Electronic Supplementary Material (ESI) for RSC Advances

Thienyl-linked Pyrenes: New Green-Emitting Triads

Supplementary Information

Contents

Experimental details:

Steady State absorption and emission spectra:

UV-vis spectral measurements were done on a Perkin Elmer Lambda 25 using Hellma quartz cells of 10mm path length.. Steady state emission measurements were done on a Horiba Jobin Yvon fluorolog 3-111. Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Quartz cell of optical path length 10mm were used for all steady state measurements.

Fluorescence decay measurements:

The measurements of spontaneous fluorescence decay were done on time correlated single-photon-counting system from HORIBA. All the molecules from **1a-c** were excited at 375 nm using N-375L picosecond diodes (IBH-NanoLed) and emission was collected at magic angle polarization using a Hamamatsu MCP photomultiplier (Model R-3809U-50). The TCSPC set up consists of an Ortec 9327 pico-timing amplifier. The data was collected with a PCI-6602 interface card as a multi-channel analyzer. FWHM at 375nm excitation was around 140 ps.

NMR and Mass spectra measurements:

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometer either in $CDCl_3$ or THF-d8. The chemical shift values have been referenced to the residual solvent signals. Due to low solubility ^{13}C NMR could not be obtained for **1b**. HRMS measurements were recorded on a microTOF-QII high resolution mass spectrometer from Bruker Daltonics coupled to a Waters Acquity UPLC system.

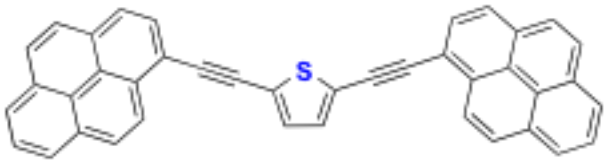
Electrochemical Measurements:

Cyclic voltammetric measurements were carried out using CH potentiostat from CHI Instruments. CV experiments were done under continuous argon flow and a conventional three-electrode electrochemical cell was used. A glassy carbon working, a platinum counter and SCE reference electrodes were used. All the measurements were done in dichloromethane solution with 0.1 M TBAP as the supporting electrolyte. All the spectra were recorded at a scan rate of 0.1 V/s.

Theoretical calculations were performed using Gaussian 09 software suite.

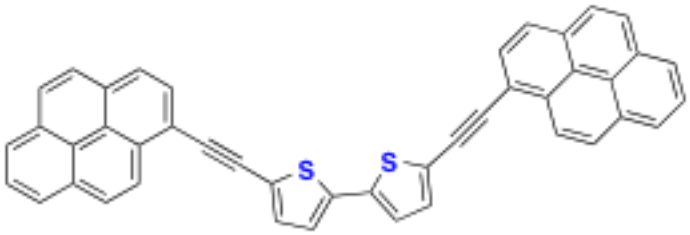
Materials: All the starting materials were purchased either from Aldrich or Alfa Aesar and were used without any further purification. Solvents employed for reactions were dried by distillation using routine procedures. All the reactions were carried under argon using dry solvents.

Compound 1a



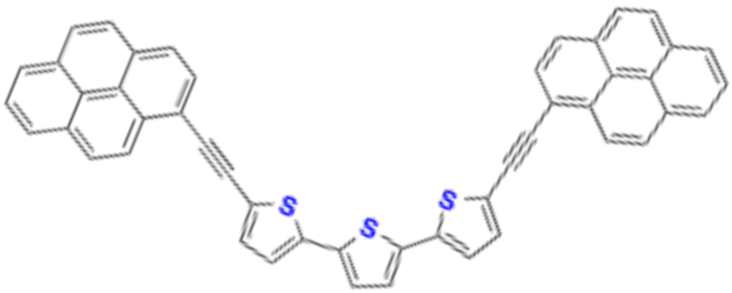
Synthesis: $PdCl_2(PPh_3)_2$(4 mol%) , CuI (2 mol%) were added to a perfectly degassed solution of Diisopropylamine and THF (3ml each) in a dried Schlenk tube. To this 2,5- Dibromo- thiophene (1 eq) was added and resulting mixture was stirred for 5 min. This is followed by an addition of 1-ethynyl pyrene (2 eq) and reaction mixture was left for stirring overnight at 70^0C. Progress of the reaction was monitored by TLC. After the completion of reaction, the reaction was quenched by 20ml of chloroform and solvent was evaporated under vacuum. Further purification was done by column chromatography on silica gel (230-400 mesh size) using distilled hexane and ethyl acetate as eluents followed by recrystallization in CH_2Cl_2/hexane. Yield (72 %).

1b



Synthesis: $PdCl_2(PPh_3)_2$(4 mol%) , CuI (2 mol%) were added to a perfectly degassed solution of Diisopropylamine and THF (3ml each). To this 5, 5′-Dibromo-2, 2′-bithiophene (1 eq) was added and resulting mixture was stirred for 5 min. This is followed by an addition of 1-ethynyl pyrene (2 eq) and reaction mixture was left for stirring overnight at 70^0C. On completion of reaction, the reaction was quenched by 20ml of chloroform and solvent was evaporated under vacuum. First purification was done by column chromatography on silica gel (230-400 mesh size) using distilled hexane and ethyl acetate as eluents to remove side products although poor solubility and stacking of molecule complicated the purification process. Further purification was done by one more filteration column followed by recrystallization in CH_2Cl_2/hexane. Yield (54 %).

