Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information for

Orthogonal electron coupling in multicentre arylamine mixed-valence compounds based on a dibenzofulvene-thiophene conjugated bridge

A. Beneduci,[a]* G. A. Corrente,[b] E. Fabiano,[c,d] V. Maltese,[a] S. Cospito,[a] G. Ciccarella,[e] G. Chidichimo,[a] G. Gigli,[f] A.-L. Capodilupo,[f]*

[a]Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 15D, 87036 Arcavacata di Rende (CS), Italy. Email: amerigo.beneduci@unical.it

[b]Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via Monteroni, 73100, Lecce, Italy

[c]Institute for Microelectronics and Microsystems (CNR-IMM), Via Monteroni, Campus Unisalento, 73100 Lecce, Italy

[d]Centre for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia (IIT), Via Barsanti, 73010 Arnesano (LE), Italy

[e]Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento & UdR INSTM di Lecce, c/o edificio "Stecca", via Monteroni, 73100 Lecce, Italy

[f]CNR NANOTEC, Institute of Nanotechnology, c/o Campus Ecotekne, University of Salento, via Monteroni, 73100 Lecce, Italy. Email: agostina.capodilupo@nanotec.cnr.it

Contents:

1. Materials and Methods

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. Flash chromatography was carried out by using silica gel (40–63 mm, Merck). Analytical TLC was performed on Merck silica gel plates. The melting point was taken on Kleinfeld Melting Point Determination Apparatus APA I. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer and performed in $CDCl_3$ ($\delta = 7.26$ ppm), in DMSO-d_6 ($\delta = 2.50$ ppm). ^{13}C NMR spectra were performed in $CDCl_3$ ($\delta = 77.16$ ppm) DMSO-d_6 ($\delta = 39.52$ ppm) solutions. Chemical shifts (δ) are given in part per million (ppm). Coupling constants J are reported in Hz. The signals are described as singlet (s), doublet (d), doublet of doublets (dd). LC-MS spectra were acquired with an Agilent 6300 Series Ion Trap interfaced to an Agilent 1200 HPLC, in the following general conditions: atmospheric pressure chemical ionization, positive ions, eluent chloroform, flow rate 0.200 mL min^{-}1, drying gas flow 5.0 l min^{-}1, nebulizer pressure 60 psi, drying gas temperature 350 °C, vaporizer temperature 325 °C, mass range 100-2200 m/z. Microwave synthesis were performed with a CEM Discover Labmate reactor. Elemental analyses were done by a Carlo Erba CHNS-O EA1108-Elemental Analyzer. Electrochemical characterization of dyes was carried out by cyclic voltammetry (CV) using a AMEL s.r.l. (Mod. 7050) potentiostat. A typical three-electrode cell was assembled with a glassy carbon disk-working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl non-aqueous reference electrode. Cyclic voltammograms were acquired at 0.05 V s^{-1} scan rate on 1 mM dye solutions prepared in the electrolyte solution, which consisted of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane (CH_2Cl_2). All the solutions were previously degassed with N_2. The CV of the Ferrocenium/Ferrocene (Fc^+/Fc) couple (0.1 mM) was also recorded in the same condition used for the MV compounds solutions and used as external reference for potential calibration. Spectroelectrochemical experiments were performed with an electrolytic cell (BAS Inc.) composed of a 1 mm path length cuvette, where a platinum gauze thin layer and a platinum wire were used as the working electrode and the auxiliary electrode, respectively.[1,2] A pseudo-reference electrode consisting of an Ag wire was calibrated against the Fc^+/Fc redox couple. The spectroelectrochemical cell was filled with dichloromethane solutions of each compound (0.1-1 mM) and $TBAPF_6$ (0.1 M). UV-vis-NIR spectra were recorded using a Vertex 80 (Bruker) spectrophotometer. The potential was supplied by means of an Amel 2049 model potentiostat. Measurements were performed at 25 °C.

2. Cyclic voltammetry of the mixed valence compounds H1, H2, T1, and T2

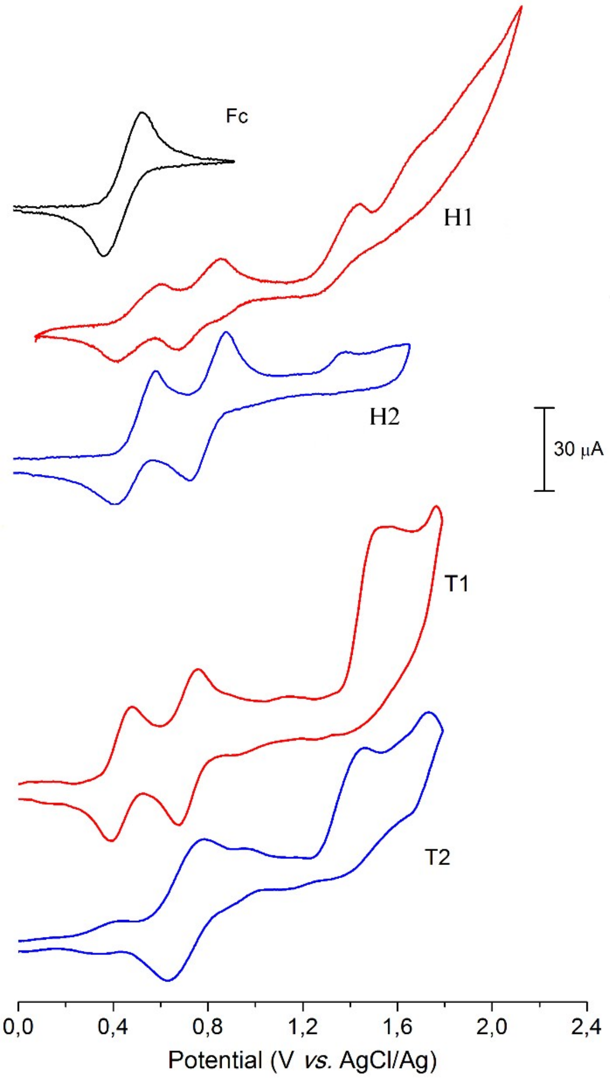


Figure S1. CVs of Ferrocene and dibenzofulvene derivatives in CH_2Cl_2/$TBAPF_6$ (0.1 M) at ambient temperature, scan rate of 50 mV/s.

3. Computational details

The molecular geometries have been optimized at the APBE-D3/def2-TZVP[3] level of theory. Ground- and excited-state properties have been computed using the PBE0-1/3 functional[4] and a def2-TZVP[1c] basis set. All calculations have been performed using the TURBOMOLE program.[5,6]

Table S1. TD-DFT calculated excitation wavelengths, oscillator strengths (o.s) and band assignment of the lowest-lying optically excited states of the

H1, **H2**, **T1**, and **T2** molecules

	Wavelength (nm)	o.s.	Character
H1	529	0.604	ππ*
	389	0.713	ππ*
H1 1+	2028	0.185	IVCT
	785	0.137	IVCT
	598	0.153	NBCT
	523	0.605	ππ*
	385	0.321	ππ*
H1 2+	1797	0.101	IVCT
	780	0.204	IVCT
	667	0.260	IVCT
	590	0.104	NBCT
	520	0.61	ππ*
H2	611	0.69	ππ*
	547	0.27	NBCT
H2 1+	1205	0.18	IVCT
	867	0.13	NBCT
	650	0.53	ππ*
	535	0.26	NBCT
H2 2+	1292	0.13	IVCT
	810	0.43	NBCT
	743	0.19	
	564	0.14	NBCT
T1	611	0.05	NBCT
	391	0.67	ππ*
T1 1+	1363	0.67	CT
	633	0.15	CT
	582	0.09	NBCT
	418	0.22	ππ*
T1 2+	785	0.30	CT
	751	0.13	CT
	605	0.08	NBCT
	521	0.21	ππ*
T2	596	0.23	NBCT
	504	0.14	NBCT
	367	0.38	ππ*
T2 1+	1107	0.59	CT
	681	0.51	CT

	585	0.24	NBCT
	380	0.72	ππ*
T2 2+	1016	0.31	CT
	681	0.34	CT
	494	0.64	NBCT
	380	0.53	ππ*

CT=charge-transfer, IVCT=inter-valence-CT, NBCT=amine-to-bridge-CT

4. IVCT bandshape analysis

The bandshape analysis of the low energy NIR bands, is summarized in Table S2. The NIR bands of the 2,7-substituted systems are evidently asymmetric (Figure 2 and Figure S2). This asymmetry is common for class III mixed valence systems or for systems at the class II/III borderline.[7,8] Table S2 shows that the bandwidth at half eight of the high energy side for **H1** and **T1** is narrower than that predicted by Hush for weakly interacting centres (class-II compounds) $\Delta \bar{\nu}_{1/2}$ (equation S1), which is consistent with strongly coupled MVs.

$$\Delta \bar{\nu}_{1/2} = 47.94\sqrt{\nu_{\max}} \qquad \text{(S1)}$$

The asymmetry, estimated by the ratio between the bandwidth at half eight of the high energy side ($\bar{\nu}_{1/2}^{high}$) and that of the low energy sides ($\bar{\nu}_{1/2}^{low}$), is larger for **T1** (Table S2).

