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SYNTHESIS AND STRUCTURAL PROPERTIES OF CYCLOPHANES CONTAINING THIOPHENE RINGS IN THE SIDE-CHAIN

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Abstract – The synthesis of some cyclophanes bearing in the linear side-chain carbon-carbon triple bonds conjugated with thiophene rings has been reported. Structure analysis of the products based on extensive NMR investigation is presented. UV-Vis absorption spectra and fluorescence spectra have been measured. The analysis of the spectra points out a correlation between the maxima and the structure of the side-chain. The replacement of a benzene ring with a thiophene ring causes a bathochromic shift when the benzene ring close to the paracyclophane moiety is replaced.

INTRODUCTION

In continuation of our study in the synthesis of [2.2]paracyclophanes, recently we described a synthetic approach to novel cyclophanes containing conjugated acetylene triple bonds in the linear side-chain[1]. In the last decade there has been much attention focused in the arylethynyl molecular systems with extended π-conjugation due to their potential applications in the field of material science[2]. We have now extended the study to the [2.2]paracyclophane-based molecules containing thiophene rings in the side-chain since the insertion of such a heterocyclic ring gives higher electron delocalisation to the molecule[3]. Since the aryl units are separated by acetylenic triple bonds rotational variations do not affect the π-overlap and, hence, the conjugation.

This note reports the synthesis and physical properties of some novel [2.2]paracyclophanes bearing thiophene rings conjugated with ethynyl units in the side-chain.

