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Synthesis and Electronic Structure of 1,2-Heteroarylethynes: Potential Monomers for Low Bandgap Conductive Polymers

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Abstract: A series of 1,2-heteroarylethynes which are potential monomers to low bandgap materials were synthesized and their He I photoelectron spectra measured and assigned with the aid of empirical arguments and semi-empirical MO calculations. The electronic structure analysis reveals that $C \equiv C$ bond is an efficient "relay" of π-electrons and that it supports inter-ring conjugation. The efficiency depends on the nature of ring heteroatom, but not on its position within the ring. The importance of $C \equiv C$ bond relay is discussed in the broader context of conjugated polymer applications. © 1997 Published by Elsevier Science Ltd.

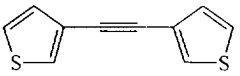
INTRODUCTION

Electrically conducting conjugated polymers, particularly those incorporating thiophenes, are an important class of "synthetic metals" that combine chemical and mechanical attributes of polymers (e.g. their ease of processibility) with electrical properties of metals. They breach the traditional view of mutual exclusion between polymers and electrical conductivity, and their development has spurred intense interdisciplinary research on a global scale over the past two decades[1, 2]. An ongoing research goal in conductive polymers has been the reduction of energy bandgap (E_g)[3], so that the absorption wavelength of the undoped polymer shifts from the visible towards the near infrared region of the electromagnetic spectrum. When fully doped, the band in the visible region would have decreased significantly so that thin films take on a nearly colorless transparent appearance. Such materials, having suitable spectral window of transparency, are potentially useful for a wide variety of applications such as electrochromic devices, replacement for ITO transparent electrodes, coatings on cathode-ray tubes to prevent static charging, applications in flexible LEDs, LCDs and transparent EMI shields[4].

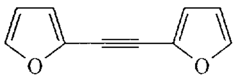
Although there are several approaches to low bandgap conducting polymers[3, 5-9], the most straightforward appears to be the incorporation of conjugative spacers such as ethenyl[5, 6] and ethynyl[7, 8] moieties into the polymer backbone. Arising from our ongoing interests in the design of novel conducting polymers , we report here studies into the electronic structures of 1,2-heteroarylethynes , which are potential monomers for conducting polymers with reduced bandgaps. Insights into the structure-electronic property correlation of these materials can then be extrapolated to the rational design of conjugated polymers with reduced bandgaps. Besides technological interest outlined above, we are interested in the electronic structure variations of C ≡ C bond when it forms part of the larger unsaturated system. C ≡ C bond is one of the most important functional groups in organic chemistry and the electronic structures of compounds containing this bond have been studied in considerable detail[10]. The triple bonds in a molecule can be considered as probes for study of conjugation, homoconjugation and π/σ interactions. The methods employed in such studies often utilize UV photoelectron spectroscopy (UPS) and quantum chemical calculations. Most UPS studies reported so far, were concerned with interactions between C ≡ C bonds, but comparatively little effort had been expended on the study of C ≡ C bond as a vehicle (relay) for π-electron interactions between other functional groups.

RESULTS AND DISCUSSION

Synthesis. Symmetrical bisarylethynes can be readily synthesized using the facile approach of *Gregory et al*[11] and *Rossi et al*[12] . Accordingly this methodology was used to synthesize 3,3'-bisthienylethyne (**TT-33**) and 2,2'-bisfurylethyne (**FF-22**).



TT33

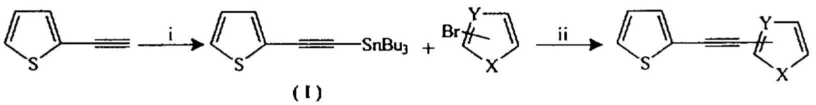


FF22

However, this approach cannot be readily extended to the non-symmetrical congeners. In addition, literature reports on the synthesis of related acetylenic compounds appears rather unsatisfactory for our purpose. Thus, although trimethylsilylacetylene was used as starting material in several methods[11-16], the high cost and lability of the reagent makes this approach less attractive. Brittain *et. al* [17] reported a Wittig-type reaction that could be used in the synthesis of 1,2-bisheteroarylethynes; unfortunately the reaction needed high temperature and high vacuum. Recently it was reported[11] that 2,2'-dithienylacetylene could be obtained by a Pd(0) catalyzed cross-coupling of 2-ethynylthiophene with 2-bromothiophene.