Table S2. IVCT band shape data

MV	$\bar{\nu}_{\max}$ (cm^{-1})	$\bar{\nu}_{1/2}^{obs}$ (cm^{-1})	$^{a}\,\bar{\nu}_{1/2}^{HTL}$ (cm^{-1})	$^{b}\,\bar{\nu}_{1/2}^{high}$ (cm^{-1})	$^{b}\,\bar{\nu}_{1/2}^{low}$ (cm^{-1})	$\bar{\nu}_{1/2}^{high} / \bar{\nu}_{1/2}^{low}$
H1	6759	3595	4036	4280	3792	1.13
H2	7562		4184		3655	
T1	6812	3151	3964	3654	2754	1.33
T2	7151		4044		2350	

[a] Calculated with equation S1; [b] Calculated as twice the measured value

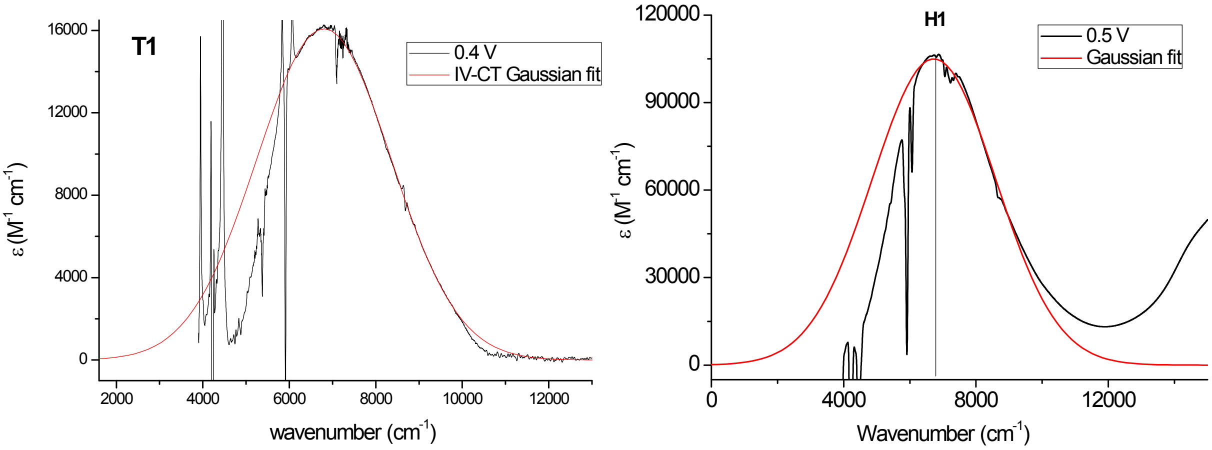


Figure S2. IVCT band fitting on the high energy side with a single Gaussian function for the 2,7-derivatives **T1** (left panel) and **H1** (right panel).

Due to the apparent band asymmetry, the IVCT bands of **T1** and **H1** were well fitted with a single Gaussian function on the high energy side.[5] The fitted curve has been extended to the low energy side in order to highlight the narrowing of the IVCT band as predicted by Hush (Figure S2).

The same bandshape analysis was hampered in the 3,6-substituted derivatives due to the sever overlap between the IVCT band with the other NIR bands occurring at higher energy in the spectrum (Figures S3).

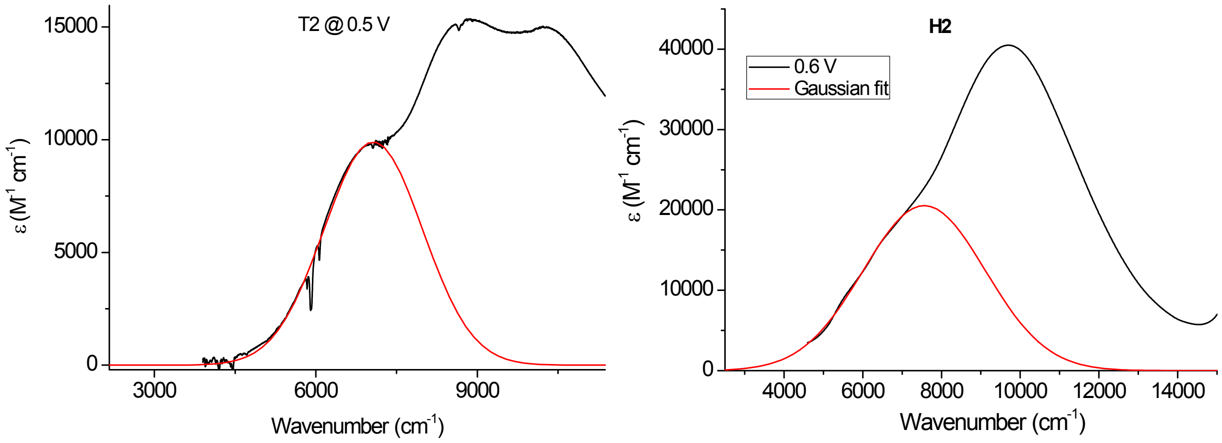


Figure S3. IVCT band fitting on the low energy side with a single Gaussian function for the 2,7-derivatives **T2** (left panel) and **H2** (right panel).

Nevertheless, information can be anyhow gained by simulating the IVCT bands with a symmetric Gaussian-shaped curve. In such a way, the value of the bandwidth of the low energy side can be calculated.[5] This analysis results in a very narrow $\bar{\nu}_{1/2}^{low}$ for **T2** and **H2** compared to the limit determined by equation S2 ($\Delta\bar{\nu}_{1/2}$) (Table S2), which proves that their IVCT bands are highly asymmetric and a strong electronic coupling occurs.

The electronic coupling integral V was determined from the shape of the IVCT band and its maximum using the equation:[7]

$$V = \frac{\mu_{eg}}{er}\bar{\nu}_{\max} \tag{S2}$$

where, r is the geometrical distance between the amine redox centres calculated from TD-DFT analysis and μ_{eg} is the transition dipole moment calculated from the integrated absorbance of the IVCT band (Table S3):[7]

$$\mu_{eg} = 0.09584\sqrt{\frac{\varepsilon(\bar{\nu})d\bar{\nu}}{\bar{\nu}_{\max}}} \tag{S3}$$

The coupling integral was also calculated with equation S4 that holds in the case of class III systems (Table S2):

$$V = \frac{\bar{\nu}_{\max}}{2} \tag{S4}$$

Table S2. Hush coupling energy

MV	$\bar{\nu}_{\max}$ (cm^{-1})	μ_{eg} (D)	r (Å) vertical; orizonthal	^{a}V (cm^{-1})	^{b}V (cm^{-1})
H1	6759	9.7	9.7; 10	1480	3380
H2	7618	7.6	7.9; 15	1519	3781
T1	6812	9.2	9.7	1341	3406
T2	7151	9.6	7.9	1623	3576

^{a}Calculated with equation S2; ^{b}Calculated with equation S4

The values of V obtained from equation S2 are smaller by a factor of 0.4-0.5 than those obtained with equation S4. This discrepancy is due to the use of r as the geometrical N-N distance in equation S2 which is larger (about 2 times) than the true diabatic electron transfer distance between the redox centers.[9]

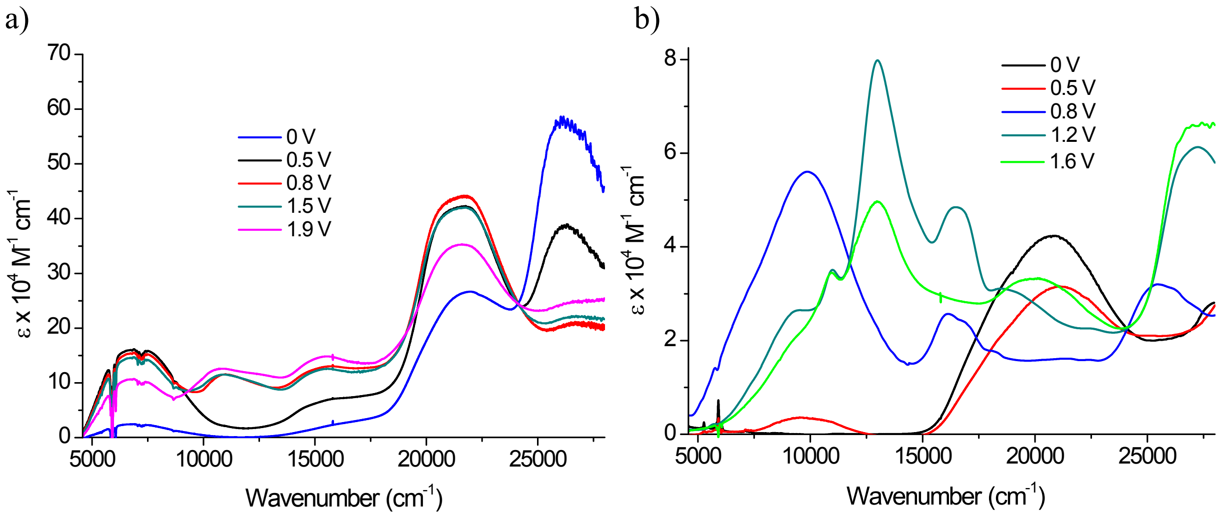
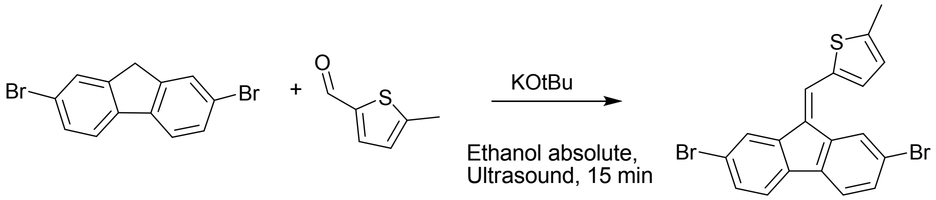


