t, *J* = 7.53 Hz, 12 H). ¹³C NMR (500 MHz, CDCl₃) δ ppm 196.77, 160.37, 137.15, 130.46, 129.85, 125.97, 124.99, 77.00, 65.75, 25.37, 11.17. FT-IR (neat, cm⁻¹) 1674 (v C=O), 1149 (v C=S). HRMS (EI)⁺ *m/z* 438.1445 (C₂₄H₂₆N₂O₂S₂ [M]⁺ requires 438.1436).

NDIS₃ as a red solid (6.5 mg, 1 %). λ_{max} (abs) = 502 nm. MS (MALDI)⁻ m/z 454.1 (C₂₄H₂₆N₂O₁S₃ [M]⁻ requires 454.12).

NIS₀: λ_{max} (abs) = 335 nm. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.59 (d, *J* = 7.15 Hz, 2 H), 8.21 (d, *J* = 8.28 Hz, 2 H), 7.76 (t, *J* = 7.78 Hz, 2 H), 4.99 - 5.12 (m, 1 H), 2.26 (spt, *J* = 7.40 Hz, 2 H), 1.92 (spt, *J* = 6.90 Hz, 2 H), 0.91 (t, *J* = 7.47 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 159.84, 133.51, 131.44, 131.13, 128.33, 126.90, 122.94, 57.33, 25.00, 11.29. HRMS (EI)⁺ *m/z* 267.1263 (C₁₇H₁₇N₁O₂ [M]⁺ requires 267.1259).

NIS₁: λ_{max} (abs) = 404 nm. ¹H NMR (400 MHz, CDCl₃) δ ppm 9.04 (d, *J* = 7.53 Hz, 1 H), 8.57 (d, *J* = 7.28 Hz, 1 H), 8.10 - 8.23 (m, 1 H), 7.69 (t, *J* = 7.91 Hz, 1 H), 7.73 (t, *J* = 7.78 Hz, 1 H), 6.33 (quin, *J* = 6.90 Hz, 1 H), 2.30 (spt, *J* = 7.50 Hz, 2 H), 2.03 (spt, *J* = 7.15 Hz, 2 H), 0.94 (t, *J*=7.47 Hz, 6 H). ¹³C NMR (400 MHz, CDCl₃) δ ppm 198.54, 161.40, 138.12, 133.55, 133.12, 131.61, 131.44, 128.21, 127.18, 126.99, 126.43, 123.48, 65.12, 25.41, 11.21. HRMS (EI)⁺ *m/z* 283.1037 (C₁₇H₁₇N₁O₁S₁ [M]⁺ requires 283.1031).

Crystallography

Single crystal X-ray diffraction experiments were performed on an Oxford Diffraction SuperNova CCD area detector diffractometer at 120 K using monochromated Cu K α radiation (λ = 1.5418 Å) (NDIS₀; NDIS₁; *trans*-NDIS₂; NIS₂-PTZ; NDIS₀-PTZ); at the UK Diamond Light Source ($\lambda = 0.6889$ Å) (NIS₀-PTZ; NDIS₃-PTZ). The structures were solved by direct methods using either SHELXS or SHELXT^{S10} and refined with SHELXL^{S11} using a least squares method. OLEX2 software was used as the solution, refinement and analysis program.^{S12} All hydrogen atoms were placed in geometrically calculated positions; non-hydrogen atoms were refined with anisotropic displacement parameters. In specific cases, geometric restraints were applied. Details of dealing with disorder of other refinement are described in the corresponding, deposited cifs. CCDC-1500966 (NIS₀-PTZ), CCDC-1500960 (NIS₂-PTZ), CCDC-1500961 (NDIS₀-PTZ), CCDC-1500963 (NDIS₃-PTZ), CCDC-1500964 (NDIS₀), CCDC-1500962 (NDIS₁), CCDC-1500965 (trans-NDIS₂). For the structure of NDIS₀-PTZ one alkyl chain (C41 to C48) is disordered over two positions. The chloroform molecule is concomitantly disordered over the same two positions as the alkyl chain. The respective occupancies were refined competively, converging at a ratio of 0.37:0.63. Chemically equivalent bonds of the disordered atoms were restrained to be approximately equal to each other and to those of the ordered equivalent. Enhanced rigid bond and similarity restraints were applied to the thermal parameters of the disordered atoms. For NDIS₁ O11 and S14 are disordered over two positions and their respective occupancies were fixed at a ratio of 0.75:0.25. O14A and S11A are also disordered over two positions and their respective occupancies were fixed at a ratio of 0.75:0.25.