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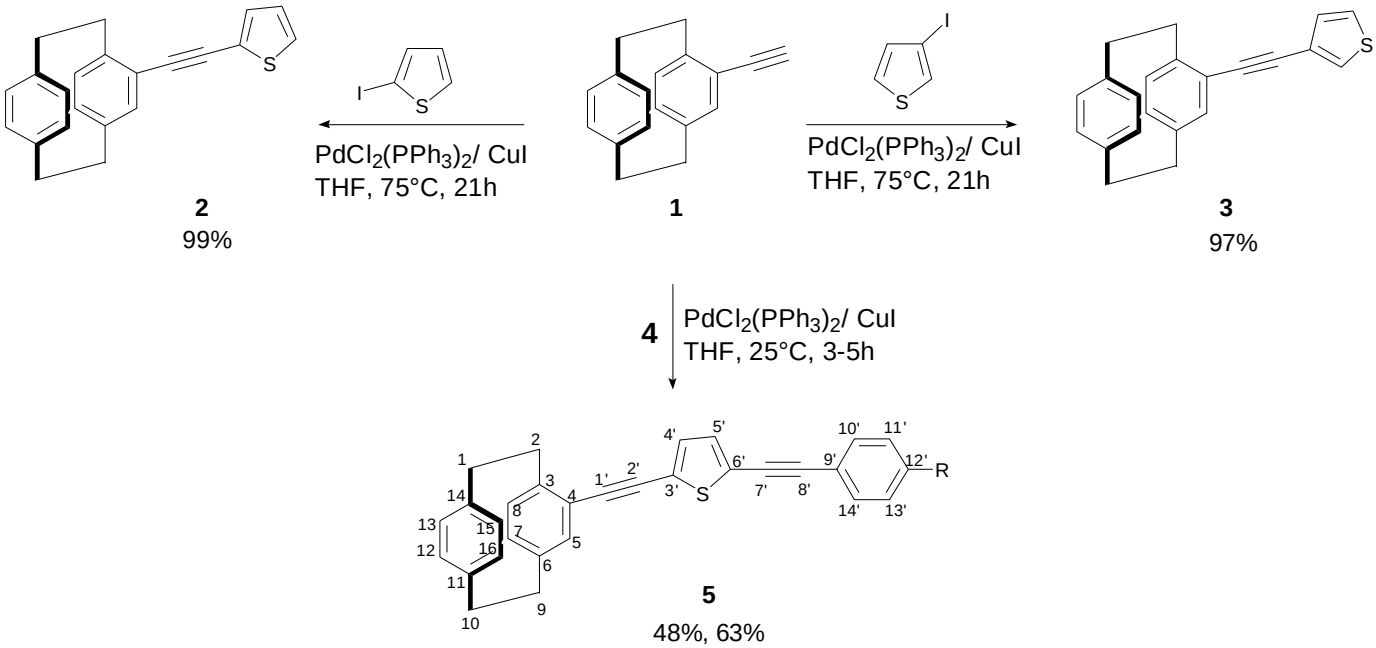
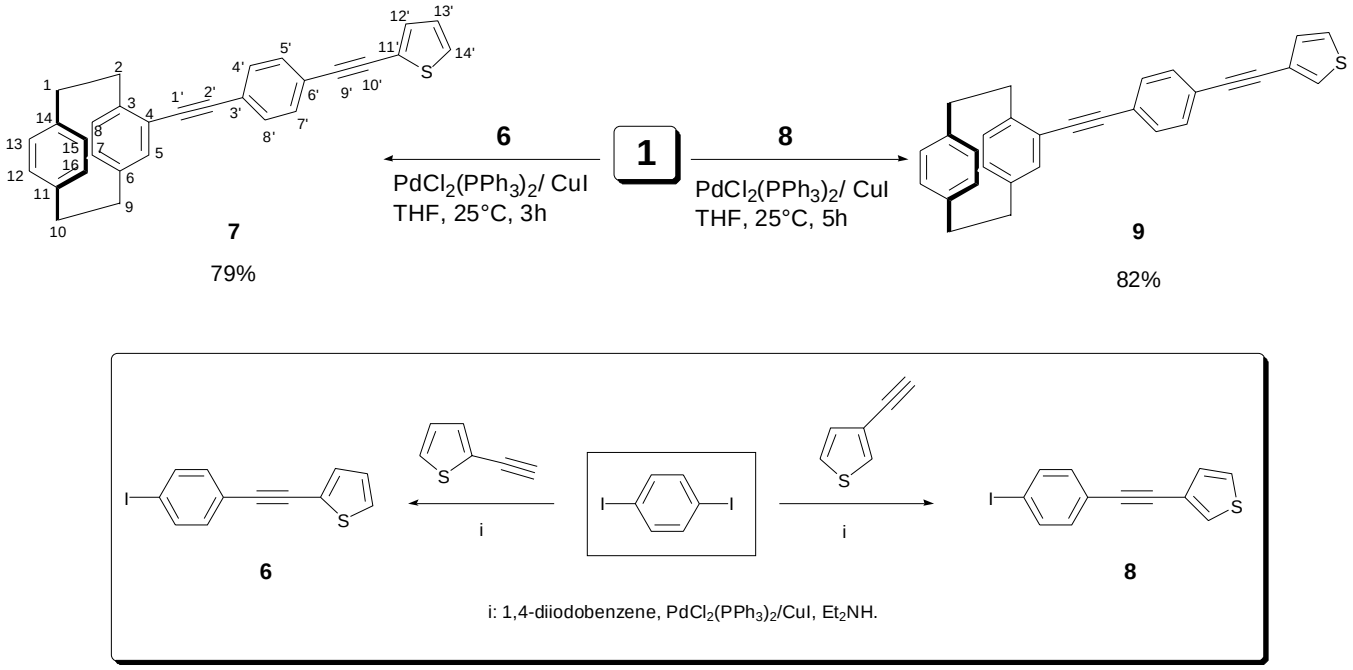
RESULTS AND DISCUSSION

The synthesis of the paracyclophanes was mainly based on the Pd/Cu catalysed Sonogashira cross coupling reaction[4] between 4-ethynyl[2.2]paracyclophane[1,5] (**1**) and the pertinent aryliodides. This methodology is known to be a powerful tool to synthesize arylethynyl systems.



Scheme 1

The couplings were carried out under argon atmosphere in dry tetrahydrofuran with $PdCl_2(PPh_3)_2$ as the catalyst, CuI as the co-catalyst, in the presence of triethylamine. Schemes 1 and 2 summarize the preparation of compounds (**2-9**).