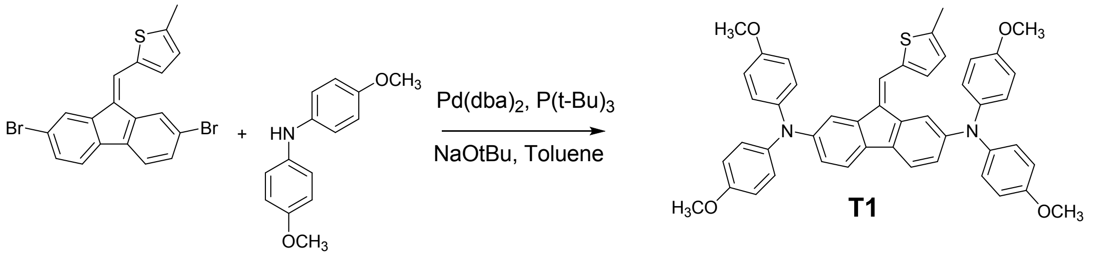
Figure S4. Spectroelectrochemistry of **H1** a) and **H2** b) up to the fourth oxidation wave.

5. Synthesis and characterization



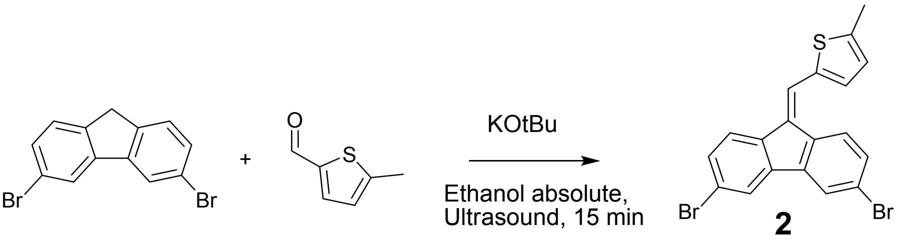
1

Synthesis of 2-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-5-methylthiophene (1):
2,7-dibromo-9H-fluorene (1.00 g, 3.0 mmol), 5-methylthiophene-2-carbaldehyde (0.390 g, 3.1 mmol) and potassium *tert*-butoxide (0.520 g, 4.65 mmol) were dissolved in 10 mL of ethanol absolute. The reaction was carried out in a ultrasound bath for 15 minutes. The precipitate obtained was filtered-off and washed different times with ethanol to remove the reagents. Was obtained 1.2 g of 2-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-5-methylthiophene as orange solid in 90% yield. Mp: 135.7-137.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.50 (d, $J = 1.6$ Hz, 1H), 7.82 (d, $J = 1.6$ Hz, 1H), 7.55 (d, $J = 8.1$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 1H), 7.49-7.44 (m, 2H), 7.31 (d, $J = 3.5$ Hz, 1H) 6.85 (d, $J = 3.3$ Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.17, 141.75, 138.59, 137.48, 136.18, 135.89, 131.76, 131.47, 131.07, 130.50, 126.94, 126.17, 123.09, 122.06, 120.91, 120.78, 120.70, 15.52. MS (APCI): calcd. for $C_{19}H_{12}Br_2S$: 432.17, found 433.32 $[M+H]^+$. $C_{19}H_{12}Br_2S$. Elemental Analysis. Calc. C, 52.81; H, 2.80; S, 7.42. Found. C, 52.88; H, 2.91; S, 7.38.



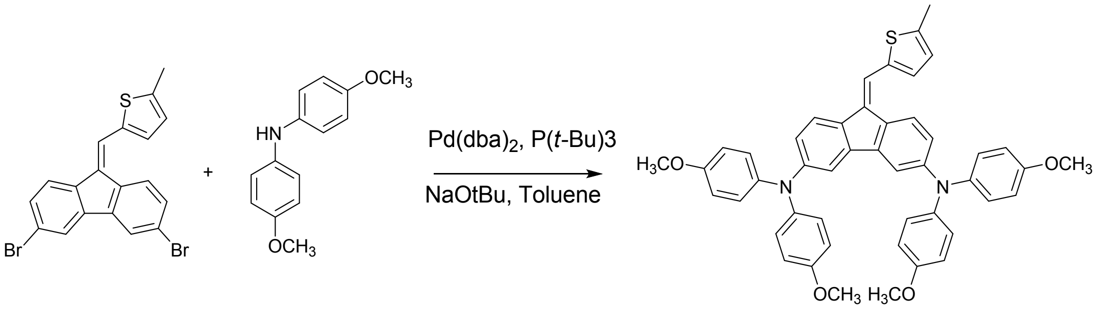
Synthesis of N2,N2,N7,N7-tetrakis(4-methoxyphenyl)-9-((5-methylthiophen-2-yl)methylene)-9H-fluorene-2,7-diamine (T1): A mixture of **1** (0.20 g, 0.46 mmol), bis(4-methoxyphenyl)amine (0.233 g, 1.02 mmol), sodium *tert*-butoxide (0.118 g,1.23 mmol), was added to a suspension of Pd(dba)$_2$ (0.013 g, 0.023 mmol), and P*t*Bu$_3$ (0.057 mmol, 1M in toluene) in anhydrous and deoxygenated toluene (5 mL), previous degassed under argon for 20 minutes. The resulting solution was heated under microwave irradiation at a constant temperature of 110°C for 50 min. The solvent was removed, and the residue was dissolved in dichloromethane and filtered on a short celite column.

After concentration by rotary evaporation, the crude product was purified by column chromatography on silica gel (eluent 8/2 hexane/CH_2Cl_2) to give a violet solid in 95% yield. Mp: 159.3-161.3. ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm) 7.86 (d, J = 2.1 Hz, 1H), 7.52-7.43 (m, 3H), 7.39 (d, J = 1.9 Hz, 1H) 7.10 (d, J = 3.7 Hz, 1H), 7.04 (d, J = 9.0 Hz, 4H), 6.95-6.92 (m, 8H), 6.87 (d, J = 9.1 Hz, 4H), 6.82 (dd, J_1 = 2.1 Hz, J_2 = 8.3 Hz, 1H), 6.77 (dd, J_1 = 2.0 Hz, J_2 = 8.2 Hz, 1H), 6.61 (d, J = 3.5 Hz, 1H), 3.74 (s, 6H), 3.72 (s, 6H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ (ppm) 155.95, 155.31, 147.81, 146.93, 142.94, 141.42, 141.01, 140.54, 136.50, 136.20, 133.16, 132.69, 127.12, 126.30, 1.25.41, 123.12, 120.71, 120.00, 119.92, 119.85, 118.36, 116.19, 115.30, 114.84, 114.76, 99.39, 55.53, 15.10. MS (APCI): calcd. for $C_{47}H_{40}N_2O_4S$: 728.27, found: 729.62 [M+H]$^+$. $C_{47}H_{40}N_2O_4S$. Elemental Analysis. Calc. C, 77.45; H, 5.53; N, 3.84; O, 8.78; S, 4.40. Found. C, 77.39; H, 5.61; N, 3.81; S, 4.44.



Synthesis of 2-((3,6-dibromo-9H-fluoren-9-ylidene)methyl)-5-methylthiophene (2): This compound (yellow solid) was prepared from 3,6-dibromo-9H-fluorene and 5-methylthiophene-2-carbaldehyde in 90% yield, using the similar procedure for the synthesis 2-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-5-methylthiophene. Mp: 130.1-132.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (d, J = 8.4 Hz, 1H), 7.81 (dd, J_1 = 2.2 Hz, J_2 = 8.9 Hz, 2H), 7.58 (d, J = 8.3 Hz, 1H), 7.57 (s, 1H), 7.44 (dd, J_1 = 1.8 Hz, J_2 = 8.3 Hz, 1H), 7.37 (dd, J_1 = 1.8 Hz, J_2 = 8.3, 1H), 7.25 (d, J = 3.5 Hz, 1H), 6.82 (d, J = 3.5 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.57, 141.30, 138.82, 138.68, 136.19, 134.77, 132.38, 130.92, 130.07, 129.93, 126.03, 125.34, 123.00, 122.79, 122.30, 121.64, 124.21, 121.00, 15.49.