The greatest drawback of this method, however, is the instability of 2-ethynylthiophene, which tends to decompose even on storage at sub-zero temperatures, requiring the material to be freshly prepared prior to reaction. Considering that organostannanes, particularly alkynylstannanes [18-20] can undergo facile reaction with a range of electrophiles as of cross-couplings with aryl halides under palladium catalysis, and that these compounds are stable under ambient storage conditions, it was envisaged that thienylethynylstannanes could be used as key starting materials instead of the unstable ethynylthiophenes. Accordingly, the organostannane (**I**) was prepared by heating 2-ethynylthiophene with methoxytributylstannane[19], or by the reaction of ethynylthiophene with diethylaminotributylstannane[20]. The palladium-catalyzed coupling reaction of arylbromide with (**I**) was found to take place under mild reaction conditions to give high yields of bisheteroarylethynes.

Scheme 1

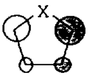


(I)

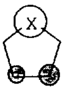
TT22,TT23: X=S, Y=C;
TF22,TF23: X=O, Y=C;
TN22: X=S, Y=N;
TSe22: X=Se, Y=C.

i: Bu_3SnOMe, 100 °C, 3 hrs; or Bu_3SnNEt_2, 22-25 °C, 17 hrs.
ii: $(MeCN)_2PdCl_2$, DMF, r.t., 10 hrs.

UPS Studies and MO Calculations. The He I photoelectron spectra of the compounds studied in this work are shown in Figs. 1 and 2. The assignments of the spectra are based on the consideration of relative band intensities and contours, AM1 calculations (PM3 for selenium derivative) and comparison with the spectra of related bisheteroarylenes[21]. The low ionization energy region ($E_i < 11.5$ eV) contains six π-orbital ionizations. The orbitals associated with these ionizations can be described as linear combinations of molecular fragment π-orbitals shown schematically below.



π_3



π_2

π''

π'

HOMO is considerably delocalized along the carbon skeleton, but other orbitals retain (to a significant degree) their fragment localization properties (Table 1). An interesting feature of the electronic structure is the ability of C ≡ C bond to act as a π-electron relay between rings. In order to study this π-electron density transfer we have selected compounds which have different types of ring heteroatoms at different ring positions. The ethyne moiety itself has two π orbitals (π_{CC}' and π_{CC}'') which are symmetric and antisymmetric with respect to molecular plane. π_{CC}'' could be expected to be delocalized into the π ring system giving rise to broad band, while π_{CC}' could not. Spectra of **TT22**, **TT23**, **TT33** and **TSe22** show repeated appearance of two bands at 10.3 eV (broad) and 11.0 eV (narrow). The pronounced difference in bandwidths suggests that the corresponding orbitals have different bonding properties; the former being more bonding than the latter. AM1 results (Table 1) indicate that the 10.3 eV band corresponds to π_{CC}' ionization and the 11.0 eV to heteroatom lone pair σ_X. This argument does not explain why π_{CC}' band is so broad, considering that it can not be delocalized into the π orbital system. The result can be rationalized in two ways:

a) π_{CC}'' = 10.3 eV π_{CC}'=11.0 eV i.e. AM1 assignment is incorrect.

b) the molecules are nonplanar because of low torsional barriers (ring rotation around -C≡C- bond axis) which allows π_{CC}' to be delocalized into ring orbitals. This explanation also invalidates the π_{CC}' π_{CC}'' labels. We have calculated torsional barrier heights and they appear to be < 1 kJmol^{-1}, which favors the explanation b).

TABLE 1. Experimental ionization (E_i) and semiempirical MO energies of arylethynes[*]

