

A β -Naphthalene-Imide Modified Terthiophene Exhibiting Charge Transfer and Polarization Through the Short Molecular Axis. Joint Spectroscopic and Theoretical Study.

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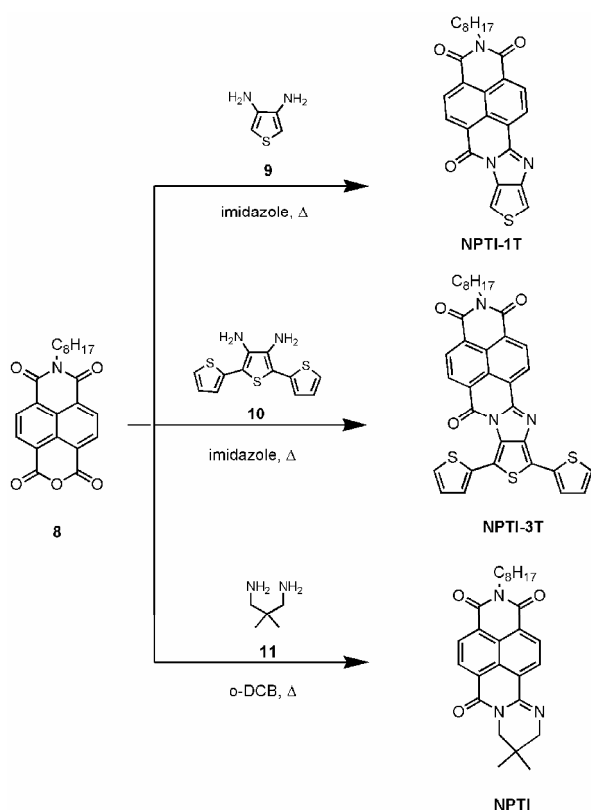
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I. Experimental and Theoretical Details

II. 1 Synthesis. It has been found that the introduction of arylimidazole to extend the conjugation in rylene-type derivatives is an efficient strategy to red-shift the absorption of these dyes.¹ The synthesis of this type of compounds can be carried out by reaction of o-phenylenediamines with anhydrides derived from naphthalene- or perylenedicarboxylic acids.² By following this strategy in Scheme 1 we synthesized naphthaleneamidinemonoimideterthiophene (**NPTI-3T**), the parent naphthaleneamidinemonoimidethiophene (**NPTI-1T**) as well as the reference **NPTI** prepared for comparison purposes.



Scheme S1. Synthesis of the compounds.

All chemicals were purchased from Aldrich and used as received without further purification unless otherwise specified. **TCV-3T**³ and **NPTI-3T**⁴ were prepared by following the previously described synthetic procedures. Column chromatography was performed on Merck Kieselgel 60 silica gel (230-240 mesh). Thin layer chromatography was carried out on Merck silica gel F-254

flexible TLC plates. Melting points were measured with an Electrothermal melting point apparatus and are uncorrected. FTIR spectra were recorded as KBr pellets in a Shimadzu FTIR 8300 spectrometer. NMR were recorded on a Bruker AC-200 and the chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm (for ^1H -NMR) and CDCl_3 at 77.16 ppm (for ^{13}C -NMR). The splitting patterns are designated as follows: s (singlet), d (doublet) and m (multiplet) and the assignments are *Naph* (naphthalene), and *Th* (thiophene) for ^1H -NMR. Mass spectra were recorded with a Varian Saturn 2000 GC-MS and with a MALDI-TOF MS Bruker Reflex 2 (dithranol as the matrix). Elemental analyses were performed on a Perkin-Elmer EA 2400. UV/Vis spectra were taken on a Perkin-Elmer Lambda 19. Cyclic voltammetry experiments were performed with a computer controlled EG & G PAR 273 potentiostat in a three electrode single-compartment cell (5 ml). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of $A = 0.785 \text{ mm}^2$, which was polished down to $0.5 \mu\text{m}$ with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was a Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene–ferricenium couple. For the measurements concentrations of $5 \times 10^{-3} \text{ mol l}^{-1}$ of the electroactive species were used in freshly distilled and deaerated dichloromethane (Lichrosolv, Merck) and 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka) which was twice recrystallized from ethanol and dried under vacuum prior to use.

