Redox-dependent properties of DTF-endcapped π-oligomers

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Table of Contents

1. Electronic Transition and Molecular Orbital Properties

Electronic transition properties for model compound **1b** in different oxidation states were simulated by the TD-DFT method at the B3LYP/6-31++(d,p) level of theory. Detailed electronic transition energies and MO assignments are listed in Tables S-1 to S-4. Eigenvalues of frontier molecular orbitals for **1b** are provided in Table S-5, and detailed contour plots for these orbitals are illustrated in Fig. S-1 and S-2.

Table S-1. Assignments of electronic transitions of **1b** in the neutral state

Wavelength (nm)	**Oscillator strength (*f*)**	**Transition**	**MO contribution**
471	2.665	HOMO→LUMO	0.70227
352.0	0.7492	HOMO-1→LUMO-1	0.5212
		HOMO-2→LUMO	-0.46202

Table S-2. Assignments of electronic transitions of **1b** in the radical cation state

Wavelength (nm)	**Oscillator strength (*f*)**	**Transition**	**MO contribution**
1823.5	1.0425	SOMO→LUMO(β)	1.07711
		LUMO→SOMO(β)	-0.42385
		SOMO→LUMO(α)	-0.14552
592.7	1.2274	SOMO→LUMO(α)	0.82471-
		SOMO→LUMO+2(β)	0.33823
		SOMO1→LUMO+1(β)	0.26939
		SOMO-3→SOMO(β)	-0.17459
		SOMO→LUMO(β)	0.16416
		SOMO-2→LUMO(α)	-0.13221
		SOMO-1→LUMO+1(β)	0.12393
		SOMO→LUMO(β)	-0.11999
		SOMO-2→LUMO+2(α)	-0.10539
421.1	0.7142	SOMO-1→LUMO+1(β)	0.5762
		SOMO→LUMO+2(β)	-0.54353
		SOMO→LUMO(α)	-0.445
		SOMO-2→LUMO(α)	-0.30482
		SOMO-1→LUMO+1(α)	0.12183
		SOMO→LUMO(β)	-0.11847
		SOMO-1→LUMO+3(β)	0.1054
		SOMO→LUMO(β)	0.10443
		SOMO-2→LUMO+2(β)	-0.101

Table S-3. Assignments of electronic transitions of 1b in the dication triplet state

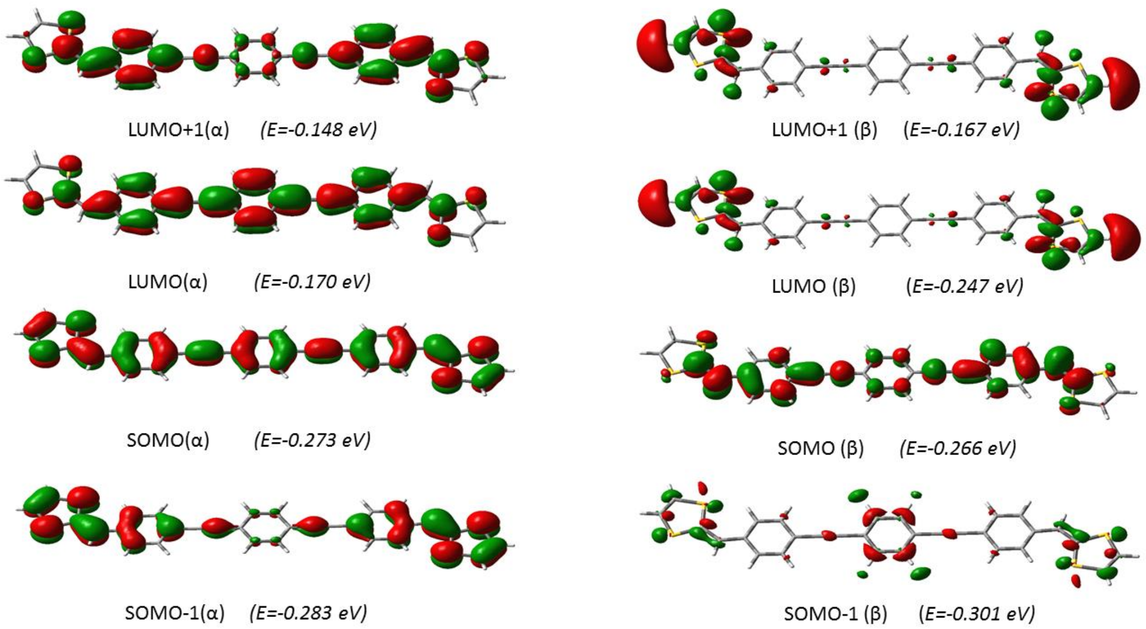
Wavelength (nm)	Oscillator strength (*f*)	Transition	MO contribution
1105.1	0.9399	SOMO→LUMO(β)	0.96778
		SOMO→LUMO(α)	-0.19161
		SOMO1→LUMO+1(α)	0.1396
554.9	1.5665	SOMO→LUMO(α)	0.77272
		SOMO1→LUMO+1(β)	0.47651
		SOMO→LUMO+2(β)	0.17438
		SOMO-2→LUMO(α)	0.16635
		SOMO→LUMO+2(α)	-0.14723
		SOMO-3→LUMO(β)	-0.12437
		SOMO→LUMO(β)	0.11664
		SOMO-2→LUMO+2(α)	-0.10259