1c:



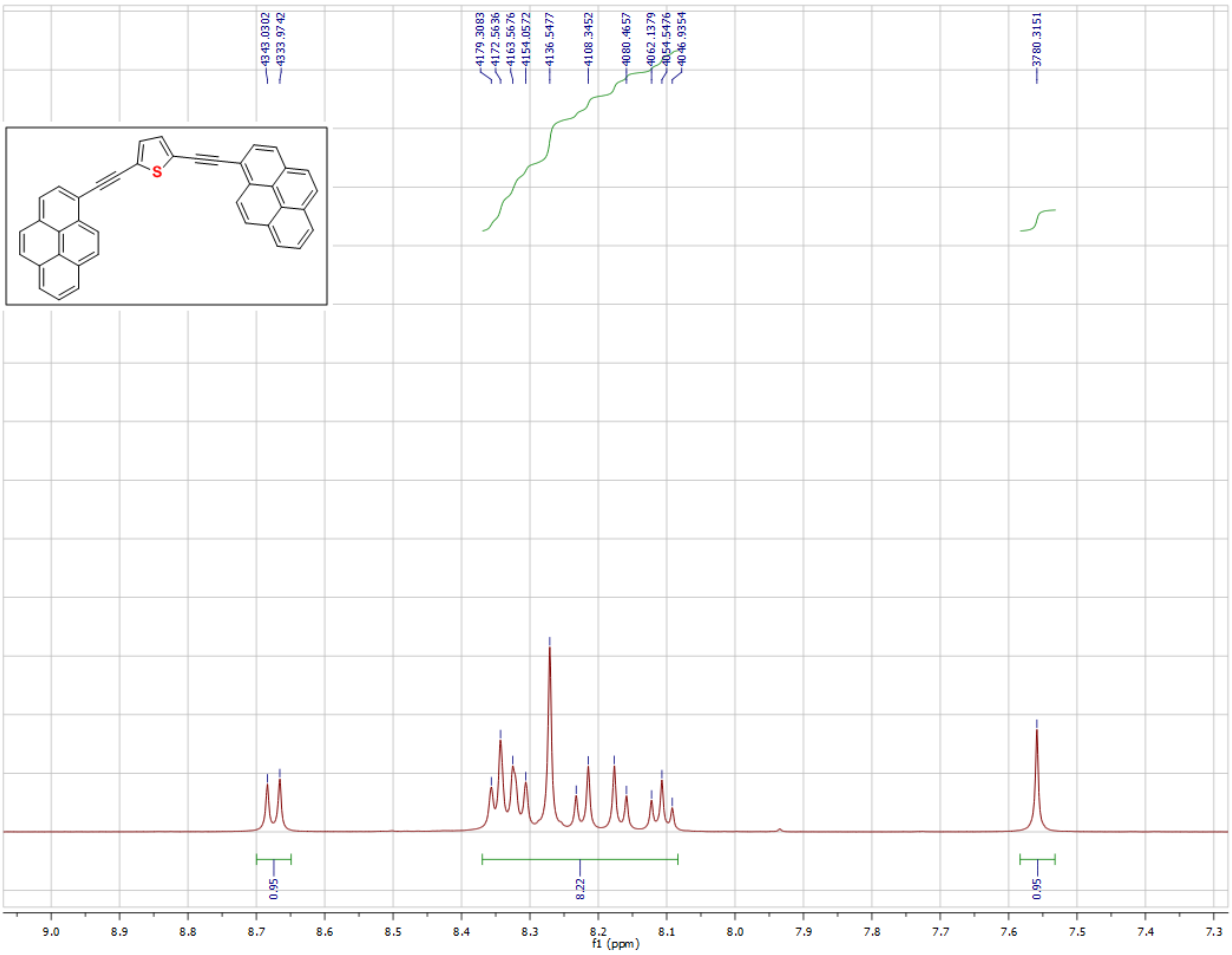
Synthesis: $PdCl_2(PPh_3)_2$(4 mol%) , CuI (2 mol%) were added to a perfectly degassed solution of Diisopropylamine and THF (3ml each). To this 5,5′′-Dibromo-2,2′:5′,2′′-terthiophene (1 eq) was added and resulting mixture was stirred for 5 min. This is followed by an addition of 1-ethynyl pyrene (2 eq) and reaction mixture was left for stirring overnight at 70^0C.After the completion of reaction, the reaction was quenched by 20ml of chloroform and solvent was evaporated under vacuum. Purification was done by column chromatography on silica gel (230-400 mesh size) using distilled hexane and ethyl acetate as eluents to remove side products. Further purification was done by one more filteration column followed by recrystallization in CH_2Cl_2/hexane. Yield (60 %).