‡ *Crystal Data for* **NIS**₀-**PTZ**; C₃₀H₁₈N₂O₂S.CHCl₃ (*M* = 589.89): orthorhombic, space group Pbca (no. 61), *a* = 9.07634(15), *b* = 18.5416(5), *c* = 31.2516(5) Å, *V* = 5259.33(19) Å³, *Z* = 8, *T* = 100(2) K, µ(synchrotron) = 0.427 mm⁻¹, *D*_{calc} = 1.490 g/cm³, 64180 reflections measured, 9248 unique (*R*_{int} = 0.032) which were used in all calculations. The final *R*₁ was 0.0387 (I > 2σ(I)) and *wR*₂ was 0.1052 (all data), S = 1.05.

Crystal Data for **NIS**₂-**PTZ**; C₃₀H₁₈N₂S₃ (*M* = 502.64): monoclinic, space group Pc (no. 7), *a* = 12.36487(18) , *b* = 9.88933(14), *c* = 9.81295(15) Å, *b* = 104.3620(15)°, *V* =1162.43(3) Å³, *Z* = 2, *T* = 120(2) K, μ (Cu- $K\alpha$) = 3.091 mm⁻¹, D_{calc} = 1.436 g/cm³, 4526 reflections measured, 3017 unique (R_{int} = 0.032) which were used in all calculations. The final R_1 was 0.0356 (I > 2 σ (I)) and wR_2 was 0.0958 (all data), S = 0.99. Flack parameter = -0.003(16).

Crystal Data for **NDIS**₀-**PTZ**; C₄₀H₃₃N₃O₄S.CHCl₃ (*M* = 771.12): triclinic, space group P-1 (no. 2), *a* = 8.7193(3), *b* = 11.6007(4), *c* = 18.7861(9) Å, α = 87.754(3)°, β = 87.804(3)°, γ = 78.925(3)°, *V* = 1862.47(13) Å³, *Z* = 2, *T* = 120(2) K, μ (Cu- $K\alpha$) = 3.128 mm⁻¹, D_{calc} = 1.375 g/cm³, 13105 reflections measured, 7323 unique (R_{int} = 0.039) which were used in all calculations. The final R_1 was 0.0930 (I > 2 σ (I)) and wR_2 was 0.2767 (all data), S = 1.03.

Crystal Data for **NDIS₃-PTZ**; C₄₀H₃₃N₃OS₄ (*M* = 699.93): monoclinic, space group P_c (no. 7), *a* = 27.4330(9), *b* = 14.3097(4), *c* = 8.5187(3) Å, *b* = 93.320(3)°, *V* = 3338.47(19) Å³, *Z* = 4, *T* = 150(2) K, μ (synchrotron) = 0.299 mm⁻¹, D_{calc} = 1.393 g/cm³, 11575 reflections measured, 9537 unique (R_{int} =

0.031) which were used in all calculations. The final R_1 was 0.0357 (I > $2\sigma(I)$) and wR_2 was 0.094 (all data), S = 1.03. Flack parameter = 0.36(4).

Crystal Data for **NDIS**₀; C₂₄H₂₆N₂O₄ (M = 406.47): monoclinic, space group P2₁/n (no. 14), a = 13.4100(3), b = 8.3348(2), c = 18.3351(4) Å, $b = 101.022(2)^\circ$, V = 2011.51(8) Å³, Z = 4, T = 120(2) K, μ (Cu- $K\alpha$) = 0.743 mm⁻¹, $D_{calc} = 1.342$ g/cm³, 7787 reflections measured, 3963 unique ($R_{int} = 0.016$) which were used in all calculations. The final R_1 was 0.0371 (I > 2 σ (I)) and wR_2 was 0.1062 (all data). S = 1.03.