Scheme 2

The structures of all products were assigned by analysis of their spectroscopic data, in particular by ^{1}H- and ^{13}C-NMR investigations, especially ^{1}H-{^{1}H}NOE experiments, HSQC and HMBC methods. In the case of the [2.2]paracyclophane derivatives (**2**), (**3**), (**5**), (**7**)**,** (**9**), the ^{1}H- and ^{13}C- chemical shifts of the paracyclophane moiety are practically the same; furthermore, as shown by an inspection of the pertinent data collected in the Experimental, a slight substituent effect of the methoxy-group can be observed in compound (**5b**), even on the carbons of the remote triple bond.

Two photophysical properties, UV-Vis absorption and fluorescence emission in chloroform, were also examined. In order to evaluate the effects of the thiophene rings on the optical properties, we have measured also the spectra of the previously described[1] compound (**10**) (Figure 1). The optical properties of the compounds (**2**), (**3**), (**5**), (**7**), (**9**), (**10**) are summarized in Table 1.

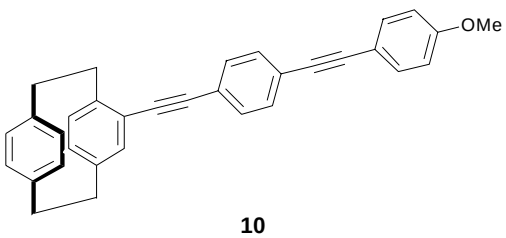


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Figure 1

Table 1. The absorption λ_{max} and fluorescence emission λ_{max} measured in $CHCl_3$ for compounds (**2**), (**3**), (**5**), (**7**), (**9**), (**10**)

Compound	UV-Vis λ_{max}, nm	log ε	Fluorescence λ_{max}, nm	Φ_f[a]
2	319	4.32	377	0.04
3	299	4.11	334	0.008
5a	356	4.46	397,419	0.27
5b	362	3.81	403,422	0.16
7	340	4.25	376,395	0.16
9	330	4.56	367,381	0.43
10	336	4.65	372,389	0.65

[a]Fluorescence quantum yield was determined relative to anthracene in ethanol.

All the UV-Vis spectra (Figure 2) were almost identical: there are two absorption bands, a weak one at 241-254 nm and a strong one at 299-362 nm. The bands are broad with little vibronic structure. The λ_{max} value of (**2**) is higher than that of (**3**) since 2-thienyl group allows a better conjugation. Moreover, the comparison of the data for compounds (**5b**), (**10**) and (**5a**), (**7**) indicates a bathochromic or an ipsochromic shift depending on the position of the thiophene ring in the side-chain.

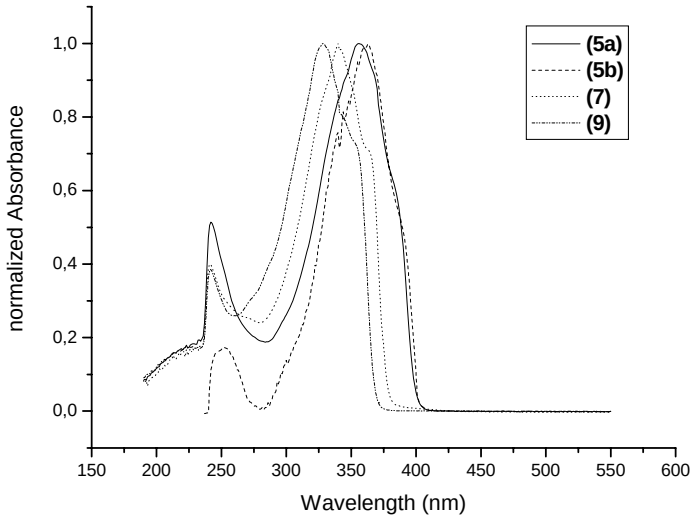

Figure 2- UV-Vis Absorption spectra of compounds (**5**), (**7**), (**9**) in $CHCl_3$

All of compounds show also fluorescence radiation emission; the wavelength and quantum yield are summarized in Table 1. Some considerations can be remarked. First the fluorescence maxima show a

dependence on the structure of the side-chain. A bathochromic effect is observed when a benzene ring close to the [2.2]paracyclophane moiety is replaced with a thiophene ring as pointed out by comparing maxima values of the methoxy-substituted compounds (**5b**), (**10**). This phenomenon, already evidenced in the UV-Vis spectra, can be rationalized considering that replacing benzenoid rings with easily delocalizable thiophene moieties favours a more extensive electron delocalization. Moreover both the absorption and fluorescence maxima depend on the position, α or β, of the thiophene ring linked to the triple bond as evidenced by the data reported in Table 1 for compounds (**2**), (**3**) and (**7**), (**9**). The quantum yields seem to depend on the chain length and presence of the thiophene rings in the side-chain.