Characterization:

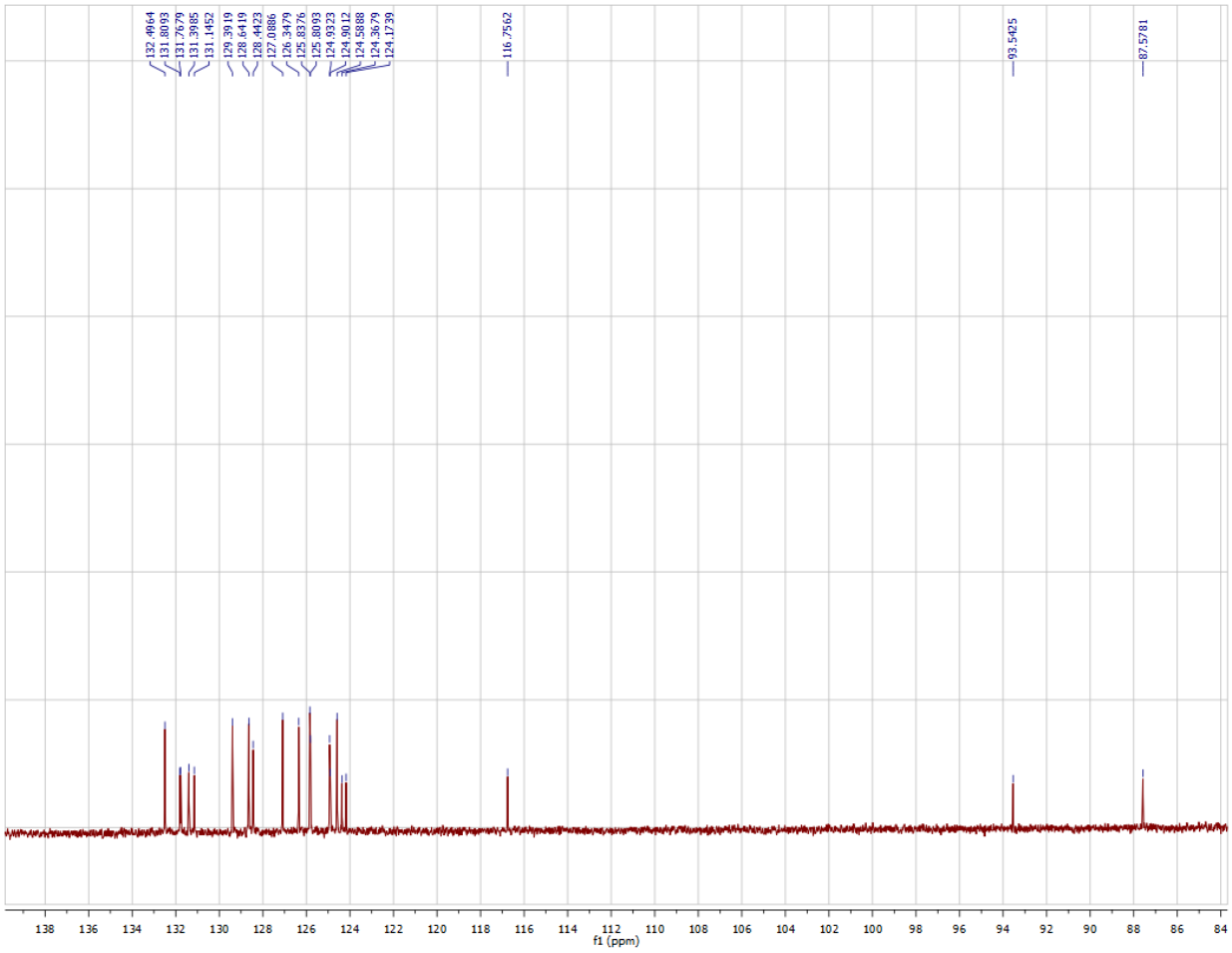
All the compounds were satisfactorily analyzed by various spectroscopic techniques including NMR and Mass. Due to the poor solubility; C^{13} NMR could not be recorded for **1b**. All the spectra were recorded in $CDCl_3$ with TMS as reference standard.

Compound	**Molecular formula**	**^{1}HNMR (500MHz) in THF-d8**	**^{13}CNMR**	**HRMS (calc.) (M+nH)**	**HRMS (obsd.)**
1a	$C_{40}H_{20}S$	8.67(d, *J*=9.1Hz, 1H), 8.05-8.36(m, 8H), 7.56(s, 1H)	132.5, 131.8, 131.78, 131.4, 131.1, 129.4, 128.6, 128.4, 127.1, 126.3, 125.8, 125.8, 124.9, 124.9, 124.6, 124.4, 124.2, 116.8, 93.5, 87.6	533.1358	533.1368
1b	$C_{44}H_{22}S_2$	8.65(d, *J*=9.0Hz, 1H), 8.08-8.27 (m, 8H), 7.49(s, 1H), 7.07(s, 1H)		615.1236	615.1233
1c	$C_{48}H_{24}S_3$	8.65(d, *J*=9.1 Hz, 1H), 8.08-8.34(m, 8H), 7.5(d,*J*=3.8 Hz,1H), 7.37(d,*J*=3.0Hz, 2H)	138.5, 136.0, 133.3, 131.7, 131.6, 131.4, 131.2, 129.2, 128.5, 128.3, 127.1, 126.3, 125.8,125.7, 125.3, 124.9, 124.6, 124.4, 124.2, 124.1, 122.3, 117.0, 93.7, 87.9	696.1035	696.1052