Crystal Data for **NDIS**₁; C₂₄H₂₆N₂O₃S (*M* = 422.53): monoclinic, space group P2₁/c (no. 14), *a* = 9.1049(7), *b* = 8.6592(7), *c* = 13.7163(8) Å, *b* = 100.773(7) °, *V* = 1062.35(13) Å³, *Z* = 2, *T* = 120(2) K, μ (Cu-*K* α) = 1.582 mm⁻¹, *D_{calc}* = 1.321 g/cm³, 3983 reflections measured, 2080 unique (*R*_{int} = 0.017) which were used in all calculations. The final *R*₁ was 0.0715 (I > 2 σ (I)) and *wR*₂ was 0.2373 (all data), S = 1.04.

Crystal Data for trans-**NDIS**₂; C₂₄H₂₆N₂O₂S₂ (*M* = 438.59): monoclinic, space group P2₁/c (no. 14), *a* = 8.7955(3), *b* = 9.4770(4), *c* = 12.8838(5) Å, *b* = 92.537(3) °, *V* = 1072.87(7) Å³, *Z* = 2, *T* = 120(2) K, μ (Cu-*K* α) = 2.436 mm⁻¹, *D_{calc}* = 1.358 g/cm³, 4286 reflections measured, 2105 unique (*R*_{int} = 0.024) which were used in all calculations. The final *R*₁ was 0.0398 (I > 2 σ (I)) and *wR*₂ was 0.1066 (all data), S = 1.03.

The single crystal X-ray structures of NDIS₀, NDIS₁ and *trans*-NDIS₂ were determined (Figure S1) revealing similar changes on bond lengths to those observed for NIS₀-PTZ, NIS₂-PTZ, NDIS₀-PTZ and NDIS₃-PTZ (See main text). The C–S bond length in NDIS₁ is 1.645(4) Å and in *trans*-NDIS₂ is 1.6519(16) Å, while the average C-O bond length is 1.241 Å (NDIS₁), 1.219(2) Å (*trans*-NDIS₂), and 1.216 Å (NDIS₀). All three compounds reported herein pack in an analogous herringbone manner, regardless of the degree of thionation. Packing arrangement is significantly influenced by the ethylpropyl imide chain. For the crystal structure of *trans*-NDIS₂, no disorder is observed, and the sulfur and oxygen atoms occupy fixed positions. In contrast, the sulfur and oxygen atoms in the crystal structure of NDIS₁ are disordered over all possible positions with 25 % and 75 % occupancies respectively, suggesting that the arrangement in the crystal structure is sufficiently flexible enough to allow for small variations in the size of the molecules.



Figure S1. Views of the crystal structures of a) **NDIS**₀; b) **NDIS**₁; c) *trans*-**NDIS**₂. Carbon – grey; nitrogen – blue; hydrogen – white; oxygen – red; sulfur – yellow.

Electrochemistry

Cyclic voltammetry was carried out using an Autolab PGSTAT20 potentiostat under an argon atmosphere using a three-electrode arrangement in a single compartment cell. Glassy carbon was used as the working electrode, platinum wire as the secondary electrode and a saturated calomel reference electrode, chemically isolated from the test solution via a fritted bridge tube containing electrolyte solution, in the cell. An analyte concentration of 1 mM was used with [ⁿBu₄N][BF₄] (400 mM) as a supporting electrolyte. Redox potentials are referenced to the ferrocinium/ferrocene couple, which was implemented as an internal reference.⁵⁸ No compensation was applied for internal resistance.

UV/vis spectroelectrochemical measurements were performed using an optically transparent quartz electrochemical cell, with a 0.5 mm path length. A three-electrode configuration of a platinum/rhodium gauze working electrode, platinum wire secondary electrode and a silver/silver chloride reference electrode (chemically isolated via a fritted bridge tube) were used in the cell. The potential at the working electrode was regulated with a Sycopel Scientific Ltd DD10M potentiostat and the spectra recorded with a Perkin Elmer 16 spectrophotometer. Temperature control was achieved with a stream of chilled nitrogen gas (cooled by passing through a tube submerged in liquid nitrogen) across the surface of the cell, adjusting the flow rate as necessary in response to a temperature sensor (± 0.3 °C). [ⁿBu₄N][BF₄] (400 mM) was used as the supporting electrolyte for the experiments.