Table S-4. Assignments of electronic transitions of **1b** the dication singlet state

Wavelength (nm)	Oscillator strength (*f*)	Transition	MO contribution
1025.4	2.9995	SOMO→LUMO(α)	0.84748
		SOMO→LUMO(β)	0.84748
		SOMO→LUMO(α)	-0.47177
		SOMO→LUMO(β)	-0.47177
397.5	0.7929	SOMO→LUMO+2(α)	0.57554
		SOMO→LUMO+2(β)	0.57554
		SOMO-1→LUMO+1(α)	0.39521
		SOMO-1→LUMO+1(β)	0.39521

Table S-5. Frontier molecular orbital energies of **1b** in various oxidation states

MO	Neu	RC (α , β)	DC(T) (α , β)	DC(S)
LUMO+3	-0.745	-2.972, -3.099	-5.479, -6.235	-5.624
LUMO+2	-0.781	-3.245, -3.870	-5.625, -6.760	-6.438
LUMO+1	-1.485	-4.027, -4.552	-6.600, -8.687	-7.116
LUMO	-2.120	-4.643, -6.709	-6.986, -8.969	-9.117
HOMO/SOMO	-5.030	-7.433, -7.244	-9.828, -10.388	-9.711
HOMO-1/SOMO-1	-5.277	-7.714, -8.193	-10.290, -11.256	-10.682
HOMO-2/SOMO-2	-6.020	-8.476, -9.038	-10.885, -11.453	-11.540
HOMO-3/SOMO-3	-6.780	-9.254, -9.536	-11.522, -11.842	-11.962
HOMO-4/SOMO-4	-7.156	-9.572, -9.539	-11.636, -11.843	-11.979