Compound	Band	E_i/eV	MO energy/eV	Qualitative Assignment
TT22	X	7.9	8.58	$\pi_3 - \pi_{CC}'' - \pi_3'$
	A	9.15	9.38	$\pi_2 - \pi_2'$
	B	9.28	9.39	$\pi_2 + \pi_2'$
	C	9.28	10.04	$\pi_3 + \pi_3'$
	D	10.3	10.68	π_{CC}'
	E	10.9	11.86	$\sigma_S - \sigma_S'$
	F	11.93	11.97	$\sigma_S + \sigma_S'$
TT23	X	8.05	8.48	$\pi_3 - \pi_{CC}'' - \pi_3$
	A	9.0	9.33	π_2
	B	9.3	9.62	π_3'
	C	9.3	9.92	$\pi_3 - \pi_2$
	D	10.3	10.69	π_{CC}'
	E	11.0	11.85	σ_S
	F	12.15	11.97	σ_S'
	G	12.15	12.10	$\pi_3 - \pi_{CC}'' - \pi_3$
TT33	X	8.1	8.38	$\pi_3 - \pi_{CC}'' - \pi_3'$
	A	8.91	9.51	$\pi_3 - \pi_3'$
	B	9.11	9.62	$\pi_2 + \pi_2'$
	C	9.11	9.85	$\pi_2 - \pi_2'$
	D	10.3	10.65	π_{CC}'
	E	11.0	11.89	$\sigma_S + \sigma_S'$
	F	12.0	11.92	$\sigma_S - \sigma_S'$
	G	12.0	12.06	$\pi_3 - \pi_{CC}'' - \pi_3'$
FF22	X	8.0	8.58	$\pi_3 - \pi_{CC}'' - \pi_3'$
	A	9.18	9.83	$\pi_3 - \pi_3'$
	B	10.2	10.78	$\pi_2 + \pi_2'$
	C	10.2	10.90	$\pi_2 - \pi_2'$
	D	11.15	11.41	π_{CC}'
	E	13.0	12.81	π_{CC}''
	F	13.0	13.81	$\sigma_o - \sigma_o$
	G	13.7	13.82	$\sigma_o + \sigma_o$

TABLE 1. (continued)

TF22	A	9.3	9.44	π_2
	B	9.3	9.90	π_3 - π_3'
	C	10.15	10.76	π_2'
	D	10.15	11.06	π_{CC}'
	E	11.0	11.98	σ_S
	F	12.0	12.41	π_{CC}"
	G	12.0	13.60	σ_o
TSe22	X	7.8	9.03	π_3 - π_{CC}" - π_3'
	A	8.8	9.58	π_2'
	B	9.21	9.70	π_2
	C	9.21	10.36	π_3 - π_3'
	D	10.3	10.75	π_{CC}'
	E	10.8	11.47	σ_{Se}
	F	11.9	12.24	π_{CC}"
	G	11.9	12.25	σ_S
TF23	X	8.12	8.66	π_3 - π_{CC}" - π_3'
	A	9.3	9.38	π_2
	B	9.3	9.72	π_2 - π_2'
	C	9.8	10.64	π_{CC}'
	D	10.55	10.79	π_3 - π_2'
	E	11.9	11.91	σ_S
	F	11.9	12.68	π_{CC}"
	G	12.6	13.52	σ_0
TN22	X	8.21	8.83	π_3 - π_{CC}" - π_3'
	A	9.32	9.50	π_2
	B	9.32	9.99	π_3 - π_3'
	C	10.16	10.59	π_2'
	D	10.16	10.74	π_{CC}'
	E	11.05	11.51	$\sigma_S + \sigma_N + \sigma_S$'
	F	12.5	12.08	σ_S
	G	12.5	12.35	π_{CC}"

[*] The π_3, π_2, π_{CC} symbols designate fragment orbitals localised on the first (left) heterocyclic ring or C ≡ C bond. π_3', π_2' symbols refer to the second (right) ring orbitals. The signs between fragment orbitals indicate relative phases in LCAO.

The inspection of Fig.1 indicates that in the bisthienyl series the relay effect is strong and slightly sensitive to heteroatom position. The result correlates well with the polythiophenes[2] whereby pronounced conjugation and consequently electrical conductivity is optimum for α-α linkage and diminishes along the sequence α-α > α-β > β-β. This can be deduced from the observed narrowing of 11.0 eV band on going from **TT22** to **TT33**. Replacement of sulfur by selenium in one of the rings does not effect the relay ability as indicated by the UPS of **TSe22**. The spectrum of **FF22** (Fig.2) also shows two π bands in the 10-11 eV region, but they are narrower than in than in bisthienylethynes, which suggests a weakening of the effect of C ≡ C bond relay.