Bulk electrolysis was performed under an argon atmosphere at 0 °C in a two-component cell: a platinum/rhodium gauze working electrode and secondary electrode are separated by a glass frit. A silver/silver chloride reference was bridged to the test solution through a vycor frit, oriented at the centre of the working electrode. The working electrode compartment, containing analyte (1 mM), was stirred rapidly with a magnetic stir bar during electrolysis. [ⁿBu₄N][BF₄] (400 mM) was used as the supporting electrolyte for the experiments. After electrolysis was completed, the prepared solution was transferred by cannula to a Schlenk-adapted quartz EPR tube for analysis at ambient temperature on an Bruker EMX spectrometer at X-band. Spectra were simulated when possible using WINEPR SimFonia software.

Transient Spectroscopy

Time-resolved infrared spectroscopy was carried out at the University of Nottingham and the apparatus is based on the PIRATE facility at the Rutherford Appleton Laboratory, which has been described previously.⁴⁶⁻⁴⁸ Briefly, a commercial Ti:sapphire oscillator (MaiTai)/regenerative amplifier system (Spitfire Pro, Spectra Physics) provides 800 nm pulses (150 fs), which is split and used to generate 355 nm pump pulses and a tuneable mid-IR pulse with a spectral bandwidth of 180 cm⁻¹ and a pulse energy of *ca.* 2 μ J at 2000 cm⁻¹. A portion of the IR pulse is reflected onto a single-element mercury cadmium telluride (MCT) detector (Kolmar Technology) to serve as a reference, while the remainder serves as the probe beam, which is focused and overlaps with the pump beam at the sample position. The 355 nm pump is optically delayed (up to 3 ns) by a translation stage (LMA Actuator, Aerotech) and focused onto the sample with a quartz lens. The polarization of the pump pulse is set at the magic angle (54.7°) relative to the probe pulse to recover the isotropic absorption spectrum. The focus spot of the probe beam is adjusted to be slightly smaller than that of the pump beam to ensure full overlap with the pump beam. The broad-band-transmitted probe pulse is dispersed with a 250 mm IR spectrograph (DK240, Spectra Product) with a 150 groves/mm grating, and detected with an MCT array detector (Infrared Associates) consisting of 128 elements (1 mm high

and 0.25 mm wide), resulting in a spectral resolution of *ca*. 4 cm⁻¹ at 2000 cm⁻¹. Signals from the array detector elements and the single-element detector are amplified with a 144-channel amplifier and digitized by a 16-bit analogue-to-digital converter (IR-0144, Infrared Systems Development Corp.). For the ns-TRIR experiments the output of a Q-switched Nd:YVO laser (1064 nm, 600 ps, Advanced Optical Technology) was frequency tripled to produce a 355 nm pump pulse. This is synchronised to the probe pulse from the regenerative amplifier and the delay is controlled by a pulse generator (DG535, Stanford Research Systems) allowing delays of 0.5 ns to 100 μ s to be used.

Transient absorption measurements are based on a similar pump-probe method as the TRIR. The pump beam is obtained with the same way as above. The probe beam is a pulsed white light continuum, generated by focusing a small amount of the 800nm output (20 nJ) onto a 4mm thick Sapphire disk or a 3mm thick CaF₂ disk. The white light beam is split into two parts. One part passes through the sample and is spatially overlapped with the pump beam. Another part serves as a reference to the probe beam change. The polarization of the pump pulse is set at the magic angle (54.7 degree) relative to the probe pulse to recover the isotropic absorption spectrum. The time difference (up to 3 ns) between the pump and probe pulses is generated by the optical delay line and longer delay between pump and probe pulses are achieved with the pulse generator. Two parts of probe beam are monitored by a duel array detector (512 pixels) (*Cronin Camera, Spectronic device Ltd, UK*). The detector is mounted in the focal plane of a 303 mm Acton spectrograph (*Acton, USA*) with a 300 g/mm grating and a 150 g/mm grating. The array detector is read out with a 16-bit analogue-to-digital digitizer.

For all experiments a Harrick flowing solution cell with 2-mm-thick CaF_2 windows and a path length of 390 μ m (750 μ m for TA) was mounted on a motorized cell mount that moves the cell rapidly in x and y dimensions throughout the experiment. Consequently, each laser pulse illuminated a different volume of the sample, reducing heating and degradation of the sample solution.

Additional Electrochemical Data.