LUMO+1(α) *(E=-0.148 eV)*

LUMO+1 (β) *(E=-0.167 eV)*

LUMO(α) *(E=-0.170 eV)*

LUMO (β) *(E=-0.247 eV)*

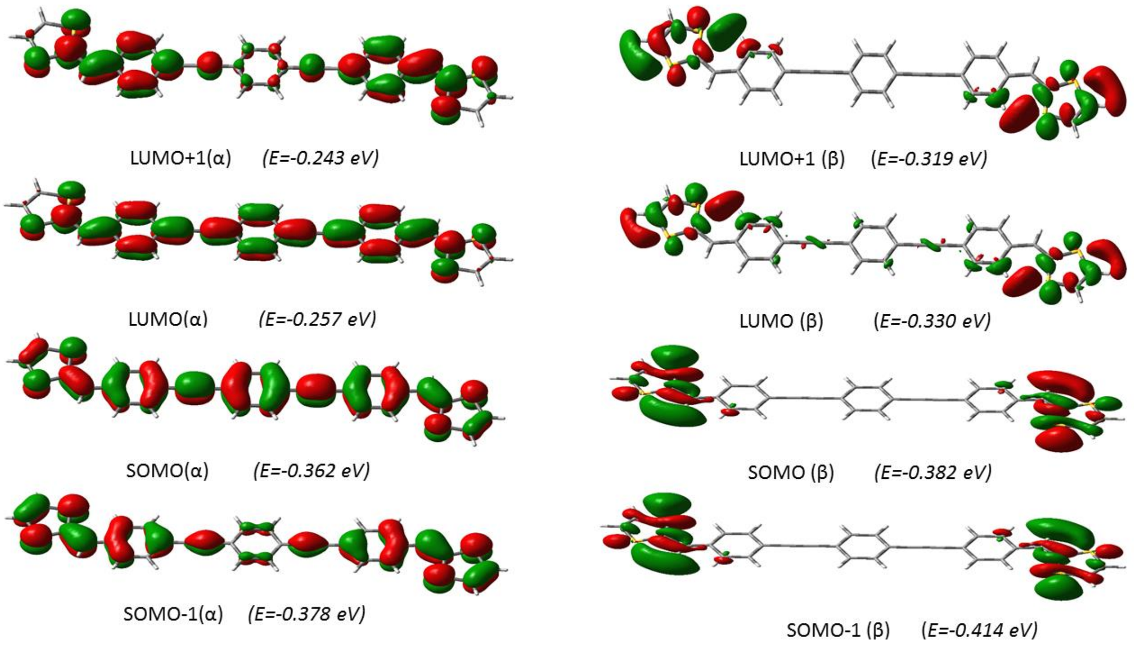
SOMO(α) *(E=-0.273 eV)*

SOMO (β) *(E=-0.266 eV)*

SOMO-1(α) *(E=-0.283 eV)*

SOMO-1 (β) *(E=-0.301 eV)*

Fig. S-1. Contours of frontier MOs for compound **1b** in the radical cation state and their eigenvalues calculated at the B3LYP/6-31++G (d,p) level.



LUMO+1(α) *(E=-0.243 eV)*

LUMO+1 (β) *(E=-0.319 eV)*

LUMO(α) *(E=-0.257 eV)*

LUMO (β) *(E=-0.330 eV)*

SOMO(α) *(E=-0.362 eV)*

SOMO (β) *(E=-0.382 eV)*

SOMO-1(α) *(E=-0.378 eV)*

SOMO-1 (β) *(E=-0.414 eV)*

Fig. S-2. Contours of frontier MOs for compound **1b** in the triplet dication state and their eigenvalues calculated at the B3LYP/6-31++G (d,p) level.

