

Supporting Information

A theoretical and spectroscopic study of a series of styryl-substituted terthiophenes.

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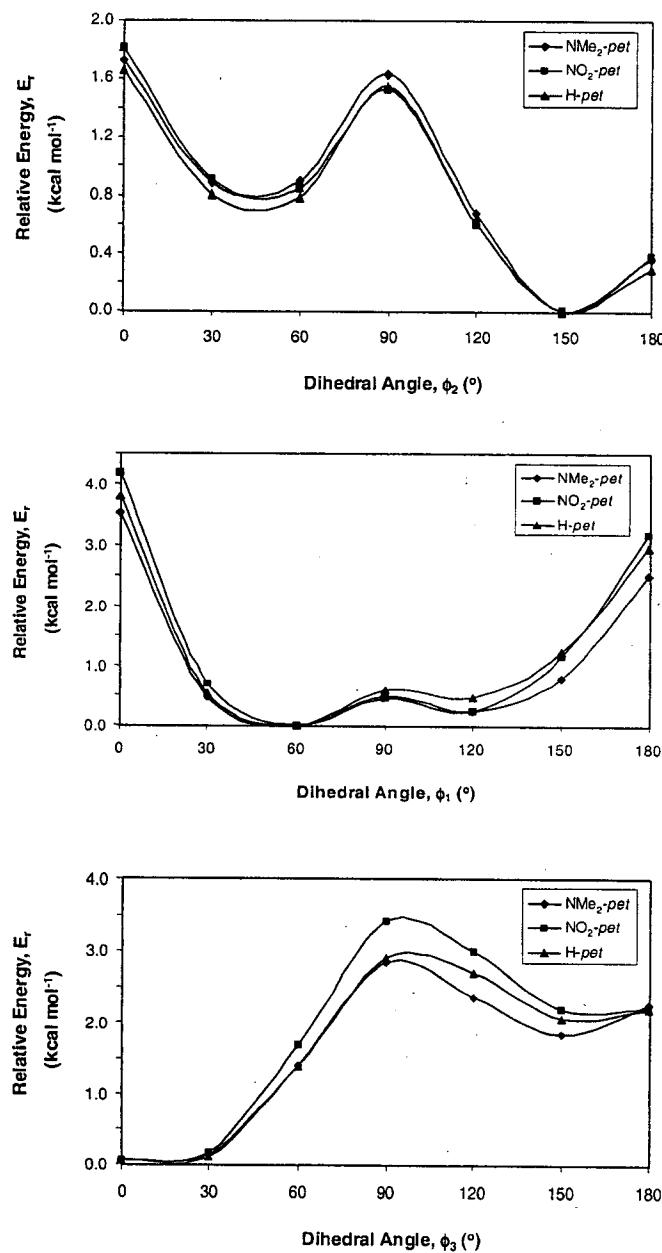


Figure 1S. The fitted potential energy surfaces of dihedral angles ϕ_2 (a), ϕ_1 (b), and ϕ_3 (c) of NMe₂-pet (◆), NO₂-pet (■), and H-pet (▲) calculated using the HF/3-21G(d) method.

Table 1S. The mode descriptions and average calculated (B3LYP/6-31G(d)) and experimental frequencies (\pm range) for each conserved mode over all R-pet molecules.