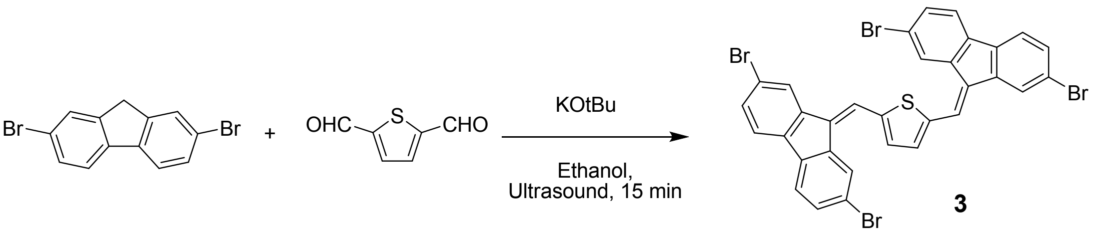
MS (APCI): calcd. for $C_{47}H_{40}N_2O_4S$: 432.17. found 433.40 $[M+H]^+$ $C_{19}H_{12}Br_2S$. Elemental Analysis. Calc. C, 52.81; H, 2.80; S, 7.42. Found. C, 52.77; H, 2.93; S, 7.39.



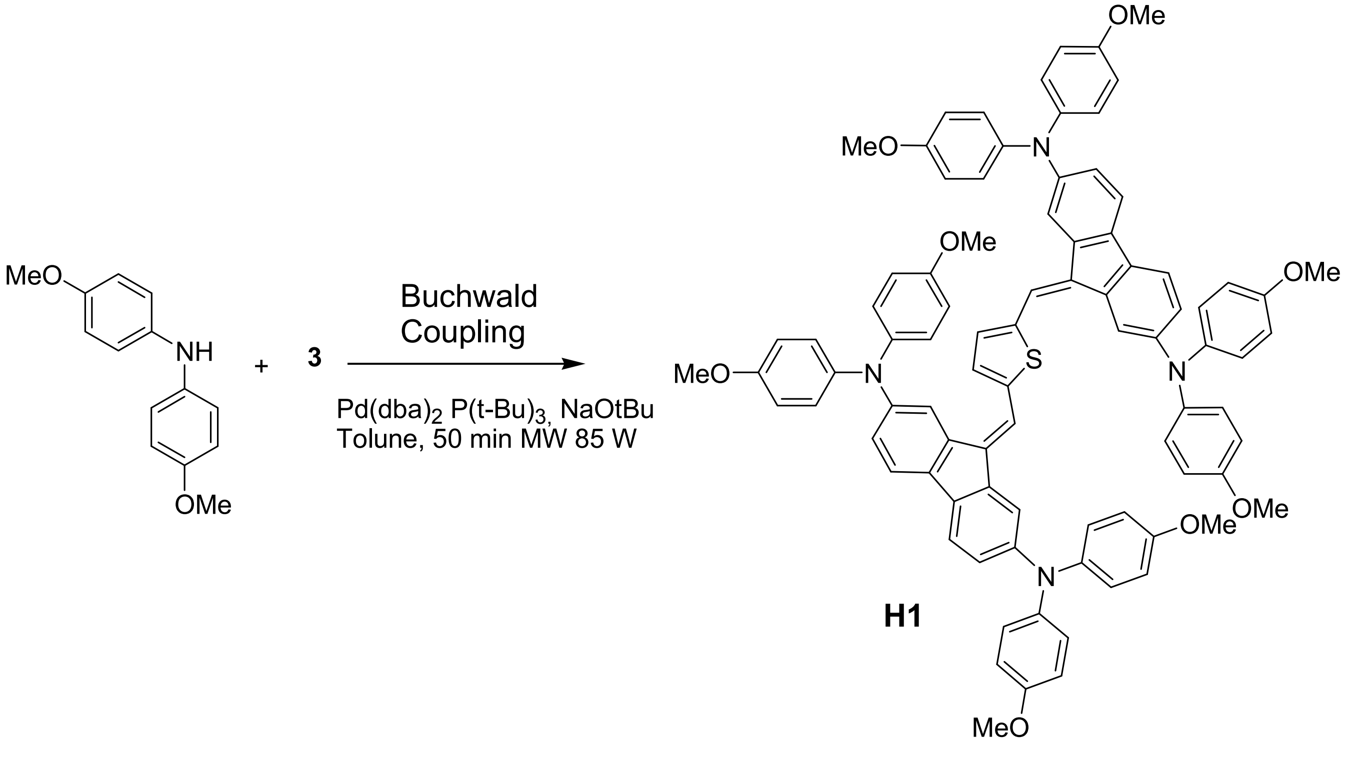
T2

Synthesis of N3,N3,N6,N6-tetrakis(4-methoxyphenyl)-9-((5-methylthiophen-2-yl)methylene)-9H-fluorene-3,6-diamine (T2):

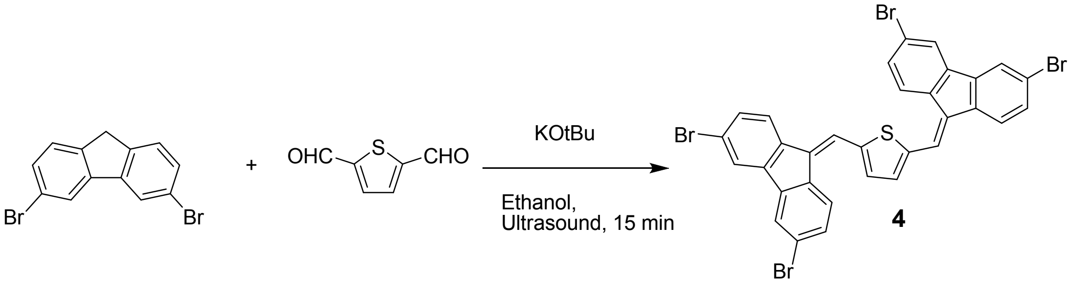
This compound was prepared from 2-((3,6-dibromo-9H-fluoren-9-ylidene)methyl)-5-methylthiophene (0.20g, 0.46 mmol) in 38% yield, using the similar procedure for the synthesis of **T1.** Mp: 159.3-161.3. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 7.87 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.4, Hz, 1H), 7.42 (s, 1H), 7.26 (d, J = 4.6 Hz, 1H), 7.11 (d, J = 3.8 Hz, 1H) 6.99 (d, J = 8.9 Hz, 4H), 6.97 (d, J = 9.0, 4H), 6.90-6.86 (m, 10H), 6.69 (dd, J_1 = 2.1, J_2 = 8.6 Hz, 1H), 6.56 (dd, J_1 = 2.2, J_2 = 8.6 Hz, 1H), 3.71 (s, 12H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 156.17, 155.84, 149.44, 149.10, 142.67, 141.84, 140.53, 140.03, 139.35, 139.01, 134.72, 133.10, 129.19, 128.35, 127.00, 126.43, 126.09, 124.95, 121.85, 120.06, 118.37, 115.24, 115.18, 115.13, 111.03, 110.36, 97.56, 55.49, 15.55. MS (APCI): calcd. for $C_{47}H_{40}N_2O_4S$: 728.27, found 729.13 $[M+H]^+$. $C_{47}H_{40}N_2O_4S$. Elemental Analysis. Calc. C, 77.45; H, 5.53; N, 3.84; O, 8.78; S, 4.40. Found. C, 77.52; H, 5.64; N, 3.95; S, 4.50.



Synthesis of 2,5-bis((2,7-dibromo-9H-fluoren-9-ylidene)methyl)thiophene, 3: 2,7-dibromo-9H-fluorene (1.00 g, 3.1 mmol), thiophene-2,5-dicarbaldehyde (0.217 g, 1.55 mmol) and potassium *tert*-butoxyde (0.520 g, 4.65 mmol) were dissolved in 15 mL of ethanol absolute. The reaction was carried out in a ultrasound bath for 15 minutes, after that, was obtained an orange precipitate that was filtered-off and washed different times with ethanol to remove the reagents. The product obtained showed a very low solubility in the common organic solvents, it was used, without more purification, for the next reaction.