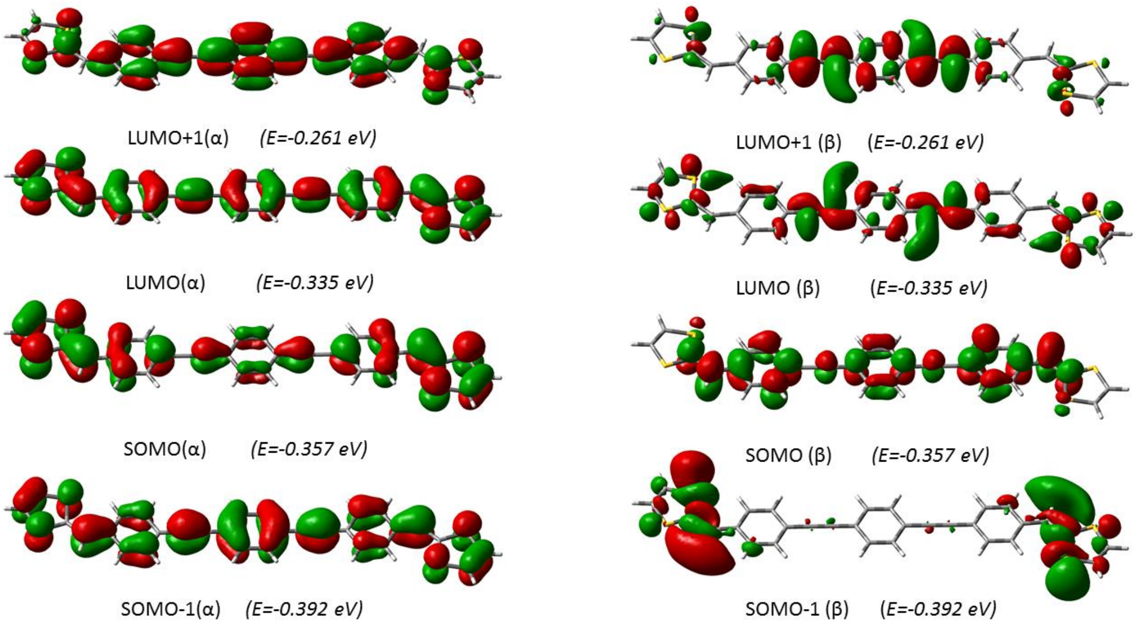


Fig. S-3. Contours of frontier MOs for compound **1b** in the singlet dication state and their eigenvalues calculated at the B3LYP/6-31++G (d,p) level.

2. Descriptions of Raman-Active Vibrational Modes

Tables S-6 to S-9 list the active vibrational modes of the Raman spectra for compound **1b** in the neutral, radical cation, dication singlet, and triplet states, respectively. DFT-calculated Raman frequencies were found to be slightly lower than experimental values, which can be rationalized by the effect of molecular orientation and inter-molecular interaction in the solid state on the vibrational energies. Fig. S-3 to S6 describe the vibrational eigenvectors of the outstanding Raman-active vibrational modes for compound **1b** in the neutral and cationic states.

Table S-6. Raman active vibrational modes for **1b** in the neutral state

Entry	**ν_{cal} (cm^{-1})**	**ν_{exp}(cm^{-1})**	**Mode**	**$\Delta\nu$ ($\nu_{exp}-\nu_{cal}$)**
1	1145.35	1126.7	C−H rocking	18.65
2	1592.35	1541.13	C=C stretching	51.22
3	1621.23	1565.1	C=C stretching	56.13
4	1640.64	1588.8	C−H rocking and C=C stretching	51.84
5	2280.39	2203.7	C≡C stretching	76.69