CONCLUSIONS

In summary some new [2.2]paracyclophanes containing conjugated ethynylthienyl units in the linear side-chain have been prepared by Pd/Cu catalysed Sonogashira reaction and characterized. Their structure has been assigned by an extensive NMR (^{1}H and ^{13}C) analysis. Photophysical properties, i.e. UV-Vis and fluorescence, have been examined and discussed. The dependence of the UV-Vis and fluorescence maxima on the position of the thiophene ring in the side-chain has been observed. A bathochromic shift was observed when the thiophene unit in the side-chain was close to the [2.2]paracyclophane framework.

ACKNOWLEDGEMENT

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EXPERIMENTAL

General Methods. Melting points were determined on a Büchi melting point apparatus and are uncorrected. MS were recorded on a Hewlett Packard 6980 Series GC System /5973 Mass Selective Detector equipped with an EI ionizer at 70 eV. Adsorption chromatography was carried out on Riedel de Haën silica gel (32-63 μm; 230-400 mesh ASTM). UV-Vis spectra were recorded on a Kontron Uvikon 923 spectrophotometer. NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument (internal Me_4Si). Fluorescence spectra were recorded on a Spex Fluorolog-2 F112A1 spectrofluorimeter. Petroleum ether refers to 40°-60°C boiling fraction.

General procedure for the synthesis of compounds (**4**)**,** (**6**)**,** (**8**)**.** The procedure described for preparing (**4a**) is that used for preparing compounds (**4**)**,** (**6**)**,** (**8**).

2-Iodo-5-(phenylethynyl)thiophene (4a). Dry diethylamine (3 mL), 2,5-diiodothiophene (0.70 g, 2.1 mmol), CuI (0.0013 g, 0.007 mmol), $PdCl_2(PPh_3)_2$ (0.010 g, 0.014 mmol) and phenylacetylene (0.068 g, 0.67 mmol) were placed in a flask and degassed with Ar. The mixture was held at –20°C for 5 h and at 25°C for further 20 h. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel. Elution with pentane afforded pure **4a** as pale yellow crystals (67% yield). mp 83-84°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 6.93 (d, 1H, J = 3.8 Hz, H-4), 7.14 (d, 1H, J = 3.8 Hz, H-3), 7.35 (m, 3H, H-9, H-11, H-13), 7.49 (m, 2H, H-10, H-12). ^{13}C-NMR ($CDCl_3$): δ 74.8 (C-2), 81.6 (C-6), 95.1 (C-7), 122.8 (C-8), 128.8 (C-10, C-12), 128.9 (C-11), 129.8 (C-5), 131.7 (C-9, C-13), 133.3 (C-4), 137.3 (C-3). MS, m/e (rel. int.) 91 (6), 139 (45), 183 (8), 310 (M^+, 100). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 243 (3.92), 311 (4.23). Anal. Calcd for $C_{12}H_7IS$: C, 46.47; H, 2.27. Found: C, 46.40; H, 2.28%.

2-Iodo-5-[(*p*-methoxyphenyl)ethynyl]thiophene (4b). Purified by column chromatography on silica gel eluting with petroleum ether/chloroform 8:1; pale yellow plates (57% yield). mp 72-73°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 3.83 (s, 3H, OMe), 6.87 (m, 2H, H-10, H-12), 6.89 (d, 1H, J = 3.8 Hz, H-4), 7.13 (d, 1H, J = 3.8 Hz, H-3), 7.43 (m, 2H, H-9, H-13). ^{13}C-NMR ($CDCl_3$): δ 55.5 (OMe), 74.1 (C-2), 80.3 (C-6), 95.2 (C-7), 114.3 (C-9, C-10, C-12), 130.3 (C-5), 132.8 (C-4), 133.2 (C-13), 133.3 (C-8), 137.2 (C-3), 160.3 (C-11). MS, m/e (rel. int.) 126 (7), 169 (26), 213 (9), 325 (35), 340 (M^+, 100). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 250 (4.07), 320 (4.39). Anal. Calcd for $C_{13}H_9IOS$: C, 45.90; H, 2.67. Found: C, 45.85; H, 2.68%.