NPTI-1T. A mixture of 3,4-diaminothiophene (**9**) (114 mg, 0.10 mmol), N-(n-octyl)-naphthalene-1,8-dicarboxyanhydride-4,5-dicarboximide (**8**) (150 mg, 0.40 mmol) and 3 g of imidazol was heated at 180°C for 2 h under argon atmosphere. The crude was allowed to reach room temperature and then HCl aq. 18% solution was added. The mixture was extracted with dichloromethane and the organic extracts dried over anhydrous magnesium sulphate and then evaporated under vacuum. The residue was purified by flash chromatography (silica gel, dichloromethane/ ethyl acetate, 95/5) to yield 55 mg (30%) of **NPTI-1T** as an orange solid. ^1H -NMR (CDCl_3 , 300 MHz). $\delta = 8.86$ (d, $J = 7.6$

Hz, 1H, *naph*), 8.85 (d, *J* = 7.6 Hz, 1H, *naph*), 8.79 (d, *J* = 7.6 Hz, 1H, *naph*), 8.76 (d, *J* = 7.6 Hz, 1H, *naph*), 7.58 (d, *J* = 2.3 Hz, 1H, *Th*), 7.40 (d, *J* = 2.3 Hz, 1H, *Th*), 4.21 (t, *J* = 7.6 Hz, 2H, -N-CH₂), 1.80 to 1.70 (m, 2H, -CH₂-), 1.30 to 1.25 (m, 10H, -CH₂-), 0.87 (t, 3H, -CH₃); FT-IR (KBr). ν = 2920, 2854, 1700, 1658, 1586, 1472, 1345, 1293, 1235, 767 cm⁻¹; MS (EI) (*m/z*): 457 (M⁺), 345 (M⁺ - C₈H₁₇). Anal. calcd. for C₂₆H₂₃N₃O₃S: C, 68.25; H, 5.07; N, 9.18; S, 7.01 Found C, 68.85; H, 5.39; N, 9.01; S, 6.90. M.p. (dichloromethane/ ethyl acetate): 279-280 °C

NPTI-3T. This was prepared by following an identical synthetic procedure as that described for **NPTI-1T** but using [2,2':5',2''-Terthiophene]-3',4'-diamine (**10**) as the starting material instead of 3,4-dimaminothiophene (**9**). In this case the residue was purified by flash chromatography (silica gel, hexane/dichloromethane, 2/8) to yield **NPTI-3T** as a deep green solid in 45% yield. ¹H-NMR (CDCl₃, 300 MHz). δ = 8.75 (d, *J* = 7.7 Hz, 1H, *naph*), 8.67 (d, *J* = 7.7 Hz, 1H, *naph*), 8.66 (d, *J* = 7.7 Hz, 1H, *naph*), 8.59 (d, *J* = 7.7 Hz, 1H, *naph*), 7.50 (dd, ³*J* = 7.5 Hz, ⁴*J* = 2.1 Hz, 1H, *Th*), 7.40 to 7.39 (m, 1H, *Th*), 7.34 to 7.32 (m, 1H, *Th*), 7.27 to 7.25 (m, 1H, *Th*), 7.17 (dd, ³*J* = 6.2 Hz, ³*J* = 7.2 Hz, 1H, *Th*), 7.06 (dd, ³*J* = 6.2 Hz, ³*J* = 7.2 Hz, 1H, *Th*), 4.14 (t, *J* = 7.4 Hz, 2H, -N-CH₂), 1.79 to 1.68 (m, 4H, -CH₂-), 1.50 to 1.35 (m, 8H, -CH₂-), 0.88 (t, 3H, -CH₃); ¹³C-NMR (CDCl₃, 75 MHz). δ = 162.60, 162.33, 156.40, 153.98, 145.05, 133.12, 132.61, 130.66, 130.38, 127.76, 127.43, 127.01, 126.52, 126.10, 125.03, 124.77, 124.51, 11.81, 40.91, 31.81, 29.30, 29.23, 28.09, 27.17, 22.64, 14.07; FT-IR (KBr). ν = 2924, 2854, 1705, 1668, 1598, 1463, 1377, 1339, 1265, 764, 690 cm⁻¹; MS (EI) (*m/z*): 621 (M⁺), 509 (M⁺ - C₈H₁₇). Anal. calcd. for C₃₄H₂₇N₃O₃S₃: C, 65.68; H, 4.38; N, 6.76; S, 15.47 Found C, 65.48 ; H, 4.85 ; N, 6.66; S, 15.41. M.p. (hexane/ dichloromethane) : M.P. = 264-265 °C.