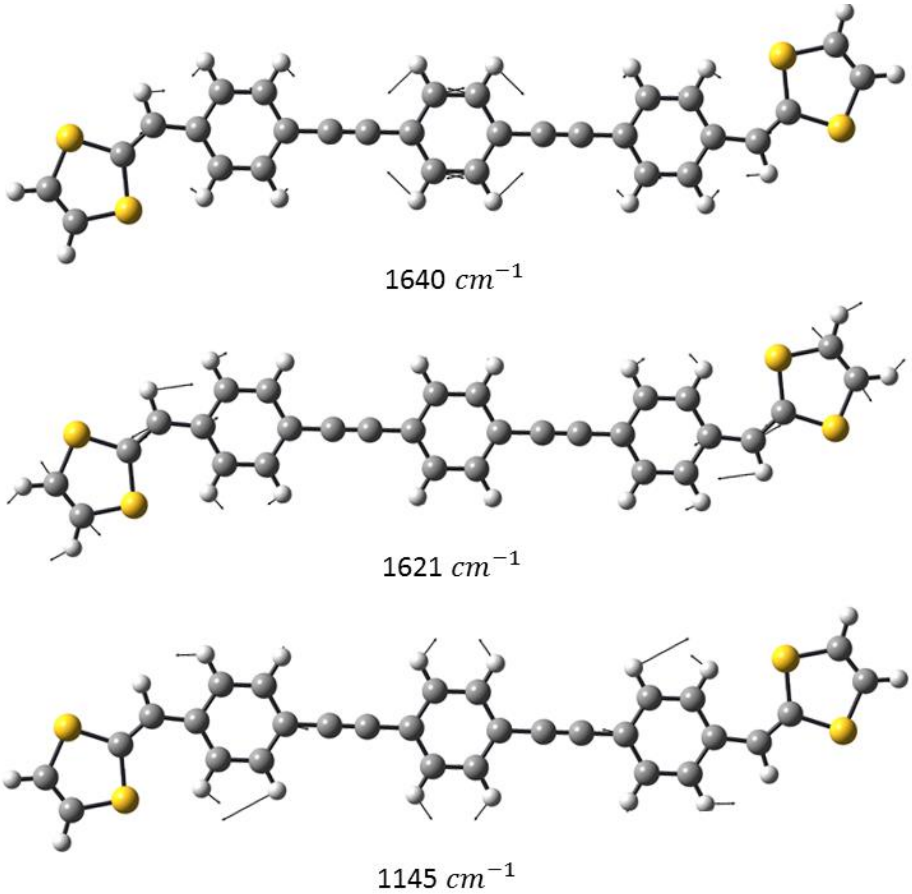


Fig. S-4. Raman active vibrational vectors for compound **1b** in the neutral state calculated at the B3LYP/6-31++G(d,p) level.

Table S-7. Raman active vibrational modes for **1b** in the radical cation state

Entry	**ν_{cal} (cm^{-1})**	**ν_{exp}(cm^{-1})**	**Mode**	**Dν (ν_{exp}-ν_{cal})**
1	747.16	722.13	C−C stretching	25.03
2	1133.50	1125.9	C−C stretching and C−H rocking	7.6
3	1225.17	1189.8	C−H rocking	35.37
4	1579.76	1567.9	C−H rocking and C=C stretching	11.86
5	1615	1588	C − H rocking and C = C stretching	27
6	2203.7	2203.7	C≡C stretching	76.69
7	3162.28	2898.7	C−H stretching	263.58