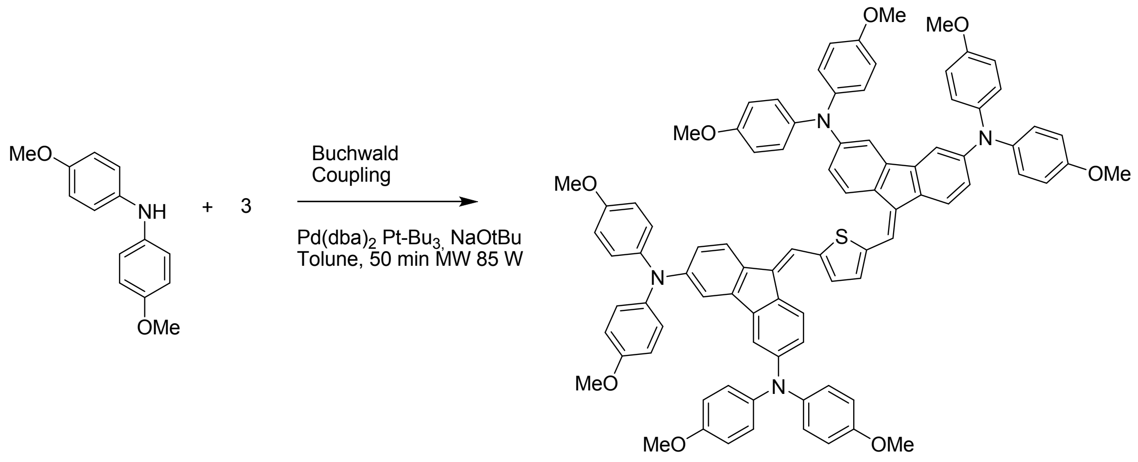


Synthesis of H1: A mixture of **3** (0.400 g, 0.532 mmol), bis(4-methoxyphenyl)amine (0.536 g, 2.3 mmol) and sodium *tert*-butoxide (0.265 g, 2.76 mmol) was added to a suspension of Pd(dba)$_2$ (0.025 g, 0.043 mmol) and P*t*Bu$_3$ (0.174 mL, 0.174 mmol, 1M in toluene) in anhydrous and deoxygenated toluene (10 mL), previous stirred under argon for 10 min. The resulting solution was heated under microwave irradiation at a constant temperature of 110°C for 50 min. The solvent was removed, and the residue was dissolved in dichloromethane and filtered on a short celite column. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography on silica gel (eluent 1/1 hexane/CH_2Cl_2) to give the pure product **H1** as a red solid, 85% yield. ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm) 7.57 (d, J = 2.0 Hz, 2H), 7.52 (dd, J_1 = 3.0 Hz, J_2 = 8.3 Hz, 4H), 7.42 (d, J = 2.0 Hz, 2H), 7.30 (s, 2H), 6.99-6.93 (m, 18H), 6.90 (d, J = 9.1 Hz, 8H), 6.83-6.79 (m, 4H), 6.74 (d, J = 9.1 Hz, 8H), 3.70 (s, 12H) 3.51 (s, 12H); ^{13}CNMR (100 MHz, DMSO-d$_6$) δ (ppm) 155.96, 155.30 147.69, 147.09, 141.21, 140.76, 140.24, 140.23, 136.54, 135.19, 133.18, 132.78, 132.25, 127.19, 125.67, 123.09, 120.06, 119.88, 119.66, 119.13, 115.64, 115.16, 114.55, 55.49, 55.20. MS (APCI) : calcd. for $C_{88}H_{72}N_4O_8S$ 1344,51; found: m/z = 1345,41[M+H]$^+$. $C_{88}H_{72}N_4O_8S$. Elemental Analysis. Calc. C, 78.55; H, 5.39; N, 4.16; O, 9.51; S, 2.38. Found. C, 78.68; H, 5.44; N, 4.25; S, 2.32.



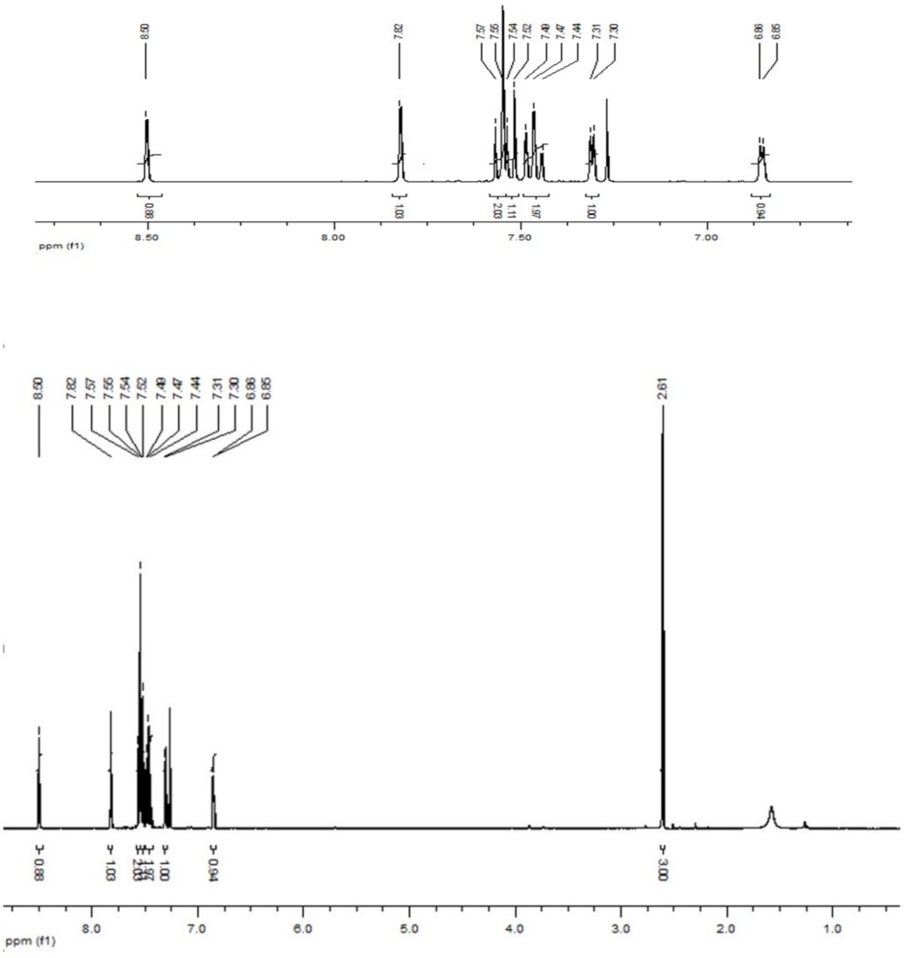
4

Synthesis of 2,5-bis((3,6-dibromo-dibenzofulvene)methyl)thiophene, 4: 3,6-dibromo-9H-fluorene (1.00 g, 3.1 mmol), thiophene-2,5-dicarbaldehyde (0.217 g, 1.55 mmol) and potassium *tert*-butoxyde (0.520 g, 4.65 mmol) were dissolved in 15 mL of ethanol absolute. The reaction was carried out in a ultrasound bath for 15 minutes, after that, was obtained a red precipitate that was filtered-off and washed different times with ethanol to remove the reagents. The product obtained showed a very low solubility in the common organic solvents, it was used, without more purification, for the next reaction.

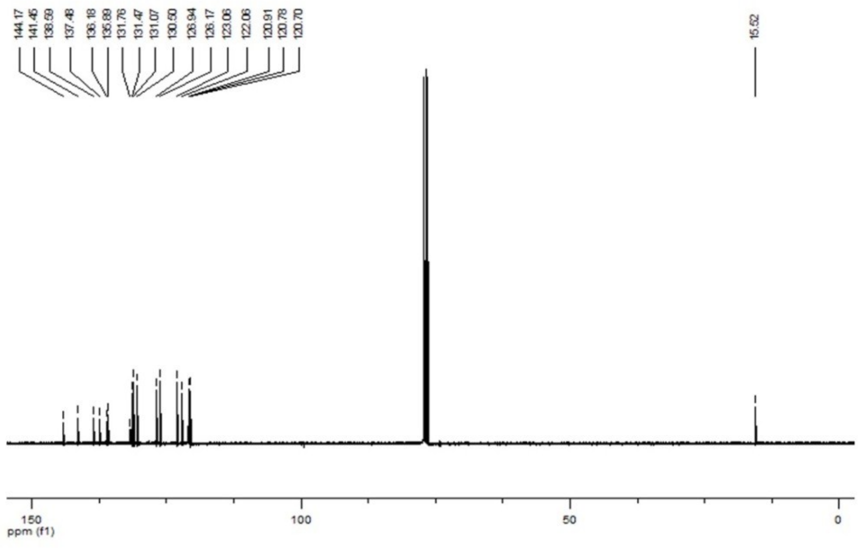


Synthesis of H2: A mixture of **4** (0.400 g, 0.532 mmol), bis(4-methoxyphenyl)amine (0.536 g, 2.3 mmol) and sodium *tert*-butoxide (0.265 g, 2.76 mmol) was added to a suspension of Pd(dba)$_2$ (0.025 g, 0.043 mmol) and P*t*Bu$_3$ (0.174 mL, 0.174 mmol, 1M in toluene) in anhydrous and deoxygenated toluene (10 mL), previous stirred under argon for 10 min. The resulting solution was heated under microwave irradiation at a constant temperature of 110°C for 50 min. The solvent was removed, and the residue was dissolved in dichloromethane and filtered on a short celite column. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography on silica gel (eluent 7/3 hexane/CH$_2$Cl$_2$) to give the pure product **H2** as a purple solid, 70% yield. ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm) 8.11 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.5 Hz, 4H), 7.47 (d, J = 10.5 Hz, 4H), 6.99-6.95 (m, 16H), 6.89-6.85 (m, 20H), 6.69 (dd, J_1 = 2.0, J_2 = 8.4 Hz, 2H), 6.58 (dd, J_1 = 2.2, J_2 = 8.6 Hz, 2H), 3.72 (s, 12H), 3.71 (s, 12H); ^{13}CNMR (100 MHz, DMSO-d$_6$) δ (ppm) 156.11, 155.83, 150.04, 149.21, 141.82, 141.19, 140.50, 140.01, 138.90, 134.16, 133.39, 131.14, 128.70, 128.25, 127.14, 127.06, 126.52, 125.23, 121.78, 119.99, 118.22, 115.24, 115.19, 114.91, 55.50.