NPTI. To a solution of 150 mg (0.40 mmol) of N-(n-octyl)-naphtalene-1,8-dicarboxyanhydride-4,5-dicarboximide (**8**) in 30 ml of 1,2-dichlorobenzene, 1.19 g (12 mmol) of 1,3-diamino-2,2-dimethylpropan (**11**) was added. The solution was refluxed for 3 h and after cooling to room

temperature, the solvent was evaporated. The residue was purified by flash chromatography (silica gel, dichloromethane/ ethyl acetate, 95/5) to yield 155 mg (87%) of **NPTI** as a yellow solid. ^1H -NMR (CDCl_3 , 200 MHz). δ = 8.74 (d, J = 7.6 Hz, 1H, *naph*), 8.71 (d, J = 7.6 Hz, 1H, *naph*), 8.66 (d, J = 7.6 Hz, 1H, *naph*), 8.63 (d, J = 7.6 Hz, 1H *naph*), 4.18 (t, J = 7.4 Hz, 2H-N- CH_2), 3.81 (s, 2H, -N- CH_2 - C_4), 3.59 (s, 2H, -N- CH_2 - C_4), 1.77 to 1.68 (m, 2H, - CH_2 -), 1.39 to 1.27 (m, 10H, - CH_2 -), 1.10 (s, 6H, - CH_3) 0.87 (t, 3H, - CH_3); ^{13}C -NMR (CDCl_3 , 75 MHz). δ = 163.32, 163.20, 160.84, 144.54, 130.88, 130.79, 129.90, 128.69, 127.45, 126.35, 125.95, 123.93, 58.25, 50.86, 40.80, 31.79, 29.29, 29.18, 28.08, 27.66, 27.10, 24.61, 22.61, 14.06; MS (EI) (m/z): 445 (M^+), 430 ($\text{M}^+ - \text{CH}_3$), 415 ($\text{M}^+ - 2\text{CH}_3$), 334 ($\text{M}^+ - \text{C}_8\text{H}_{17}$). FT-IR (KBr). ν = 2924, 2853, 1703, 1661, 1627, 1468, 1353, 1264, 768 cm^{-1} ; Anal. calcd. for $\text{C}_{27}\text{H}_{31}\text{N}_3\text{O}_3$: C, 72.78; H, 7.01; N, 9.43 Found C, 72.21 ; H, 7.09 ; N, 9.26. M.p. (dichloromethane/ ethyl acetate): 198-199 $^\circ\text{C}$

Photophysical properties.

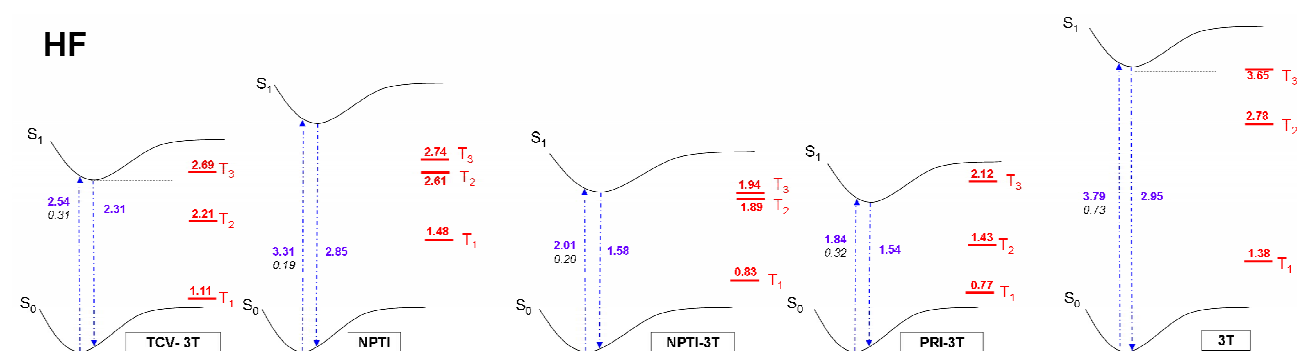


Figure S1. TD-DFT/B3LYP/6-31G** excited states data over the S₀ (HF/6-31G**) and S₁ (RCIS/6-31G**) optimized geometries. This compares with the TD-DFT/B3LYP/6-31G** excited states data over the S₀ (DFT/B3LYP//6-31G**) and S₁(RCIS/6-31G**) optimized geometries in Figure 7.