Mode Number, <i>v</i>	Mode Description	Calc. Freq (cm ⁻¹)	Exp. Freq (cm ⁻¹)
63	$\gamma(\text{CH})_{\text{ethene}}$	965 \pm 6	956 \pm 6
64	$\gamma(\text{CH})_{\text{ethene}}$	972 \pm 3	975 \pm 15
65	$\nu(\text{CC})_{\text{phenyl skeletal}}$	987 \pm 12	991 \pm 18
66	$\delta(\text{CH})_{\text{terthiophene}}$	1039 \pm 1	
67	$\delta(\text{CH})_{\text{terthiophene}}$	1039 \pm 1	1050 \pm 2
68	$\delta(\text{CH})_{\text{terthiophene}}$	1071 \pm 1	
69	$\delta(\text{CH})_{\text{terthiophene}}$	1072 \pm 1	1080 \pm 1
71	$\delta(\text{CH})_{\text{phenyl}}$	1103 \pm 23	1115 \pm 11
72	$\delta(\text{CH})_{\text{phenyl}}$	1168 \pm 11	1178 \pm 9
73	$\nu(\text{C-S})$ and $\delta(\text{CH})_{\text{terthiophene}}$	1173 \pm 1	1184 \pm 9
74	$\nu(\text{C-S})$ and $\delta(\text{CH})_{\text{terthiophene}}$	1177 \pm 2	1189 \pm 0
75	$\delta(\text{CH})_{\text{phenyl}}$ and $\delta(\text{CH})_{\text{ethene}}$	1197 \pm 5	
76	$\nu(\text{C-S})$ and $\delta(\text{CH})_{\text{terthiophene}}$	1207 \pm 0	1213 \pm 5
77	$\delta(\text{CH})_{\text{terthiophene}}$ and $\delta(\text{CH})_{\text{ethene}}$	1214 \pm 1	1230 \pm 11
78	$\delta(\text{CH})_{\text{terthiophene}}$	1223 \pm 1	1242 \pm 4
79	$\delta(\text{CH})_{\text{delocalised}}$	1270 \pm 15	1278 \pm 13
80	$\delta(\text{CH})_{\text{delocalised}}$	1298 \pm 8	1307 \pm 6
81	$\delta(\text{CH})_{\text{delocalised}}$	1311 \pm 9	1314 \pm 15
82	$\delta(\text{CH})_{\text{ethene}}$ and $\delta(\text{CH})_{\text{terthiophene}}$	1324 \pm 3	1334 \pm 4
85	$\delta(\text{CH})_{\text{ethene}}$	1340 \pm 2	1350 \pm 2
86	$\nu(\text{C-C})_{\text{terthiophene}}$	1373 \pm 2	1386 \pm 3
87	$\nu_a(\text{C=C})_{\text{phenyl}}$	1415 \pm 21	1422 \pm 26
88	$\nu(\text{Delocalised})$	1417 \pm 3	1418 \pm 4
89	$\nu_s(\text{C=C})_{\text{terthiophene}}$	1432 \pm 1	1432 \pm 1
90	$\nu_s(\text{C=C})_{\text{terthiophene}}$	1446 \pm 2	1460 \pm 2
91	$\nu_s(\text{C=C})_{\text{phenyl}}$	1495 \pm 19	1509 \pm 15
92	$\nu_a(\text{C=C})_{\text{terthiophene}}$	1501 \pm 2	1503 \pm 6
93	$\nu_a(\text{C=C})_{\text{terthiophene}}$	1524 \pm 1	1527 \pm 3
94	$\nu_a(\text{C=C})_{\text{phenyl}}$	1547 \pm 21	1555 \pm 37
95	$\nu_a(\text{C=C})_{\text{terthiophene}}$	1548 \pm 0	1558 \pm 3
96	$\nu_s(\text{C=C})_{\text{phenyl}}$ and $\nu(\text{C=C})_{\text{ethene}}$	1592 \pm 10	1599 \pm 6
98	$\nu(\text{C=C})_{\text{ethene}}$	1625 \pm 5	1625 \pm 4

Table 2S. The predicted transition wavelengths (from the molecular orbital energy differences), and the experimental transition wavelengths of R-*pet*, as measured in CH₂Cl₂ at room temperature. The superscript * indicates a shoulder.

Molecule	HOMO-LUMO Transition		HOMO-LUMO+1 Transition	
	Calculated ΔE (cm ⁻¹)	Measured λ (cm ⁻¹)	Calculated ΔE (cm ⁻¹)	Measured λ (cm ⁻¹)
NO ₂ - <i>pet</i>	23753	24096	29674	28986
CN- <i>pet</i>	26385	27778	30769	30960
pyr- <i>et</i>	27624	28653	31847	32154
H- <i>pet</i>	27624	28490	32154	32051
MeO- <i>pet</i>	27027	27397	31847	30960
NH ₂ - <i>pet</i>	26247	26596	31250	29851
NMe ₂ - <i>pet</i>	25381	25316	30488	28490