Compound	1 st Reduction E _{1/2} / V	2 nd Reduction E _{1/2} / V	Difference Between Reduction Potentials / V	Change from NDIS ₀ 1 st Reduction / V	Change from NDIS ₀ 2 nd Reduction / V
NDISo	-1.07	-1.53	0.46	0.00	0.00
	-0.88	-1.29	0.41	0.19	0.24
trans -NDIS₂	-0.75	-1.08	0.33	0.32	0.45
cis-NDIS₂	-0.73	-1.05	0.32	0.34	0.48
NDIS ₃	-0.61	-0.91	0.30	0.46	0.62

Table S1. Reduction potentials of a thionated NDI compound series.

Potentials quoted against $E_{1/2} Fc^+/Fc$ at 100 mVs⁻¹ used as the internal standard. Recorded in dichloromethane at ambient temperature containing [ⁿBu₄N][BF₄] (0.4 M) as the supporting electrolyte.



Additional UV-vis Spectra and Spectroelectrochemistry and Data.



Figure S2. UV-vis absorption spectra showing the inter-conversion between the various charge states of **NDIS**₀-**PTZ**, arrows indicate the progress of the oxidation/reduction. a) from neutral (blue) to monocationic (purple), b) from neutral (blue) to monoanionic (red), c) from monoanionic (red to dianionic (green) species. Spectra were recorded in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) as the supporting electrolyte at 273 K.





Figure S3. UV-vis absorption spectra showing the inter-conversion between the various charge states of **NDIS₃-PTZ**, arrows indicate the progress of the oxidation/reduction. a) from neutral (blue) to monocationic (purple), b) from neutral (blue) to monoanionic (red), c) from monoanionic (red to dianionic (green) species. Spectra were recorded in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) as the supporting electrolyte at 273 K.



Figure S4. UV-vis absorption spectra showing the inter-conversion between the various charge states of **NIS₀-PTZ**, arrows indicate the progress of the oxidation/reduction. a) from neutral (blue) to monocationic (purple), b) from neutral (blue) to monoanionic (red) species. Spectra were recorded in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) as the supporting electrolyte at 273 K.



Figure S5. UV-vis absorption spectra showing the inter-conversion between the various charge states of **NIS₂-PTZ**, arrows indicate the progress of the oxidation/reduction. a) from neutral (blue) to monocationic (purple), b) from neutral (blue) to monocanionic (red) species. Spectra were recorded in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) as the supporting electrolyte at 273 K.



Figure S6. UV-vis absorption spectra showing the inter-conversion from neutral (blue) to monocationic (purple) species for PTZ-NH₂, arrows indicate the progress of the oxidation. Spectra were recorded in dichloromethane containing [${}^{n}Bu_{4}N$][BF₄] (0.4 M) as the supporting electrolyte at 273 K.







Figure S7: UV-vis absorption spectra showing the inter-conversion from neutral (blue) to monoanionic (red) species for a thionated NDI series, arrows indicate the progress of the reduction. Spectra were recorded in CH_2Cl_2 containing [${}^{n}Bu_4N$][BF₄] (0.4 M) as the supporting electrolyte at 273 K. a) **NDIS**₀, b) **NDIS**₁, c) *trans*-**NDIS**₂, d) *cis*-**NDIS**₂ and e) **NDIS**₃.







Figure S8. UV-vis absorption spectra showing the inter-conversion from monoanionic (red) to dianionic (green) species for a thionated NDI series, arrows indicate the progress of the reduction. Spectra were recorded in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) as the supporting electrolyte at 273 K. a) **NDIS**₀, b) **NDIS**₁, c) *trans*-**NDIS**₂, d) *cis*-**NDIS**₂ and e) **NDIS**₃. Inset are spectra from the monoanionic NDIs (red) against the spectra from the monoanionic form regenerated from the dianionic form (blue) when this process was not completely reversible.



Figure S9. FT-IR spectra showing the neutral (black) from monocationic (red) and monoanionic (blue) species for (a) **NDIS**₀-**PTZ**, (b) **NIS**₀-**PTZ**, and (c) **NIS**₂-**PTZ** in CH₂Cl₂.

Table S2. Summary of optical spectroscopy for the thionated NDI and NI series. The transitions giving rise to the lowest-energy peaks in the electronic absorption spectra of the compounds are included. H and L refer to HOMO and LUMO respectively.