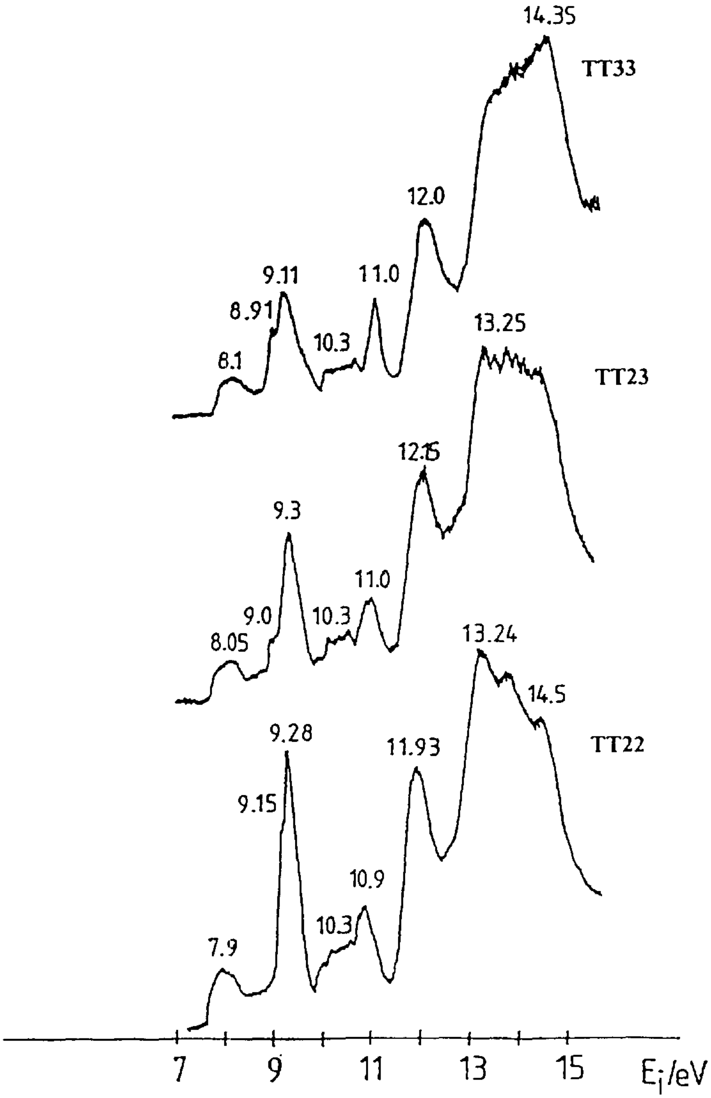


Fig. 1. He I photoelectron spectra of TT33, TT23 and TT22.