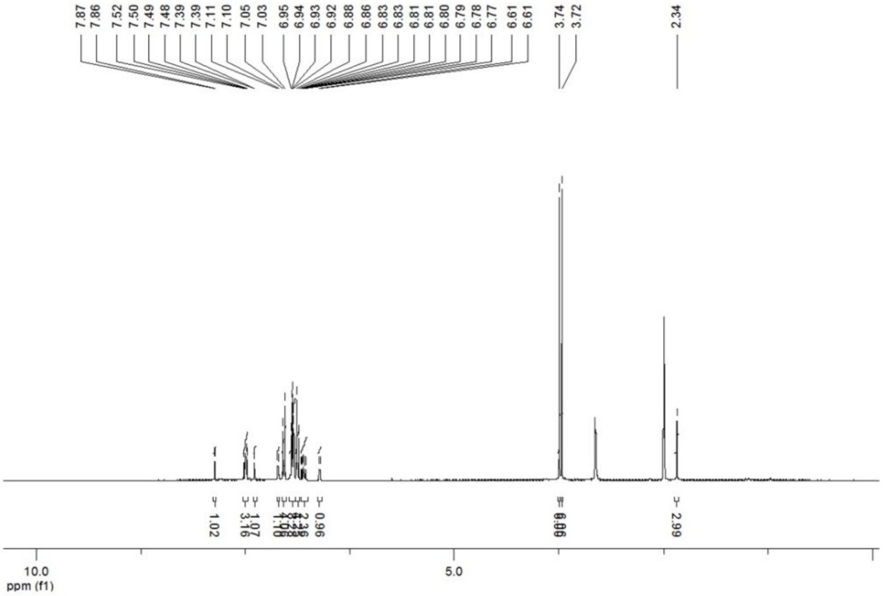
MS (APCI) : calcd. for $C_{88}H_{72}N_4O_8S$ 1344,51; found 1345,36 $[M+H]^+$. $C_{88}H_{72}N_4O_8S$. Elemental Analysis. Calc. C, 78.55; H, 5.39; N, 4.16; O, 9.51; S, 2.38. Found. C, 78.71; H, 5.45; N, 4.21; S, 2.41.



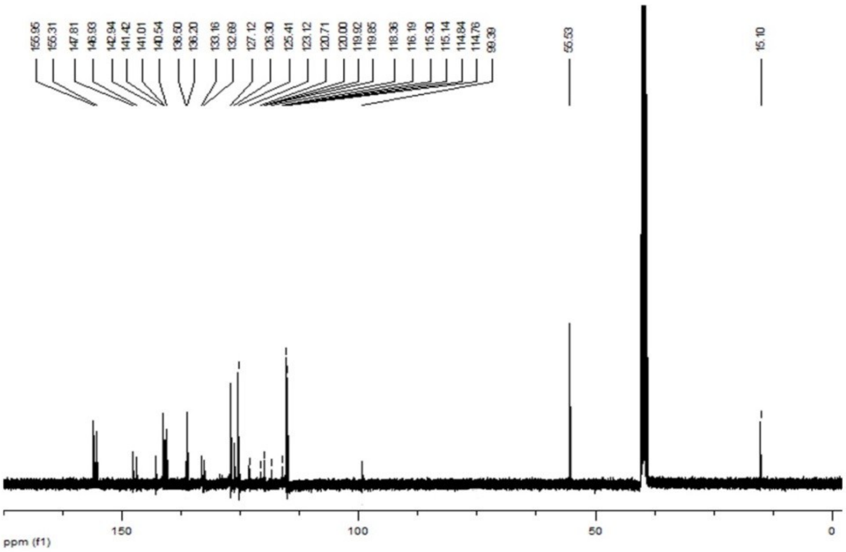
^{1}H NMR spectrum of compound **1** (top, partial enlarging).



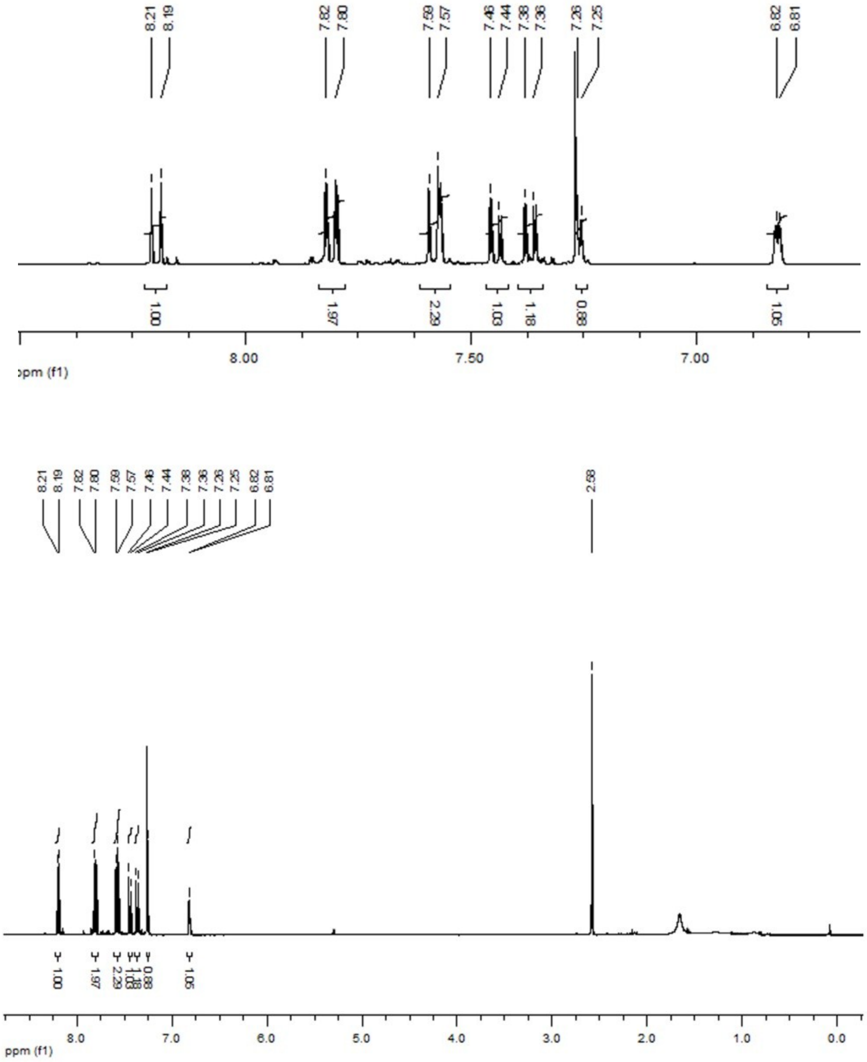
^{13}C NMR spectrum of compound **1**.



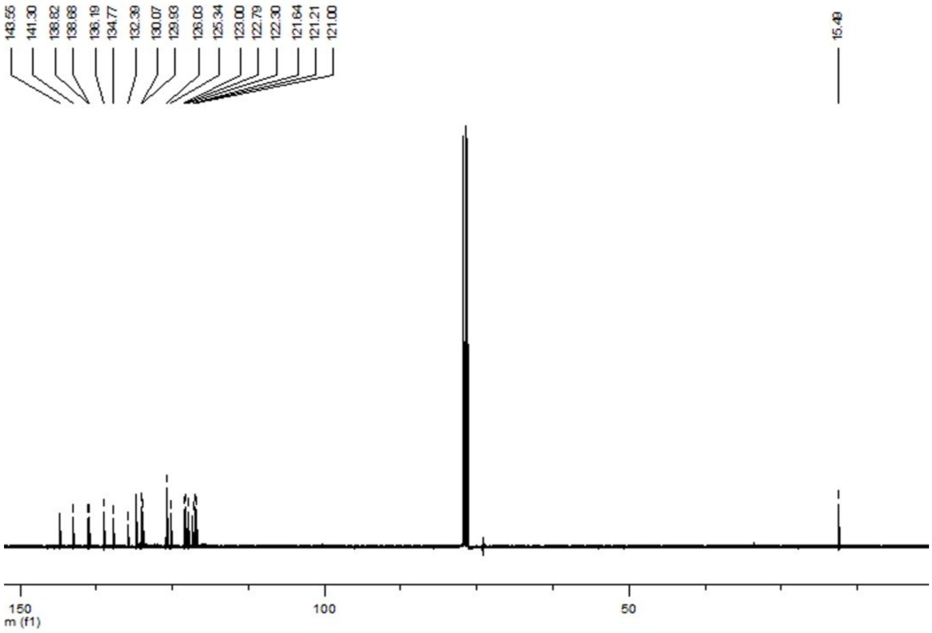
^{1} H NMR spectrum of compound **T1** (top, partial enlarging).