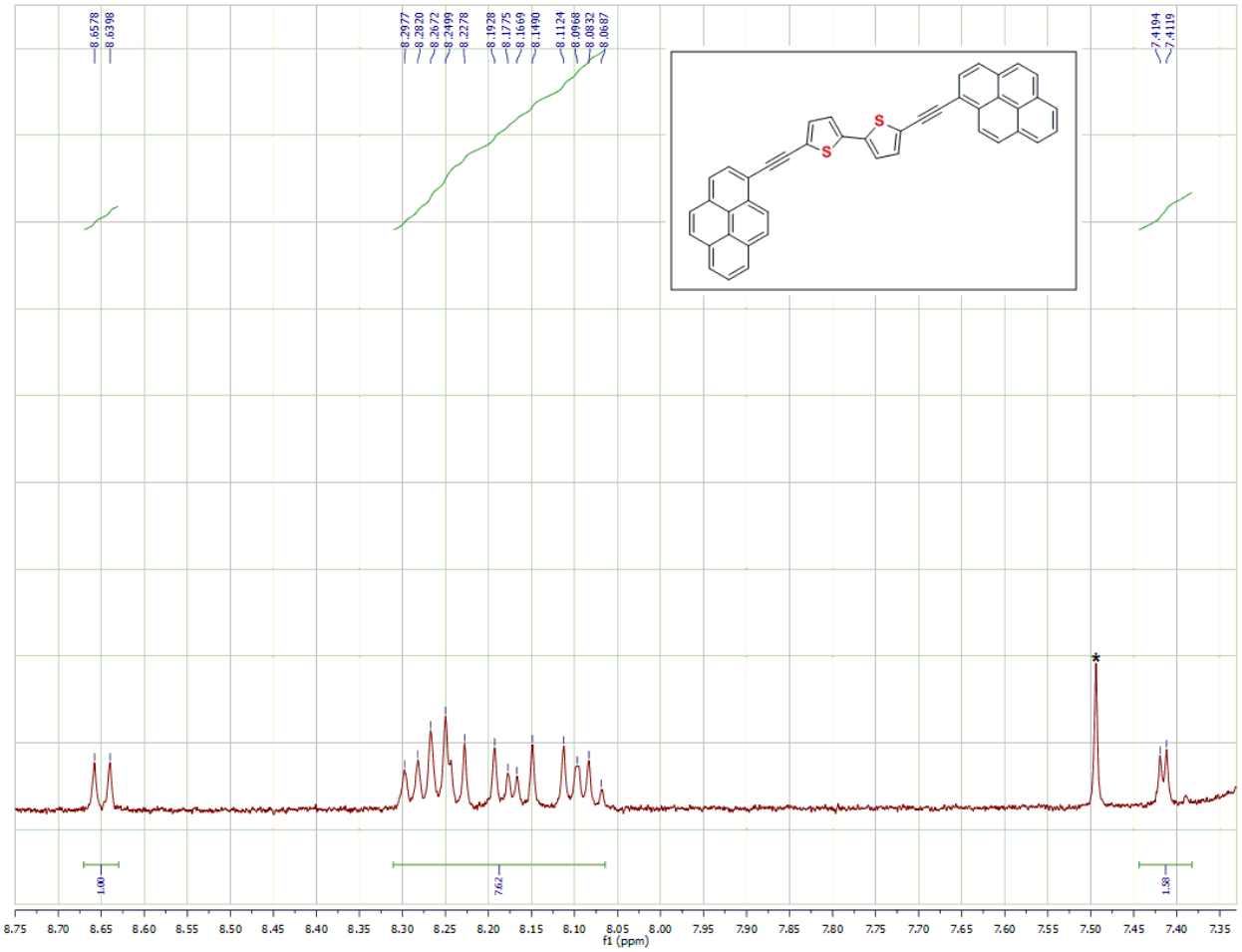
NMR spectra of reported compounds



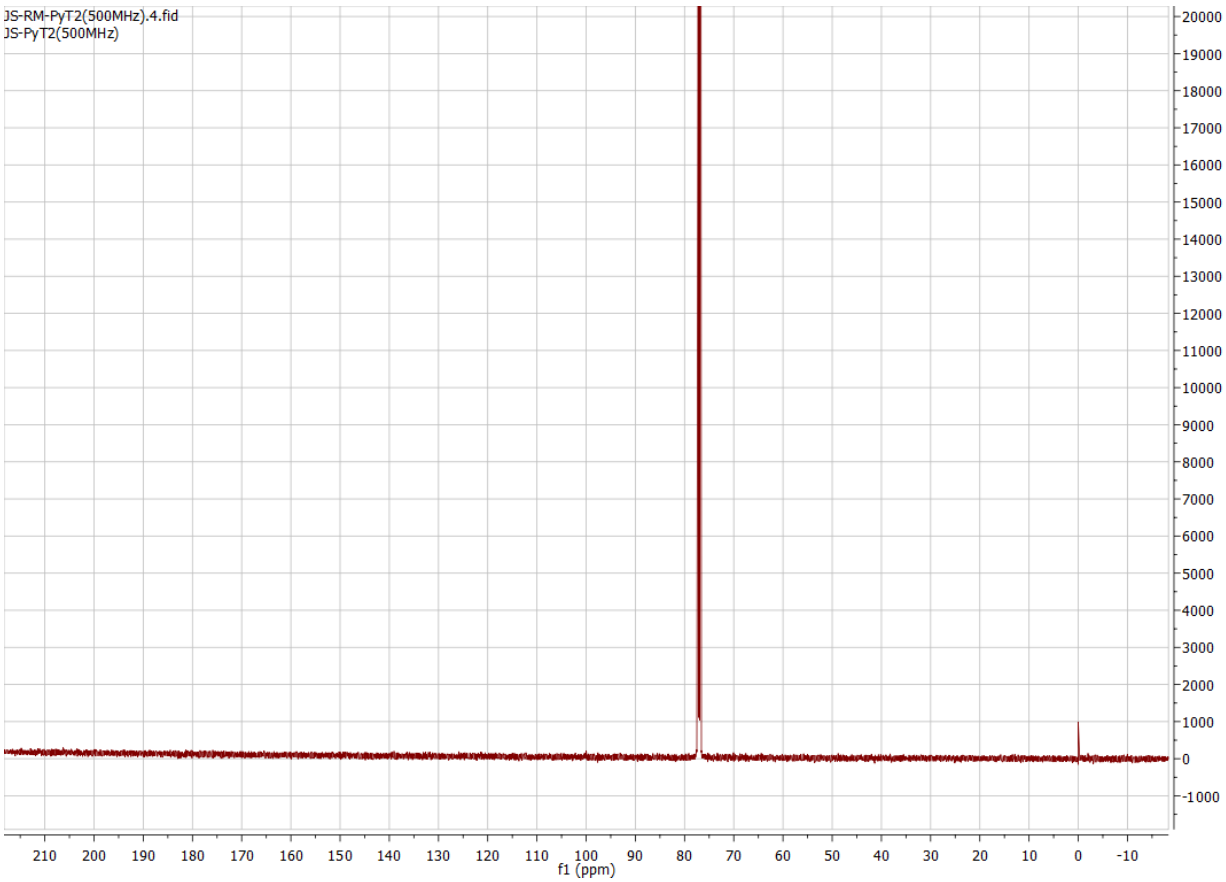
500 MHz ^{1}H NMR of Compound **1a** in THF-d8.