2-[(*p*-Iodophenyl)ethynyl]thiophene (6). Purified by column chromatography on silica gel eluting with pentane; white plates (60% yield). mp 105-106°C (MeOH) [lit.[6], 89-91°C, hexane]. ^{1}H-NMR ($CDCl_3$): δ 7.01 (dd, 1H, J =5.1, 3.6 Hz, H-4), 7.24 (m, 2H, H-9, H-13), 7.27 (dd, 1H, J =3.6, 1.2 Hz, H-3), 7.29 (dd, 1H, J =5.1, 1.2 Hz, H-5), 7.69 (m, 2H, H-10, H-12). ^{13}C-NMR ($CDCl_3$): δ 84.3 (C-6), 92.3 (C-11), 94.5 (C-7), 122.7 (C-8), 123.2 (C-2), 127.4 (C-5), 127.8 (C-4), 132.4 (C-3), 133.1 (C-9, C-13), 137.8 (C-10, C-12). MS, m/e (rel. int.) 91 (3), 139 (25), 183 (6), 310 (M^+, 100). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 261 (4.09), 309 (4.40). Anal. Calcd for $C_{12}H_7IS$: C, 46.47; H, 2.27. Found: C, 46.65; H, 2.26%.

3-[(*p*-Iodophenyl)ethynyl]thiophene (8). Purified by column chromatography on silica gel eluting with petroleum ether/dichloromethane 24:1; white plates (62% yield). mp 139-140°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 7.18 (dd, 1H, J = 5.0, 1.2 Hz, H-4), 7.23 (m, 2H, H-9, H-13), 7.30 (dd, 1H, J = 5.0, 3.0 Hz, H-5), 7.53 (dd, 1H, J = 3.0, 1.2 Hz, H-2), 7.67 (m, 2H, H-10, H-12). ^{13}C-NMR ($CDCl_3$): δ 86.2 (C-6), 88.2 (C-11), 94.2 (C-7), 122.2 (C-3), 123.0 (C-8), 125.7 (C-5), 129.1 (C-2), 130.1 (C-4), 133.2 (C-9, C-13), 137.8 (C-10, C-12). MS, m/e (rel. int) 91 (4), 139 (30), 183 (6), 310 (M^+, 100). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 292 (4.36), 309 (4.30). Anal. Calcd for $C_{12}H_7IS$: C, 46.47; H, 2.27. Found: C, 46.40; H, 2.27%.

General procedure for the Sonogashira coupling reaction of 4-ethynyl[2.2]paracyclophane (1). The following discussion of the reaction of **4a** with 4-ethynyl[2.2]paracyclophane (**1**) is a typical procedure used for all coupling reactions.