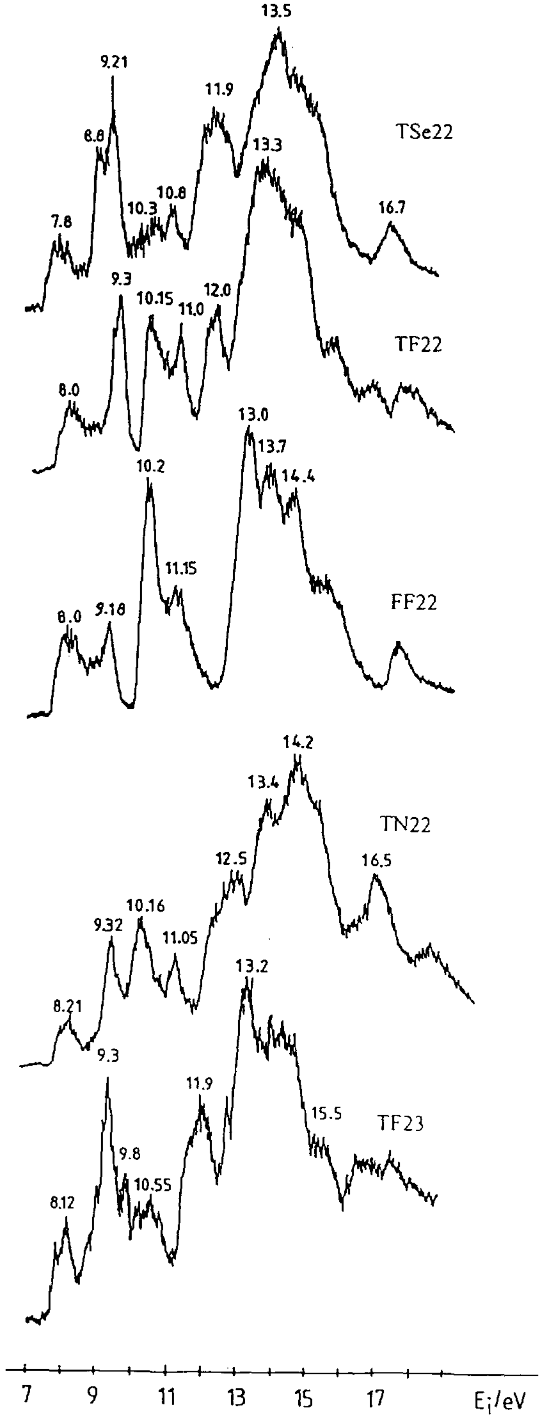


Fig. 2. He I photoelectron spectra of TSe22, TF22, FF22, TN23 and TF23.

HOMO-LUMO energy gap (ΔE) in dimer is important because it has some influence on the electrical conductivity of the related polymer and its conduction-valence band gap. We have estimated ΔE values from UV spectra of **TT22-TT33** and they are 3.76, 4.0 and 4.2 eV, respectively. Polymerisation trials of these compounds are currently in progress and will be reported in due course.

CONCLUSION

Our results showed that 1,2-bisthienylethynes are good candidates for the preparation of conducting polymers while other 1,2-heteroarylenes are not. This is a direct consequence of small, but observable variations in their electronic structures.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. Mass spectra were obtained using a micromass VG 7035E mass spectrometer at a source temperature of 200 °C and an ionizing voltage of 70 eV. NMR spectra were obtained on a Bruker ACF300 spectrometer using $CDCl_3$ as solvent unless otherwise specified and $SiMe_4$ as internal reference. Elemental analyses were performed on a Perkin-Elmer Model 240C elemental analyzer. Reagents and solvents, obtained from commercial sources, were purified and dried in accordance with standard procedures prior to use. Completion of reactions was monitored by thin layer chromatography (TLC) on Polygram precoated plastic sheets of silica gel. Visualization of the TLC was effected by inspection under UV light (254 nm) or by staining with a solution of ammonium molybdate (10 g)-cerium(IV) sulphate (2 g) dissolved in 2 M H_2SO_4 (500 mL).

The HeI UPS spectra were recorded on a UPG-200 Leybold-Heraeus spectrometer under the spectral resolution of 18-25 meV, measured as FWHM of Ar^+ $^2P_{3/2}$ and $^2P_{1/2}$ calibration lines. Elevated sample inlet temperatures (100-150^0 C) were used during measurements of less volatile compounds in order to obtain sufficient sample vapour pressures. The electronic structure calculations were performed by semiempirical MO methods (AM1 and PM3) implemented in SPARTAN program package[22]. This method was found suitable for the calculation of electronic properties in electroactive polymers[23]. All molecular geometries were fully optimized and correspond to genuine minima on the potential energy surface which was confirmed by the absence of imaginary vibrational frequencies. The calculations suggest that molecules are planar in ground state. UV spectra of **1-3** were measured in hexane solvent at ambient temperatures.

Isomeric ethynylthiophenes were prepared from corresponding bromothiophenes and 2-methyl-3-butyn-2-ol as reported previously[24], 2-ethynylfuran was prepared from 2-bromofuran and ethynyltrimethylsilane[14]. All other required starting materials and catalysts were synthesized using literature procedures referenced: 2-

bromofuran[25], 2-bromoselenophene[26], tributylmethoxystannane[27], tributyl (diethylamino)stannane[28], $(CH_3CN)_2PdCl_2$[29] and $(Ph_3P)_2PdCl_2$[30].

Tributyl(2-thienylethynyl)stannane. *Method A:* A mixture of (9.5 g, 30 mmol) of methoxytributylstannane and (7.0 g, 62 mmol) of 2-ethynylthiophene was heated at 90 °C for 3 hrs. Purification was accomplished by bulb-to-bulb distillation to afford the product 10.1 g (85%) as a colorless liquid: bp 143 °C / 1.2 mbar; ^1H NMR ($CDCl_3$) δ: 0.89-1.65 (27H, m, 3-Bu), 6.90 (1H, dd, J = 3.61 and 5.16 Hz), 7.13-7.16 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 131.6, 126.6, 126.1, 124.2, 102.1, 98.5. ^{119}Sn NMR ($CDCl_3$) δ: -112.1. IR ν_{max} (KBr) cm^{-1}: 3070, 2900, 2100,1449, 1148, 1067, 845, 688 .