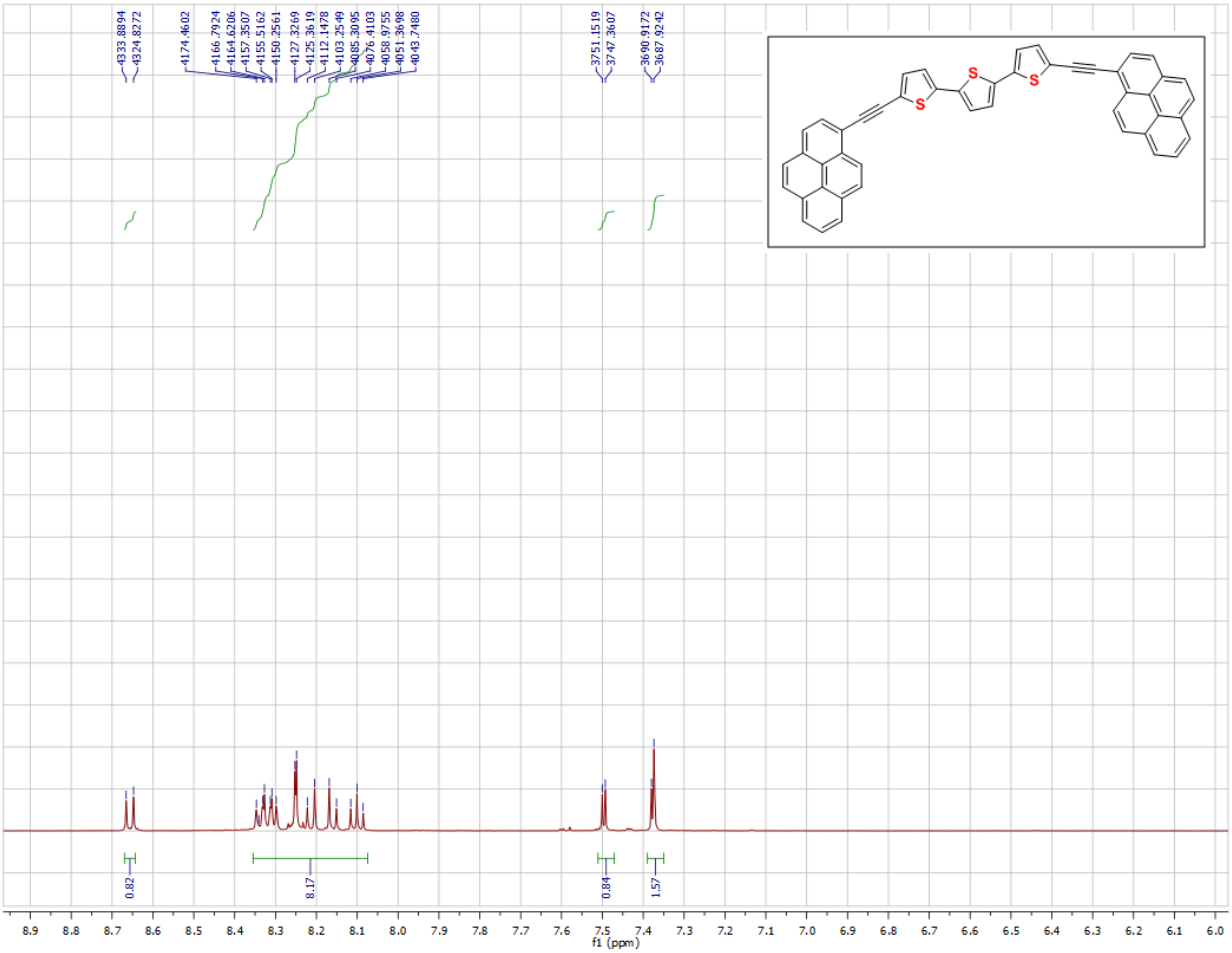
^{13}C NMR of Compound **1a** in THF-d8.