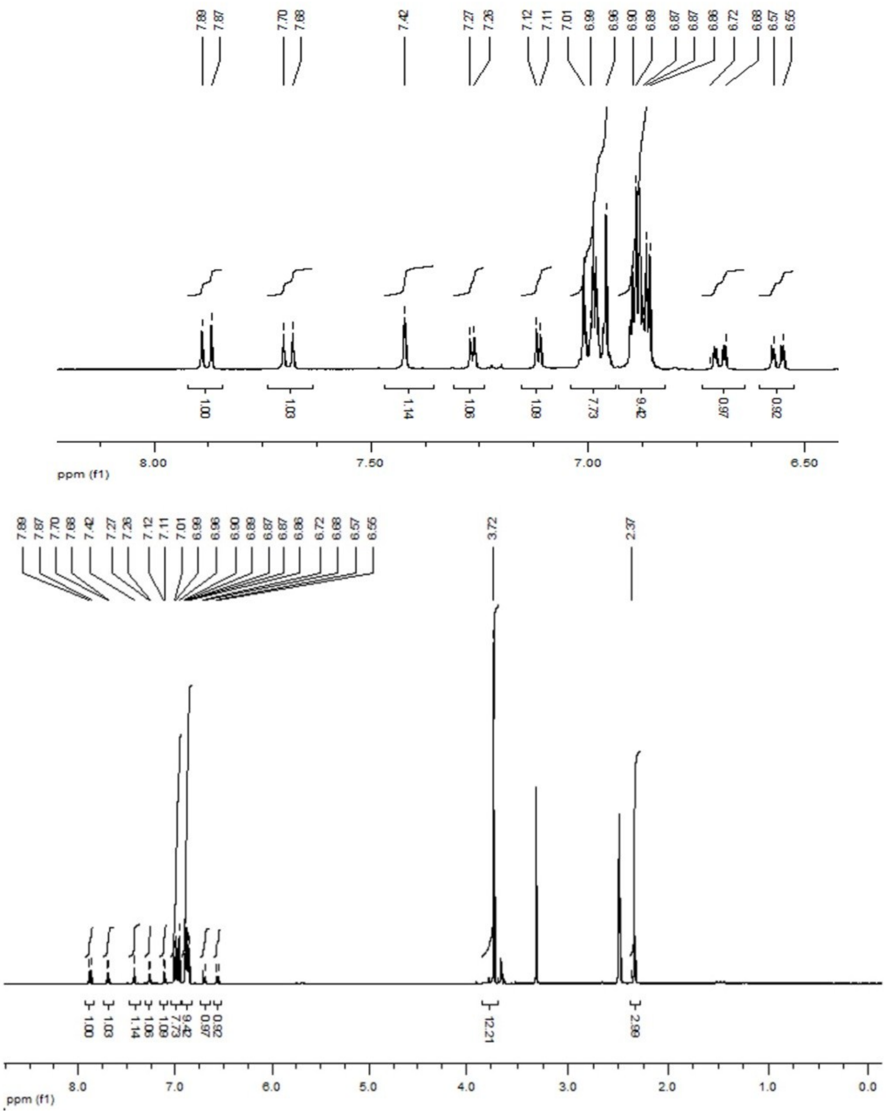
^{13} C NMR spectrum of compound **T1**



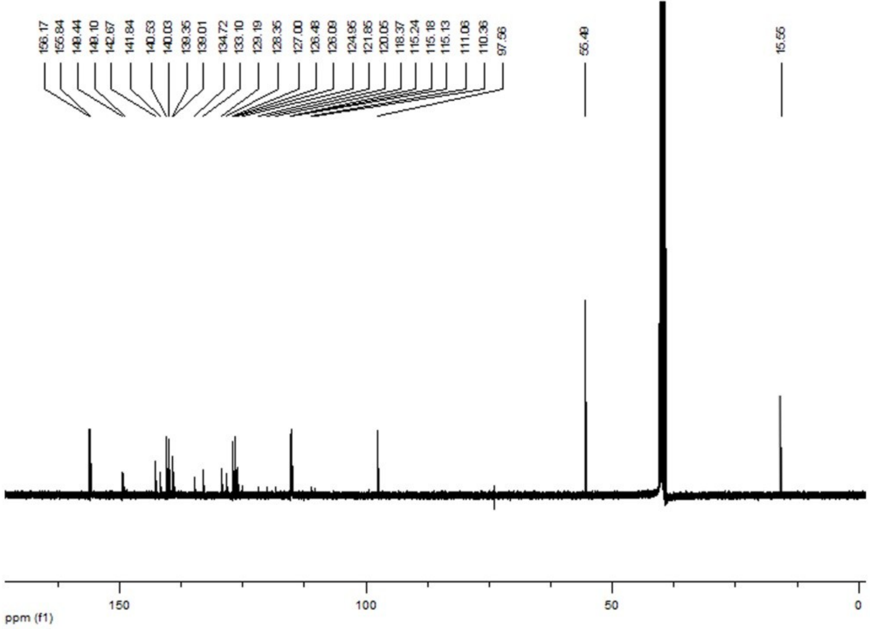
^{1} H NMR spectrum of compound **2** (top, partial enlarging).