Method B: A mixture of (10.9 g, 30 mmol) of (diethylamino)trimethylstannane and (7.1 g, 6.6 mmol) of thienylethenyl was stirred at ambient temperature (25 °C) for 17 hrs. Purification was accomplished by bulb-to-bulb distillation, to yield 10.3 g (87%) of a colorless liquid.

2,2'-Bisthienylethyne (TT-22) To a solution of $(MeCN)_2PdCl_2$ in dry DMF (30 mL) was added 2-bromothiophene (0.98 g, 6 mmol) under nitrogen. Tributyl(2-ethynylthiophene)stannane (2.6 g, 6.5 mmol) was then added dropwise at ambient temperature (25 °C). The reaction mixture which turned black immediately was stirred overnight (16 hrs), whence TLC indicated complete consumption of 2-bromothiophene. Water (50 mL) was added and the aqueous mixture extracted with ether (3x30 mL). The combined ethereal extracts were washed successively with water (2x25 mL), brine(50 mL) and then dried over $MgSO_4$. Removal of solvent under reduced pressure, followed by flash chromatography using Hexane as eluent afforded the product as a light yellow solid 0.92 g (81%): mp 94-95 °C (lit.[11] mp 95 °C). ^1H NMR ($CDCl_3$) δ: 7.01 (2H, dd, J = 3.66 and 5.13 Hz), 7.26-7.28 (4H, m). IR ν_{max} (KBr) cm^{-1}: 3098, 2139. EI-MS m / z 190 (M^+ ,100), 158 (12), 145 (18), 93 (10); UV λ_{max} (Hexane) nm: 355, 335, 280, 202.

2,3-Bisthienylethyne (TT-23) was prepared from I and 3-bromothiophene in 78% yield as light yellow solid: mp 92-93 °C; ^1H-NMR δ 6.99 (1H, dd, J= 3.73 and 5.10 Hz), 7.18 (1H, dd, J = 1.05 and 4.91 Hz), 7.25-7.30 (3H, m), 7.51 (1H, dd, J = 1.05 and 2.89 Hz). IR ν_{max} (KBr) cm^{-1}: 3096, 2367. EI-MS m / z 190 (M^+, 100), 158 (12), 145 (22), 93 (12). UV λ_{max} (Hexane) nm: 312, 244, 212. Anal. Calcd for $C_{10}H_6S_2$: C, 63.16; H, 3.16. Found: C, 63.60, H, 3.53.

2-[(2'-Thienyl)ethynyl]furan (TF22) was prepared from I and 2-bromofuran in 80% yield as a yellow solid: mp 37-38 °C (lit.[17] mp 38.5 °C). ^1H NMR (CDCl3) δ: 6.41 (1H, dd, J = 1.89 and 3.46 Hz), 6.65 (1H, d, J = 2.97 Hz), 6.99 (1H, dd, J = 3.78 and 5.04 Hz), 7.30 (1H, dd, J = 1.08 and 4.95 Hz), 7.41(1H, d, J = 1.26 Hz). IR ν_{max} (KBr) cm^{-1}: 3107, 2209. EI- MS m / z 174 (M^+, 100), 145 (30). UV λ_{max} (Hexane) nm: 322, 304, 290, 252, 210.

3-[(2'-Thienyl)ethynyl]furan (TF-23) was prepared from I and 3-bromofuran in 70% yield as light yellow oil: ^{1}H NMR ($CDCl_3$) δ: 6.98 (1H, dd, J = 4.78 and J = 8.81 Hz), 7.22-7.38 (4H, m), 7.49 (1H, dd, J = 2.01 and 5.58 Hz). IR ν_{max} (KBr) cm^{-1}: 3016, 2204. EI- MS m / z 174 (M$^+$, 100), 145 (50). UV λ_{max} (Hexane) nm: 334, 314, 300, 290, 236, 226, 204. Anal. Calcd for $C_{10}H_6OS$: C, 68.97; H, 3.448. Found: C, 68.81; H, 3.21.