3'-{[2.2]Paracyclophan-4-ylethynyl}-6'-[phenylethynyl]thiophene (5a). Dry THF (3 mL), 4-ethynyl[2.2]paracyclophane (**1**) (0.094 g, 0.57 mmol), triphenylphosphine (0.010 g, 0.04 mmol), CuI (0.004 g, 0.02 mmol), aryliodide (**4a**) (0.084g, 0.27 mmol), $PdCl_2(PPh_3)_2$ (0.014 g, 0.02 mmol) and dry triethylamine (1.3 mL) were placed in a flask and degassed with Ar. The mixture was kept at 25°C for 3h. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel (elution: petroleum ether/chloroform 24:1) to obtain **5a** as pale yellow crystals (48% yield). mp 145-146°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 2.90 (ddd, 1H, J = 13.1, 10.2, 5.3 Hz, H-2), 2.96-3.16 (m, 5H, H-1, H_s-9, H_s-10), 3.23 (m, 1H, H-1), 3.59 (ddd, 1H, J = 13.1, 10.2, 2.8 Hz, H-2), 6.47-6.53 (m, 5H, H-7, H-8, H-12, H-13, H-16), 6.57 (d, 1H, J = 1.8 Hz, H-5), 6.97 (dd, 1H, J = 7.8, 1.9 Hz, H-15), 7.17 (d, 1H, J = 3.8 Hz, H-4' or H-5'), 7.19 (d, 1H, J = 3.8 Hz, H-4' or H-5'), 7.36 (m, 2H, H-11', H-13'), 7.37 (m, 1H, H-12'), 7.53 (m, 2H, H-10', H-14'). ^{13}C-NMR ($CDCl_3$): δ 34.6 (C-1), 34.8 (C-2), 35.4, 35.7 (C-9, C-10), 82.6, 85.8 (C-2', C-7'), 94.3, 94.9 (C-1', C-8'), 122.9 (C-9'), 124.5, 124.7 (C-3', C-6'), 125.5 (C-4), 128.6 (C-11', C-13'), 128.8 (C-12'), 130.4 (C-15), 131.4, 132.1 (C-4', C-5'), 131.7 (C-10', C-14'), 132.7, 132.9, 133.5 (C-12, C-13, C-16), 133.4 (C-7), 134.2 (C-8), 137.0 (C-5), 139.5 (C-11), 139.6 (C-14), 140.1 (C-6), 142.8 (C-3). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 242 (4.14), 356 (4.46). Anal. Calcd for $C_{30}H_{22}S$: C, 86.92; H, 5.35. Found: C, 86.98; H, 5.34%.

3'-{[2.2]Paracyclophan-4-ylethynyl}-thiophene (2). Reaction temperature: 75°C; reaction time: 21 h. Purified by column chromatography on silica gel eluting with petroleum ether/chloroform 4:1; white plates (99%). mp 122-123°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 2.88 (ddd, 1H, J = 13.1, 10.3, 5.5 Hz, H-2), 2.90-3.15 (m, 5H, H-1, H_s-9, H_s-10), 3.24 (ddd, 1H, J = 13.2, 10.2, 5.3 Hz, H-1), 3.61 (ddd, 1H, J = 13.1, 10.3, 2.6 Hz, H-2), 6.48 (d, 1H, J = 7.9 Hz, H-8), 6.50-6.54 (m, 4H, H-7, H-12, H-13, H-16), 6.56 (d, 1H, J = 1.7 Hz, H-5), 7.00 (dd, 1H, J = 7.8, 1.8 Hz, H-15), 7.05 (dd, 1H, J = 4.9, 3.9 Hz, H-5'), 7.31 (dd, 1H, J = 4.9, 1.1 Hz, H-6'), 7.32 (dd, 1H, J = 3.9, 1.1 Hz, H-4'). ^{13}C-NMR ($CDCl_3$): δ 34.6 (C-1), 34.8 (C-2), 35.4, 35.7 (C-9, C-10), 86.2 (C-2'), 93.7 (C-1'), 124.2 (C-3'), 124.8 (C-4), 127.2 (C-6'), 127.4 (C-5'), 130.4 (C-15), 131.6 (C-4'), 132.7 (C-12), 132.9 (C-16), 133.2 (C-7), 133.5 (C-13), 134.2 (C-8), 137.0 (C-5), 139.6 (C-11), 139.7 (C-14), 140.0 (C-6), 142.7 (C-3). UV-Vis ($CHCl_3$) [λ_{max} nm (logε)] 244 (4.19), 319 (4.32). Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77. Found: C, 84.10; H, 5.78%.