	UV-Vis λ_{abs} / nm ($\epsilon \times 10^{-3}$ / mc	ol ⁻¹ dm ³ cm ⁻¹)		B3LYP			CAM-B3LYP		
	Neutral	Monoanionic	Monocationic	λ / nm (ƒ)	Donor	Acc.	λ / nm (ƒ)	Donor	Acc.
NDIS ₀	382 (33.6), 361 (26.0), 343	756 (8.9), 682 (5.0), 612 (11.3),	604 (24.5), 556 (14.2),	378 (0.4336)	Н	L	336 (0.5322)	Н	L
	(14.9), 312 (7.8), 238 (40.6)	594 (6.4), 530 (13.1), 480	514 (5.0), 427 (45.5), 403						
		(40.4), 403 (3.5), 378 (3.0), 332	(30.9), 242 (41.0)						
		(7.0), 272 (25.9), 233 (32.3)							
NDIS ₁	428 (10.7), 396 (10.9), 379	784 (6.8), 682 (8.1), 635 (7.9),	760 (0.8), 615 (16.2), 566	444 (0.4149)	H-1	L	385 (0.5610)	H-1, H	L
	(9.8), 367 (9.6), 317 (3.9),	529 (24.4), 408 (4.1), 383 (3.5),	(10.1), 525 (4.5), 452						
	304 (3.8), 252 (17.3)	361 (5.0), 283 (11.0)	(23.6), 428 (18.2)						
cis-NDIS ₂	428 (10.7), 396 (10.9), 379	784 (6.8), 682 (8.1), 635 (7.9),	760 (0.8), 615 (16.2), 566	496 (0.4845)	H-2	L	423 (0.6145)	H-2, H-1, H	L
	(9.8), 367 (9.6), 317 (3.9),	529 (24.4), 408 (4.1), 383 (3.5),	(10.1), 525 (4.5), 452						
	304 (3.8), 252 (17.3)	361 (5.0), 283 (11.0)	(23.6), 428 (18.2)						
trans-NDIS ₂	585 (0.1), 476 (24.4), 410	876 (14.5), 806 (13.8), 696	639 (53.7), 586 (25.2),	496 (0.5263)	H-2	L	421 (0.6927)	Н	L
	(10.8), 387 (9.1), 367 (13.9),	(28.8), 555 (22.1), 473 (5.8),	541 (6.6), 454 (35.0), 428						
	290 (6.1), 261 (30.7), 233	406 (13.2), 324 (5.3), 289	(26.6), 322 (8.3), 309						
	(20.2)	(15.4), 255 (33.7)	(8.0), 251 (44.9)						
NDIS ₃	502 (8.9), 400 (3.2), 384	836 (4.2), 787 (4.4), 627 (14.0),	643 (11.0), 589 (5.7), 544	526 (0.5194)	H-3, H-2	L	444 (0.6562)	Н-3, Н	L
	(3.2), 271 (9.2)	500 (2.0), 425 (3.0), 314 (3.8),	(2.3), 504 (21.1), 472						
		291 (6.8), 252 (9.1)	(10.6), 309 (4.7), 255						
			(13.1), 233 (14.9)						
NISo	350 (12.9), 335 (14.0)	819 (6.1), 736 (3.3), 494 (4.1),		338 (0.2423)	Н	L	305 (0.2994)	Н	L
		422 (27.3), 351 (5.4), 273							
		(20.2), 267 (7.4), 237 (27.9)							
NIS ₁	527 (0.1), 404 (13.4), 368	786 (6.4), 714 (3.1), 568 (3.8),		400 (0.3375)	H-1	L	358 (0.42)	Н	L
	(8.8), 341 (9.9), 256 (20.6),	536 (3.2), 444 (29.5), 390 (4.8),							
	251 (20.3)	351 (10.4), 318 (5.3), 286 (9.2),							
		269 (8.2), 241 (17.9)							