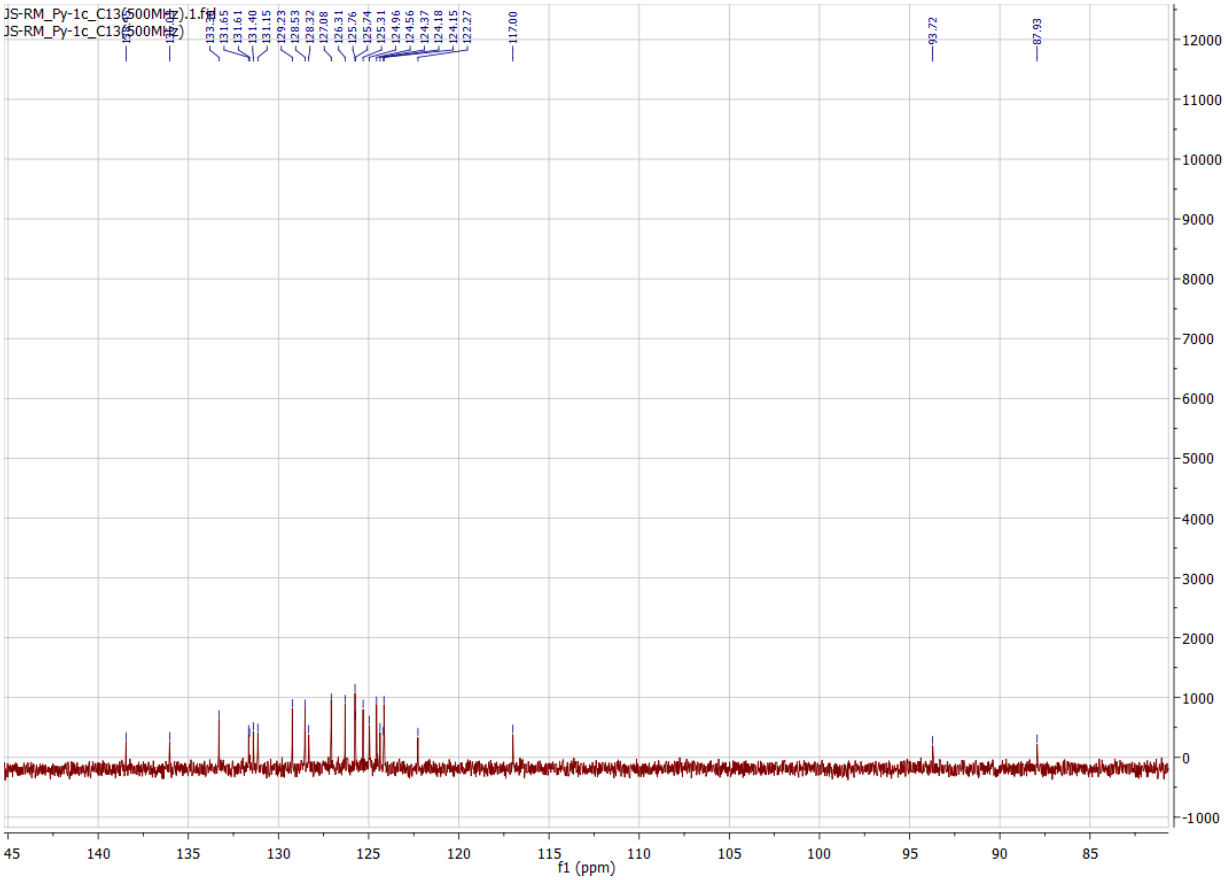
500 MHz ^{1}H NMR of Compound **1b** in $CDCl_3$.



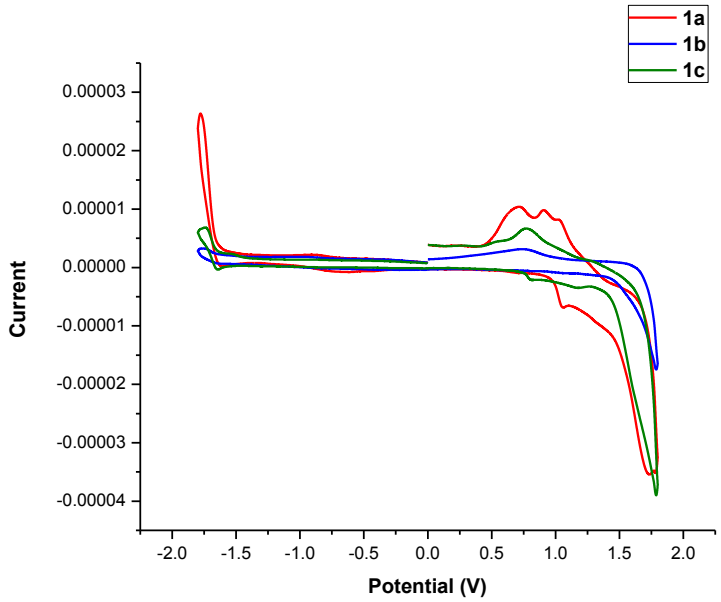
500 MHz ^{1}H NMR of Compound **1b** in $CDCl_3$ (Number of scans: 20480)



500 MHz ^{1}H NMR of Compound **1c** in THF-d8.



^{13}C NMR of Compound **1c** in THF-d8.