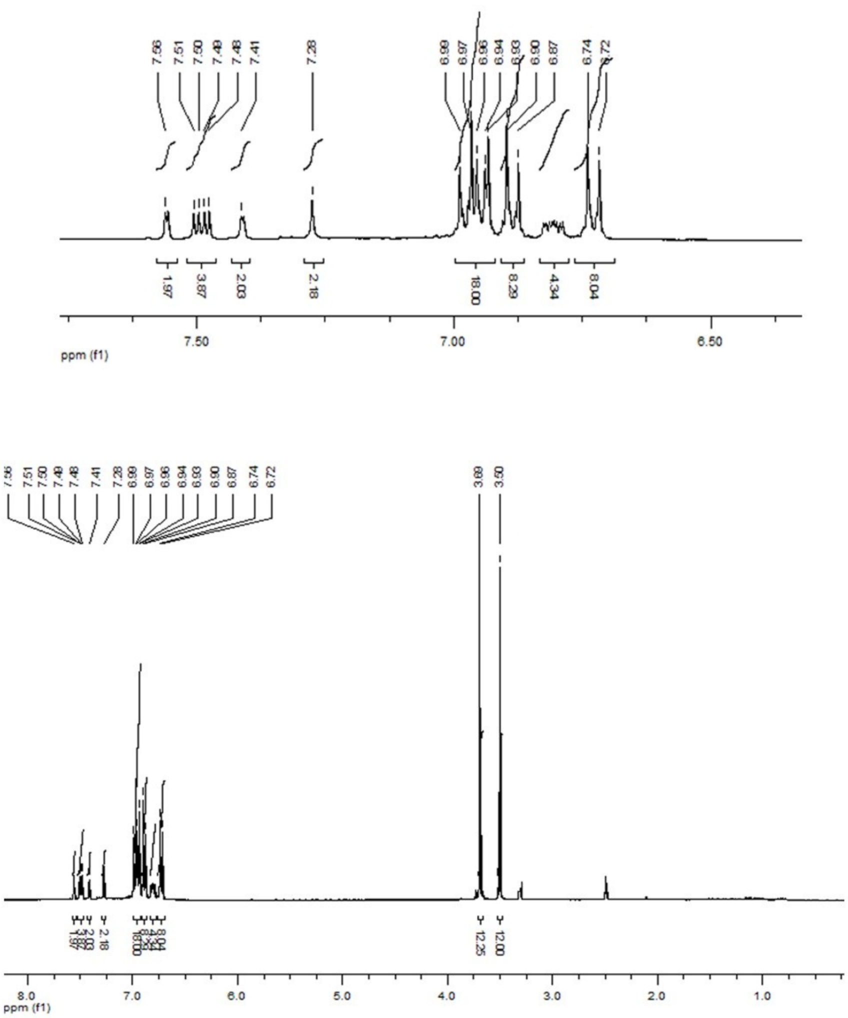
^{13}C NMR spectrum of compound **2**



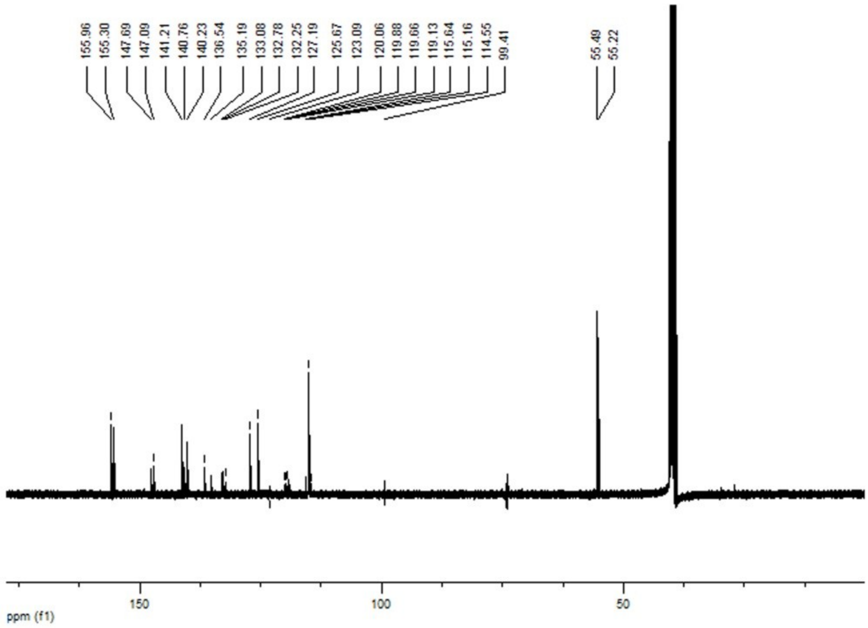
^{1}H NMR spectrum of compound T**2** (top, partial enlarging).



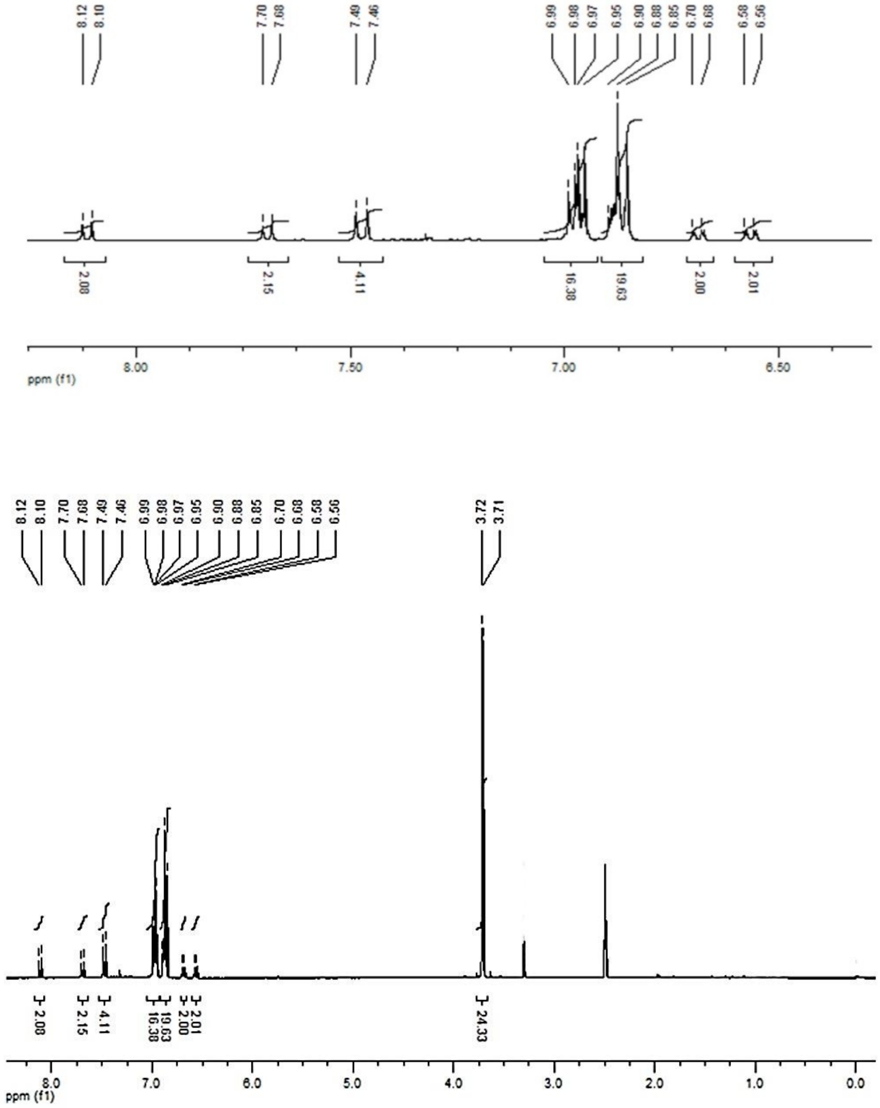
^{13}C NMR spectrum of compound **T2**



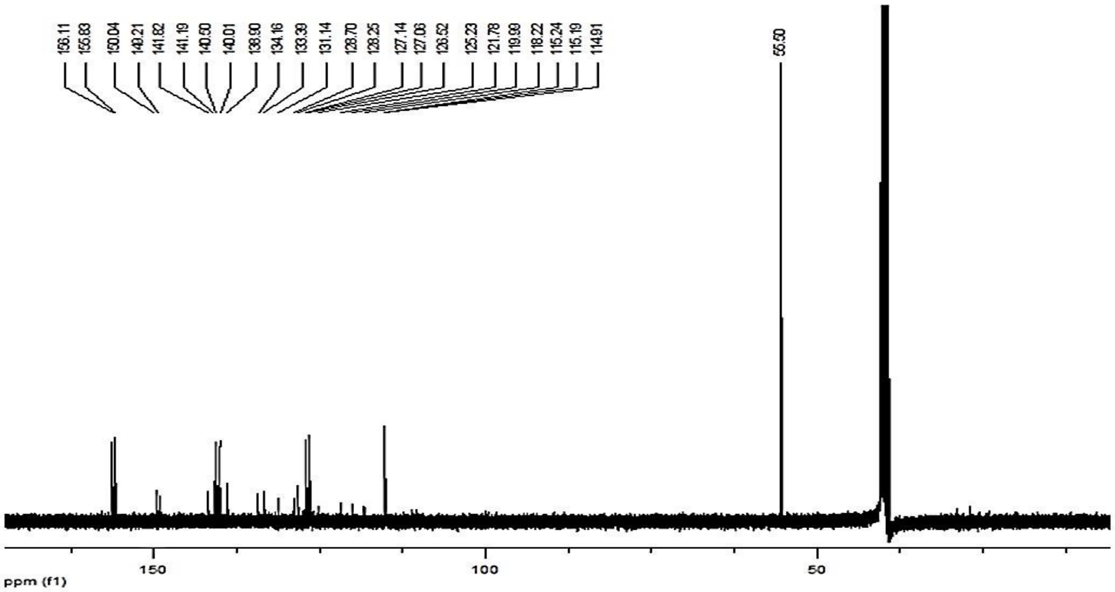
^{1} H NMR spectrum of compound **H1** (top, partial enlarging).



^{13}C NMR spectrum of compound **H1**



^{1}H NMR spectrum of compound **H2** (top, partial enlarging).



^{13}C NMR spectrum of compound **H2**

References

1 V. Maltese, S. Cospito, A. Beneduci, B. C. De Simone, N. Russo, G. Chidichimo, R. A. J. Janssen, *Chemistry A European Journal* 2016, *22*, 10179-10185.

2 S. Cospito, A. Beneduci, M. Salamonczykc, G. Chidichimo, *Physical Chemistry and Chemical Physics* 2015, *17*, 17670.

3 a) L. A. Constantin, E. Fabiano, S. Laricchia, F. Della Sala, *Physical Review Letters* 2011, *106*, 186406; b) E. Fabiano, L. A. Constantin, P. Cortona, F. Della Sala, *Journal of Chemical Theory and Computation* 2015, *11*, 122-131; cF. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chemical Physics Letters* 1998, *294*, 143-152.

4 C. A. Guido, E. Brémond, C. Adamo, P. Cortona, *The Journal of Chemical Physics* 2013, *138*, 021104.

5 TURBOMOLE V7.1. A development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH (2012) 1989–2007, TURBOMOLE GmbH, since 2007 http://www.turbomole.com

6 F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, Wi*ley Interdisciplinary Reviews: Computational Molecular Science 20*14, 4, 91-100.

7 A. Heckmann, C. Lambert, An*gewandte Chemie International Edition 20*12, 51*,* 326-392.

8 a) N. S. Hush, Co*ordination Chemistry Reviews 19*85, 64*,* 135-157; b) C. Lambert, G. Nöll, Jo*urnal of the American Chemical Society 19*99, 12*1,* 8434-8442.

9 K. Lancaster, S. A. Odom, S. C. Jones, S. Thayumanavan, S. R. Marder, J-L. Brédas, V. Coropceanu, and S. Barlow, *Journal of the American Chemical Society*, 2009, **131**, 1717-1723.