2-[(2'-Thienyl)ethynyl]thiazole (TN-22) was prepared from (I) and 2-bromothiazole in 78% yield as light yellow solid: mp 42-43 °C. ^{1}H NMR ($CDCl_3$) δ: 7.04 (1H, dd, J = 3.66 and 5.13 Hz), 7.38-7.42 (3H, m), 7.86 (1H, d, J = 3.33 Hz). IR ν_{max} (KBr) cm^{-1}: 3072, 2191. EI-MS m / z 191 (M$^+$, 95), 58 (100). UV λ_{max} (Hexane) nm: 340, 332, 325, 318, 290. Anal. Calcd for $C_9H_5NS_2$: C, 56.54; H, 2.62; N, 7.33. Found C, 56.59; H, 2.89; N, 7.07.

2-[(2'-Selenienyl)ethynyl]thiophene (TSe-22) was prepared from land 2-bromoselenophene in 80% yield as yellow solid: mp 91-92 °C; ^{1}H NMR ($CDCl_3$) δ: 7.01 (1H, dd, J = 3.60 and 5.16 Hz), 7.22-7.31 (3H, m), 7.45 (1H, dd, J = 1.05 and 3.87 Hz), 8.02 (1H, dd, J = 1.11 and 5.46 Hz). IR ν_{max} (KBr) cm^{-1}: 3076, 2335. EI-MS m / z 238(100), 236 (M$^+$, 50), 158 (80). UV λ_{max} (Hexane) nm: 322, 254, 206, 290. Anal. Calcd for $C_{10}H_6SSe$: C, 50.85; H, 2.54. Found: C, 51.09; H, 2.71.

3,3'-Bisthienylethyne (TT-33) was prepared from 3-ethynylthiophene and 3-bromothiophene. To a solution of $(Ph_3P)_2PdCl_2$ (0.007 g, 0.01 mmol), CuI (0.01 g, 0.05 mmol) and Ph_3P (0.01 g, 0.04 mmol) in dry triethylamine was added 3-bromothiophene (1.8 g, 11 mmol) and 3-ethynylthiophene (0.54 g, 5 mmol) under nitrogen. The reaction mixture was refluxed for 2 hrs, then cooled to room temperature. 3-Ethynylthiophene (0.54 g, 5 mmol) was added again, and the mixture was kept refluxing. After 3 hrs, the reaction was completed and cooled to room temperature. Solvent was removed under reduced pressure, cool water was added, the aqueous mixture was extracted with ether (3x20 mL). The combined ether extracts were washed with water and dried over MgSO4 . The dried extracts were filtered . Solvent was evaporated to afford a crude product which was purified by chromatography using hexane as eluent. The product was light yellow solid in 70% yield: mp 95-96 °C; ^{1}H NMR ($CDCl_3$) δ: 7.16-7.18 (2H, dd, J = 1.14 and 5.07 Hz), 7.27-7.30 (2H, dd, J = 2.99 and 4.99 Hz), 7.49-7.50 (2H, dd, J = 1.15 and 2.92 Hz). IR ν_{max} (KBr) cm^{-1}: 3099, 2361. EI-MS m / z 190 (M$^+$, 100), 158 (20), 145 (58). UV λ_{max} (Hexane) nm: 298, 228, 218. Anal. Calcd for $C_{10}H_6S_2$: C, 63.16; H, 3.16; Found: C, 63.56; H, 3.21.

2,2'-Bisfurylethyne (FF-22) was prepared from 2-ethynylfuran and 2-bromofuran in 75% yield as solid by the same route: mp 20 °C (lit.[31] mp 21 °C); ^{1}H NMR ($CDCl_3$) δ: 6.42 (2H, dd, J = 1.90 and 3.49 Hz), 6.69 (2H, dd, J = 0.64 and 3.51 Hz.), 7.43 (2H, dd, J = 0.66 and 1.98 Hz.). IR ν_{max} (KBr) cm^{-1}: 3156, 3119, 2195 . EI-MS m /z 158 (M$^+$, 100), 102 (75), 76 (70). UV λ_{max} (Hexane) nm: 340, 312, 300, 292, 282, 252.

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