4'-{[2.2]Paracyclophan-4-ylethynyl}-thiophene (3). Reaction temperature: 75°C; reaction time: 21 h. Purified by column chromatography on silica gel eluting with petroleum ether/chloroform 4:1; white plates (97%). mp 143-144°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 2.88 (ddd, 1H, J = 13.1, 10.4, 5.3 Hz, H-2), 2.92-3.15 (m, 5H, H-1, H_s-9, H_s-10), 3.25 (ddd, 1H, J = 13.1, 10.2, 5.4 Hz, H-1), 3.63 (ddd, 1H, J = 13.1, 10.3, 2.7 Hz, H-2), 6.49-6.53 (m, 5H, H-7, H-8, H-12, H-13, H-16), 6.58 (d, 1H, J = 1.8 Hz, H-5), 7.02 (dd, 1H, J = 7.8, 1.8 Hz, H-15), 7.27 (dd, 1H, J = 5.0, 3.0 Hz, H-5'), 7.35 (dd, 1H, J = 5.0, 1.2 Hz, H-6'), 7.55 (dd, 1H, J = 3.0, 1.2 Hz, H-3'). ^{13}C-NMR ($CDCl_3$): δ 34.6 (C-1), 34.8 (C-2), 35.4, 35.7 (C-9, C-10),

88.1 (C-2'), 89.4 (C-1'), 123.1 (C-4'), 125.1 (C-4), 125.7 (C-6'), 128.2 (C-3'), 130.2 (C-5'), 130.3 (C-15), 132.7 (C-12), 133.0 (C-7, C-16), 133.5 (C-13), 134.1 (C-8), 137.2 (C-5), 139.6 (C-11), 139.8 (C-14), 140.0 (C-6), 142.6 (C-3). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 241 (4.05), 299 (4.11). Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77. Found: C, 84.15; H, 5.74%.

3'-{[2.2]Paracyclophan-4-ylethynyl}-6'-[(*p*-methoxyphenyl)ethynyl]thiophene (5b). Reaction temperature: 25°C; reaction time: 5 h. Purified by column chromatography on silica gel eluting with petroleum ether/chloroform 4:1; pale yellow plates (63%). mp 142-143°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 2.90 (ddd, 1H, J = 13.1, 10.3, 5.2 Hz, H-2), 2.95-3.16 (m, 5H, H-1, H_s-9, H_s-10), 3.23 (m, 1H, H-1), 3.59 (ddd, 1H, J = 13.1, 10.2, 2.7 Hz, H-2), 3.84 (s, 3H, OMe), 6.47 (d, 1H, J = 7.9 Hz, H-8), 6.49-6.54 (m, 4H, H-7, H-12, H-13, H-16), 6.57 (d, 1H, J = 1.9 Hz, H-5), 6.87 (m, 2H, H-11', H-13'), 6.97 (dd, 1H, J = 7.8, 1.8 Hz, H-15), 7.14 (d, 1H, J = 3.8 Hz, H-4' or H-5'), 7.16 (d, 1H, J = 3.8 Hz, H-4' or H-5'), 7.47 (m, 2H, H-10', H-14'). ^{13}C-NMR ($CDCl_3$): δ 34.6 (C-1), 34.8 (C-2), 35.4, 35.7 (C-9, C-10), 55.5 (OMe), 81.3, 85.9 (C-2', C-7'), 94.4, 94.6 (C-1', C-8'), 114.4 (C-11', C-13'), 115.0 (C-9'), 124.5 (C-3'), 125.0 (C-6'), 125.2 (C-4), 130.4 (C-15), 131.4, 131.6 (C-4', C-5'), 132.7, 132.9, 133.5 (C-12, C-13, C-16), 133.3 (C-10', C-14'), 133.4 (C-7), 134.2 (C-8), 137.0 (C-5), 139.5 (C-11), 139.6 (C-14), 140.0 (C-6), 142.8 (C-3), 160.2 (C-12'). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 254 (2.99), 362 (3.81). Anal. Calcd for $C_{31}H_{24}OS$: C, 83.75; H, 5.44. Found: C, 83.68; H, 5.43%.