Cyclic voltammogram for compound 1a-1c

DFT optimized coordinates for the reported compounds:

1a:

C	6.82428600	-2.76951300	-0.00032100
C	7.86857900	-1.83062300	-0.00016900
C	7.54483700	-0.44136900	-0.00002200
C	6.18352500	-0.01876300	-0.00003700
C	5.15485800	-1.00068600	-0.00019500
C	5.50219700	-2.36572100	-0.00033200
C	8.59204100	0.52750100	0.00014100
C	8.28074800	1.91846400	0.00029200
C	6.90148200	2.30875800	0.00027300
C	5.90278500	1.38644800	0.00011600
C	9.24712700	-2.22128300	-0.00015300
C	10.24401700	-1.29700900	0.00000000
C	9.95581900	0.10852900	0.00015400
C	10.96719200	1.08018100	0.00031700
C	10.65325600	2.43553100	0.00046600
C	9.32676300	2.85315100	0.00045400
C	3.78818800	-0.63184400	-0.00021900
C	2.61328900	-0.32448900	-0.00024400
C	1.25931100	0.02952300	-0.00027600
C	0.70326600	1.29726900	-0.00034200
C	-0.70327100	1.29726900	-0.00032700
C	-1.25931600	0.02952300	-0.00023200
S	-0.00000200	-1.19385700	-0.00030000
C	-2.61329200	-0.32449400	-0.00014200
C	-3.78819000	-0.63185700	-0.00005700
C	-10.96718800	1.08019000	0.00011900
C	-9.95581700	0.10853500	0.00020800
C	-8.59203800	0.52750300	0.00004800
C	-8.28074100	1.91846500	-0.00019800
C	-9.32675300	2.85315500	-0.00028100
C	-10.65324800	2.43553900	-0.00012400
C	-7.54483700	-0.44137000	0.00013400
C	-6.18352500	-0.01876800	-0.00002100
C	-5.90278000	1.38644100	-0.00026500
C	-6.90147400	2.30875500	-0.00035100
C	-10.24402000	-1.29700200	0.00045500
C	-9.24713300	-2.22127900	0.00053600
C	-7.86858400	-1.83062300	0.00037900
C	-6.82429300	-2.76951600	0.00045700
C	-5.50220400	-2.36572800	0.00030500
C	-5.15486100	-1.00069300	0.00006800
H	7.06389200	-3.82735800	-0.00043100
H	4.70871000	-3.10295500	-0.00045100
H	6.66520900	3.36771200	0.00038800
H	4.86704900	1.70293600	0.00010600
H	9.48138800	-3.28059700	-0.00026500
H	11.28258900	-1.61075500	0.00001100
H	12.00438800	0.76233600	0.00032800

H	11.44913200	3.17173000	0.00059200
H	9.08918900	3.91158500	0.00057000
H	1.31050100	2.19190800	-0.00037300
H	-1.31050500	2.19190800	-0.00034100
H	-12.00438500	0.76234800	0.00024000
H	-9.08917600	3.91158900	-0.00046800
H	-11.44912100	3.17174100	-0.00019000
H	-4.86704300	1.70292700	-0.00038300
H	-6.66519700	3.36770800	-0.00053700
H	-11.28259300	-1.61074600	0.00057600
H	-9.48139700	-3.28059300	0.00072200
H	-7.06390200	-3.82736000	0.00064300
H	-4.70871800	-3.10296400	0.00037400

1b:

C	-11.21771800	2.00789000	-0.33738200
C	-12.03889200	0.92640800	-0.40088000
C	-11.51715200	-0.40860200	-0.33773100
C	-10.10772900	-0.58753600	-0.20654400
C	-9.24459000	0.54652200	-0.14163800
C	-9.79871900	1.85937200	-0.20601900
C	-9.56596200	-1.90428800	-0.14071900
C	-8.14615900	-2.05230900	-0.00932600
C	-7.32238000	-0.97256900	0.05085400
C	-7.83661300	0.36348000	-0.01331100
C	-12.34461600	-1.53925600	-0.39988600
C	-11.80638400	-2.82047000	-0.33451800
C	-10.43384300	-3.00444100	-0.20622100
C	-6.99409400	1.50727500	0.04676500
C	-7.56774300	2.79234400	-0.01526800
C	-8.93380100	2.96358900	-0.13834900
C	7.32235400	0.97253400	0.05119400
C	8.14611100	2.05231000	-0.00861500
C	9.56591600	1.90436300	-0.14007900
C	10.10770700	0.58764500	-0.20637500
C	9.24459000	-0.54645200	-0.14185900
C	7.83661200	-0.36348300	-0.01345100
C	11.51713200	0.40878400	-0.33764200
C	12.03889700	-0.92619400	-0.40126800
C	11.21774500	-2.00771400	-0.33814200
C	9.79874500	-1.85926900	-0.20670900
C	10.43377500	3.00455600	-0.20520200
C	11.80631900	2.82065600	-0.33358100
C	12.34457400	1.53947500	-0.39940700
C	8.93384800	-2.96352600	-0.13941700
C	7.56778800	-2.79235100	-0.01626200
C	6.99411500	-1.50731500	0.04622900
C	-5.58865000	1.38251100	0.16187700
C	5.58867000	-1.38261900	0.16139800
C	-4.37986400	1.30694400	0.25182300