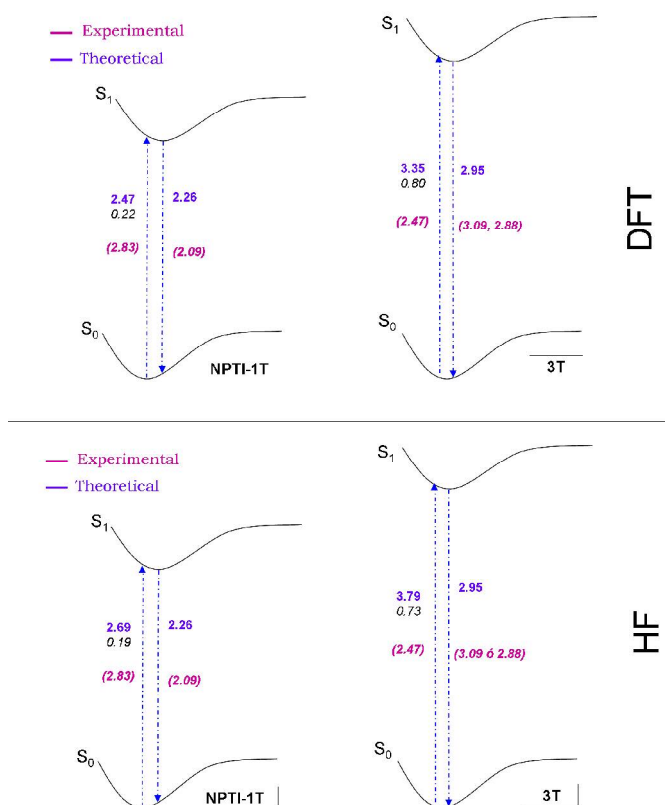


Figure S2. Experimental (see Figure R3 for the spectra), theoretical DFT [HF(S_0)/RCIS-HF(S_1) and DFT(S_0)/RCIS-HF(S_1)] and theoretical HF [HF(S_0)/RCIS-HF(S_1) and HF(S_0)/RCIS-HF(S_1)] of the absorption and emission properties of **3T** and **NPTI-1T**.

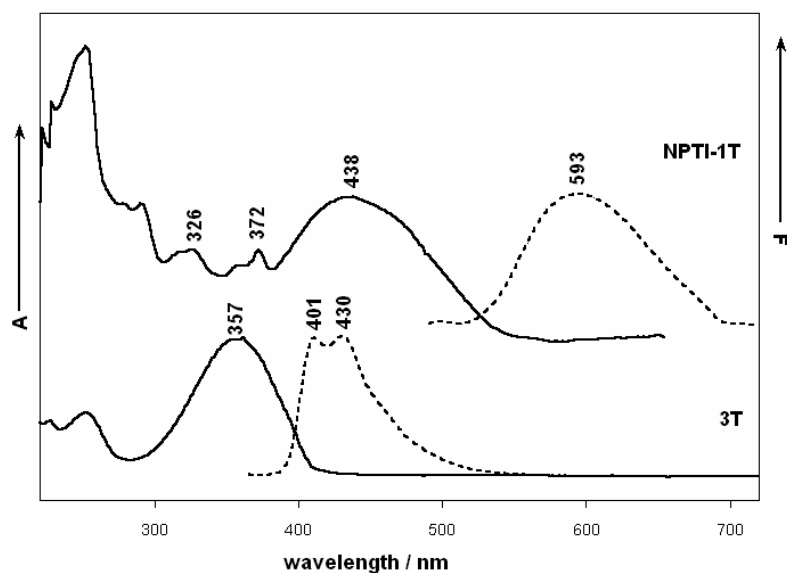


Figure S3. Absorption and emission spectra of **3T** and **NPTI-1T** in dichloromethane.

References

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