	UV-Vis λ _{abs} / nm (ε	x 10 ⁻³ / mol ⁻¹ dm ³ cm ⁻¹)			B3LYP			CAM-B3LYP		
	Neutral	Monocationic	Monoanionic	Dianionic	λ / nm (ƒ)	Donor	Acc.	λ / nm (ƒ)	Donor	Acc.
NDIS ₀ -PTZ	381 (31.9) <i>,</i> 360	784 (1.6), 517 (10.2),	762 (6.4), 688 (3.7),	608 (14.4), 561 (8.2),	378 (0.4663)	H-2	L	335 (0.6105)	H-2	L
	(25.4), 342	381 (31.9), 360	609 (10.0), 478 (35.1),	423 (39.5), 400 (27.6),						
	(16.0), 326	(25.6), 342 (15.5),	402 (3.2), 379 (3.0),	316 (7.5), 257 (76.6)						
	(11.6), 257	326 (10.2), 276	325 (8.4), 258 (55.7),							
	(42.1), 237 (52.5)	(53.2), 237 (47.8)	234 (43.6)							
cis-NDIS ₂ -	473 (8.9) <i>,</i> 387	788 (0.8), 500 (9.6),	812 (3.5), 702 (5.6),	609 (7.2), 560 (4.6),	495 (0.5842)	H-4	L			
PTZ	(5.8), 368 (5.2),	475 (10.7), 387 (6.1),	596 (19.8), 526, (3.0),	490 (27.3), 459 (15.0),						
	319 (5.4) <i>,</i> 257	367 (5.2), 352 (3.6),	414 (3.2), 326 (6.5),	434 (5.7), 309 (5.3),						
	(23.3)	331 (4.1), 319 (4.8),	257 (23.8)	257 (26.6), 245 (46.2)						
		276 (23.0), 268 (20.8)								
NDIS ₃ -PTZ	534 (21.1), 505	784 (1.5), 509 (31.0),	877 (7.0), 820 (14.1),	644 (31.5), 590 (15.9),	540 (0.6500)	H-4	L	456 (0.8243)	H-3	L
	(25.1), 398 (9.4),	399 (10.5), 381 (9.1),	770 (8.7), 716 (12.5),	543 (5.7), 502 (62.8),						
	383 (8.7) <i>,</i> 369	368 (9.7), 350 (8.6),	620 (41.6), 424 (8.1),	471 (30.7), 306 (18.4),						
	(9.4), 293 (14.4),	275 (60.0)	368 (6.7), 288 (21.8),	257 (77.7)						
	258 (61.1)		258 (65.3)							
NIS ₀ -PTZ	352 (15.0), 337	784 (1.8), 714 (1.1),	832 (4.8), 749 (2.5),		339 (0.3245)	H-2	L	305 (0.4039)	H-2	L
	(18.0), 325	517 (11.0), 353	490 (3.6), 419 (27.6),							
	(15.3), 258	(15.3), 338 (17.2),	351 (6.7), 298 (9.2),							
	(43.1), 234 (56.8)	325 (14.1), 276	258 (53.4), 237 (47.6)							
		(53.7), 234 (51.1)								
NIS ₂ -PTZ	442 (26.9), 373	783 (2.2), 516 (12.6),	833 (10.2), 748 (4.0),		454 (0.4054)	H-3	L	401 (0.5170)	H-2	L
	(12.1), 357 (7.6),	442 (30.1), 373	650 (2.4), 400 (1.9),							
	313 (8.5), 257	(12.9), 317 (6.9), 276	458 (36.3), 369 (22.9),							
	(74.1)	(65.9), 269 (56.6),	344 (11.0), 325 (11.7),							
		254 (46.0)	307 (12.4), 291 (20.2),							
			257 (67.1)							
PTZ-NH ₂	322 (5.1), 258	642 (4.8), 515 (7.9),			308 (0.0573)	Н	L+1	273 (0.0401)	Н	L+1
	(58.0)	373 (9.6), 309 (9.0),			308 (0.0287)	Н	L+2	267 (0.1026)	H-2, H	L, L+2, L+3
		274 (26.0), 257 (22.2)								, , -

Table S3. Summary of optical spectroscopy for phenothiazine-NDI and –NI compounds. The transitions giving rise to the lowest-energy peaks in the electronic absorption spectra of the compounds are included. H and L refer to HOMO and LUMO respectively.

Additional EPR Spectra and Data.



Figure S10. EPR Spectra of reduced NI-phenothiazine dyads. a) **NIS₀-PTZ**, b) **NIS₂-PTZ**. Experimental data (blue), simulated data (red).

Compound	g iso
PTZ-NH ₂	2.0053
NDIS ₀ -PTZ	2.0055
cis-NDIS2-PTZ	2.0055
NDIS ₃ -PTZ	2.0055
NIS ₀ -PTZ	2.0055
NIS ₂ -PTZ	2.0055

Table S4. Experimentally determined g_{iso} values for oxidised phenothiazine species.