C	4.37988400	-1.30709900	0.25138000
C	-2.98706100	1.21385400	0.34582700
S	-2.17426500	-0.34100400	0.22041900
C	-0.60060300	0.39939800	0.43245000
C	-0.72987100	1.76718500	0.57500200
C	-2.06191200	2.22427500	0.52540000
C	0.60062600	-0.39959900	0.43232000
C	0.72989600	-1.76742600	0.57448300
C	2.06193500	-2.22450400	0.52472500
C	2.98708100	-1.21403300	0.34542500
S	2.17428200	0.34085800	0.22043300
H	-11.62737000	3.01133000	-0.38551400
H	-13.11130100	1.05702800	-0.50037700
H	-7.73459800	-3.05486900	0.04164400
H	-6.25236000	-1.10728100	0.15061200
H	-13.41633700	-1.40406100	-0.49956700
H	-12.46236700	-3.68226400	-0.38398500
H	-10.02108000	-4.00636800	-0.15610900
H	-6.91396000	3.65459400	0.03257900
H	-9.34892400	3.96457700	-0.18539200
H	6.25233200	1.10718900	0.15101400
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H	13.11130700	-1.05675800	-0.50082400
H	11.62741500	-3.01112900	-0.38663100
H	10.02099400	4.00645700	-0.15473300
H	12.46228400	3.68248000	-0.38275200
H	13.41629700	1.40433600	-0.49914900
H	9.34899000	-3.96448900	-0.18681800
H	6.91402200	-3.65463000	0.03128800
H	0.11861600	2.42084400	0.72965500
H	-2.35345400	3.26055900	0.62630200
H	-0.11858900	-2.42112600	0.72897800
H	2.35347800	-3.26081500	0.62533800

1c:

C	-11.94692700	-5.72297000	0.17843300
C	-12.90777600	-5.68536300	-0.78252500
C	-12.70673200	-4.96684600	-2.00806500
C	-11.46977400	-4.28364900	-2.20624000
C	-10.46077600	-4.32208200	-1.19844400
C	-10.69490400	-5.04744000	0.00730600
C	-11.24680300	-3.56340800	-3.41593000
C	-9.99414300	-2.88739900	-3.58632800
C	-9.03183900	-2.92323500	-2.62675300
C	-9.22599800	-3.63876000	-1.40042800
C	-13.68256400	-4.91471300	-3.01399700
C	-13.45547200	-4.20911800	-4.19134400
C	-12.25292700	-3.54012000	-4.39310200
C	-8.23305600	-3.69138400	-0.38402200
C	-8.48974200	-4.41607500	0.79636800

C	-9.68912000	-5.07624900	0.98676300
C	8.70897300	-0.03028400	3.55343700
C	9.23929200	-0.70311500	4.60900700
C	10.60721300	-0.52521700	4.99934700
C	11.41361200	0.38178800	4.25196700
C	10.85854300	1.08815400	3.14364800
C	9.49400900	0.88769300	2.78251500
C	12.77878700	0.57967200	4.61660100
C	13.57045900	1.49756300	3.84921400
C	13.04298300	2.17073100	2.79250000
C	11.67599400	1.99194200	2.40232900
C	11.17470900	-1.20952500	6.08455400
C	12.50640800	-1.01040800	6.43267900
C	13.30136400	-0.12698600	5.70957400
C	11.11300900	2.67670500	1.31322200
C	9.79081900	2.48621900	0.95819300
C	8.96116800	1.60088100	1.67380700
C	-6.99016000	-3.03051700	-0.53290700
C	7.61314300	1.44115600	1.27213400
C	-5.91891200	-2.46896400	-0.64293900
C	6.46156600	1.32873100	0.90307200
C	-1.02073300	-0.70208800	0.14582800
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C	1.37373600	0.04166300	0.45153000
C	0.81279900	-0.50905200	1.58416700
C	-0.52535800	-0.92474700	1.41312900
C	2.69690400	0.58351200	0.26221000
C	3.15050900	1.43115700	-0.72937200
C	4.51220100	1.77410500	-0.60947700
C	5.13434300	1.19715100	0.48089900
S	3.99739900	0.18859300	1.36729300
H	-12.11379900	-6.27116600	1.09966300
H	-13.85008300	-6.20279800	-0.63667600
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H	-14.62296900	-5.43425100	-2.86416500
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H	-9.86078200	-5.62680200	1.90539800
H	7.67304000	-0.18032400	3.27514500
H	8.62604100	-1.39396800	5.17797600
H	14.60771700	1.64498100	4.13105200
H	13.65467900	2.86124400	2.22151700
H	10.56057800	-1.89993900	6.65271700
H	12.92863600	-1.54805700	7.27415900
H	14.33917800	0.02319500	5.98747200
H	11.72941000	3.36516900	0.74535200
H	9.37145400	3.02297700	0.11604600
H	1.34409600	-0.58193300	2.52412200
H	-1.12275000	-1.35037000	2.20857700
H	2.50635000	1.81233800	-1.51091200

H	5.03561000	2.43284700	-1.28858500
C	-2.33423800	-0.98082400	-0.38012300
C	-4.68032100	-1.82878600	-0.75739300
C	-4.23042300	-0.98002300	-1.75022400
H	-4.84448800	-0.70678300	-2.59710200
S	-3.43265300	-2.05429000	0.46226500
C	-2.92059800	-0.50597700	-1.53691200
H	-2.42095400	0.18439800	-2.20373100

Reference:

16. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A. 02; Gaussian, Inc., Wallingford CT, 2009.