11'-{[*p*-([2.2]Paracyclophan-4-ylethynyl)phenyl]ethynyl}thiophene (7). Reaction temperature: 25°C; reaction time: 3h. Purified by column chromatography on silica gel eluting with petroleum ether/chloroform 8:1; pale yellow plates (79%). mp 170-171°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 2.91 (ddd, 1H, J = 13.1, 10.5, 5.4 Hz, H-2), 2.87-3.16 (m, 5H, H-1, H_s-9, H_s-10), 3.26 (m, 1H, H-1), 3.65 (ddd, 1H, J = 13.1, 10.3, 2.8 Hz, H-2), 6.49 (dd, 1H, J = 7.8, 1.8 Hz, H-16), 6.49-6.53 (m, 2H, H-12, H-13), 6.50-6.54 (m, 2H, H-7, H-8), 6.59 (d, 1H, J = 1.8 Hz, H-5), 6.99 (dd, 1H, J = 7.8, 1.8 Hz, H-15), 7.02 (dd, 1H, J = 5.0, 3.8 Hz, H-13'), 7.29 (dd, 1H, J = 5.0, 1.2 Hz, H-14'), 7.31 (dd, 1H, J = 3.8, 1.2 Hz, H-12'), 7.51-7.56 (m, 4H, H-4', H-5', H-7', H-8'). ^{13}C-NMR ($CDCl_3$): δ 34.6, 34.7 (C-1, C-2), 35.4, 35.7 (C-9, C-10), 84.7 (C-10'), 92.1 (C-1'), 92.8 (C-2'), 93.1 (C-9'), 122.8, 123.4 (C-3', C-6'), 124.1 (C-11'), 124.8 (C-4), 127.3 (C-14'), 127.7 (C-13'), 130.4 (C-15), 131.6 (C-4', C-5', C-7', C-8'), 132.3 (C-12'), 132.7, 132.9 (C-12, C-16), 133.2 (C-7), 133.5 (C-13), 134.1 (C-8), 137.2 (C-5), 139.6, 139.7, 140.0 (C-6 , C-11, C-14), 142.8 (C-3). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 241 (4.17), 340 (4.25). Anal. Calcd for $C_{30}H_{22}S$: C, 86.92; H, 5.35. Found: C, 86.70; H, 5.35%.

12'-{[*p*-([2.2]Paracyclophan-4-ylethynyl)phenyl]ethynyl}thiophene (9). Reaction temperature: 25°C; reaction time: 5h. Purified by column chromatography on silica gel eluting with petroleum ether/chloroform 6:1; white plates (82%). mp 176-177°C (MeOH). ^{1}H-NMR ($CDCl_3$): δ 2.91 (ddd, 1H, J = 13.2, 10.5, 5.5 Hz, H-2), 2.96-3.16 (m, 5H, H-1, H_s-9, H_s-10), 3.25 (m, 1H, H-1), 3.66 (ddd, 1H, J =

13.2, 10.2, 2.7 Hz, H-2), 6.49 (dd, 1H, *J* = 7.8, 1.8 Hz, H-16), 6.49-6.53 (m, 4H, H-7, H-8, H-12, H-13), 6.59 (d, 1H, *J* = 1.8 Hz, H-5), 7.00 (dd, 1H, *J* = 7.8, 1.8 Hz, H-15), 7.22 (dd, 1H, *J* = 5.0, 1.2 Hz, H-13'), 7.33 (dd, 1H, *J* = 5.0, 3.0 Hz, H-14'), 7.51-7.57 (m, 5H, H-4', H-5', H-7', H-8', H-11'). ^{13}C-NMR ($CDCl_3$): δ 34.6, 34.8 (C-1, C-2), 35.4, 35.7 (C-9, C-10), 86.6 (C-10'), 89.0, 91.9 (C-1', C-9'), 92.8 (C-2'), 122.4 (C-12'), 123.1, 123.8 (C-3', C-6'), 124.8 (C-4), 125.7 (C-14'), 129.1 (C-11'), 130.1 (C-13'), 130.4 (C-15), 131.6, 131.7 (C-4', C-5', C-7', C-8'), 132.7, 133.0 (C-12, C-16), 133.2 (C-7), 133.5 (C-13), 134.2 (C-8), 137.3 (C-5), 139.6, 139.7, 140.0 (C-6 , C-11, C-14), 142.8 (C-3). UV-Vis ($CHCl_3$): [λ_{max} nm (logε)] 241 (4.17), 330 (4.56). Anal. Calcd for $C_{30}H_{22}S$: C, 86.92; H, 5.35. Found: C, 86.50; H, 5.36%.

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