Table S5. Experimentally determined EPR parameters for reduced phenothiazine dyad species.

Compound	g iso	$a_{iso} / x 10^{-4} cm^{-1}$	Linewidth / G	Lineshape
NDIS ₀ -PTZ	2.0038	1.872 (2H), 1.656 (2H), 0.206 (2H), 0.903 (2N)	0.13	Lorentzian
cis-NDIS ₂ -PTZ	2.0085			
NDIS ₃ -PTZ	2.0110			
NIS ₀ -PTZ	2.0032	5.331 (2H), 4.695 (2H), 0.797 (2H), 1.324 (1N)	0.11	Gaussian
NIS ₂ -PTZ	2.0062	4.674 (2H), 4.402 (2H), 1.227 (2H), 2.285 (1N)	0.20	Lorentzian

Compound	g _{iso}	a_{iso} / x 10 ⁻⁴ cm ⁻¹	Linewidth / G	Lineshape
NDIS ₀	2.0037	1.740 (4H)	0.21	0.8
NDIS ₁	2.0058	-	-	-
trans-NDIS₂	2.0078	1.569 (2H) 1.346 (2H)	0.31	Lorentzian
		0.956 (2N)		
cis-NDIS₂	2.0085	1.219 (2H) 0.835 (2N)	0.30	Lorentzian
NDIS ₃	2.0105	-	-	-

Table S6. EPR measurements for the reduced thionated NDI series.

DFT Calculations.







Table S8. Calculated molecular orbital diagrams for the thionated NDI-phenothiazine dyads. Alkyl chains are omitted from the figures for the sake of clarity, no MOs were observed for the HOMO, LUMO or anion SUMO on the alkyl chain for any of the compounds.





Table S9. Calculated molecular orbital diagrams for the thionated NI-phenothiazine dyads.



Figure S11. Comparison of LUMO energies and first reduction potential values for the thionated NDI series.

Compound			Gap/ol/	Change from NDIS / oV
Compound		LUNIO/ EV	Gap/ ev	Change Ironi NDIS ₀ / eV
NDIS ₀	-7.08	-3.47	3.61	0.00
NDIS ₁	-6.49	-3.71	2.78	0.83
cis-NDIS ₂	-6.40	-3.86	2.54	1.07
gem-NDIS ₂	-6.44	-3.88	2.56	1.05
trans-NDIS ₂	-6.48	-3.89	2.59	1.02
NDIS ₃	-6.44	-4.03	2.41	1.2
NDIS ₄	-6.43	-4.19	2.24	1.37
NDIS ₀ -PTZ	-5.39	-3.56	1.83	
cis-NDIS ₂ -PTZ	-5.39	-3.98	1.41	
NDIS ₃ -PTZ	-5.40	-4.15	1.25	
NIS ₀ -PTZ	-5.36	-2.72	2.64	
NIS ₂ -PTZ	-5.37	-3.46	1.91	

Table S10. Calculated HOMO-LUMO gaps for the thionated NDI series and NDI- and NI-phenothiazine dyads.

Additional Time Resolved Spectroscopy



Figure S12. Simulated TRIR difference spectra generated by subtracting the calculated ground state from the calculated triplet state spectra. All calculations were done at the B3LYP/6-311g(d,p) level of theory in a dichloromethane solvent field and no scale factor has been applied. (a) NDIS₀, (b) NDIS₁, (c) *cis*-NDIS₂, (d) *trans*-NDIS₂, (e) NDIS₀-PTZ, (f) NDIS₃-PTZ, (g) NIS₀-PTZ, (h) NIS₂-PTZ.



Figure S13. (a) Transient absorption spectra of *trans*-NDIS₂ acquired in CH_2Cl_2 at selected timedelays after photoexcitation with a 355 nm pulse. (b) TRIR spectra of *trans*-NDIS₂ acquired in CH_2Cl_2 at selected time-delays after photoexcitation with a 355 nm pulse.



Figure S14. (a) Transient absorption spectra of **NDIS₃-PTZ** acquired in CH₂Cl₂ at selected time-delays after photoexcitation with a 355 nm pulse. (b) TRIR spectra of **NDIS₃-PTZ** acquired in CH₂Cl₂ at selected time-delays after photoexcitation with a 355 nm pulse.

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