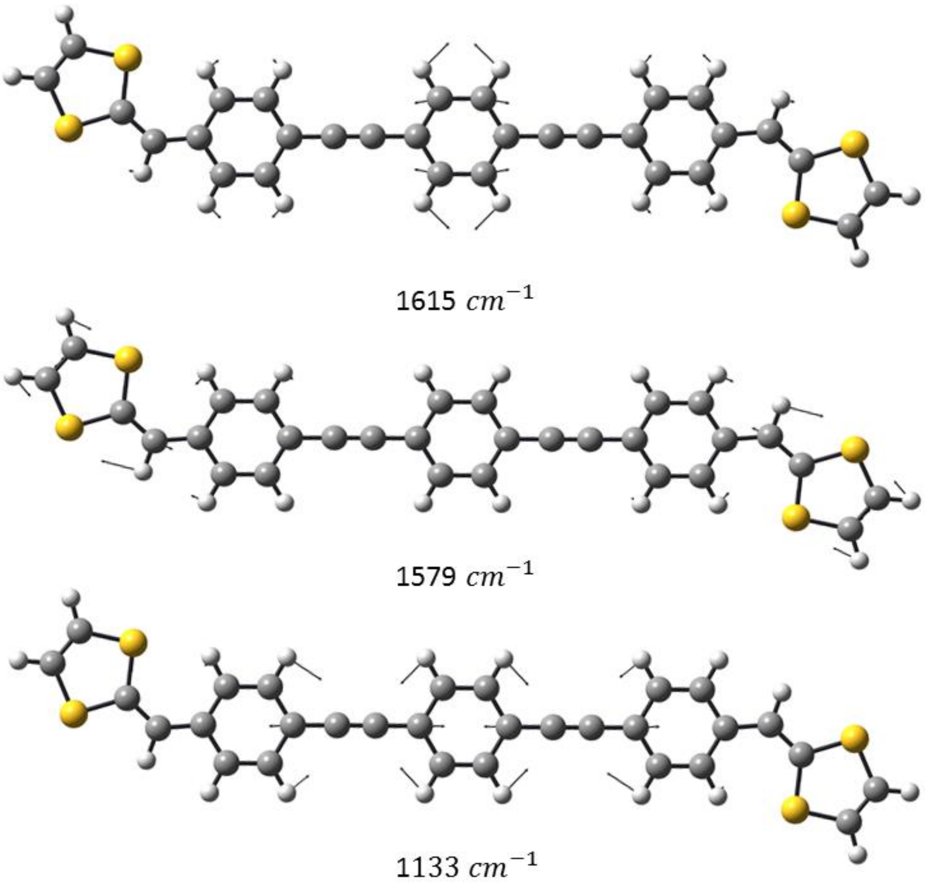


Fig. S-5. Raman active vibrational vectors for compound **1b** in the radical cation state calculated at the B3LYP/6-31++G(d,p) level.

Table S-8. Raman active vibrational modes for **1b** in the dication triplet state

Entry	**ν_{cal} (cm^{-1})**	**ν_{exp}(cm^{-1})**	**Mode**	**Dν (ν_{exp}-ν_{cal})**
1	478.99	514.81	C=C−C bending	35.82
2	1143.76	1108.8	C−H rocking	34.96
3	1209.25	1129.2	C−H rocking and C−C stretching	80.05
4	1329.71	1234.6	C−H scissoring	95.11
5	1384.91	1293.2	C−H rocking	91.71
6	1468.39	1369.7	C−H rocking and C=C stretching	98.69
7	1514.06	1411.3	C−H rocking and C=C stretching	102.76
8	1549.07	1471.5	C−H scissoring and C=C stretching	77.57
9	1631.18	1596.2	C−H scissoring and C=C stretching	34.98

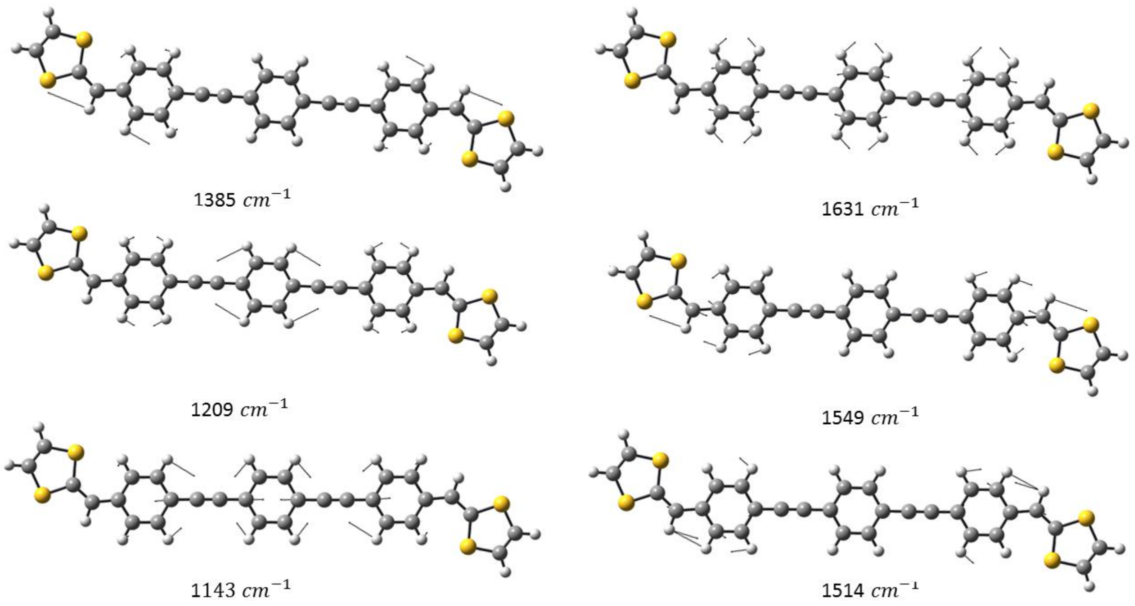
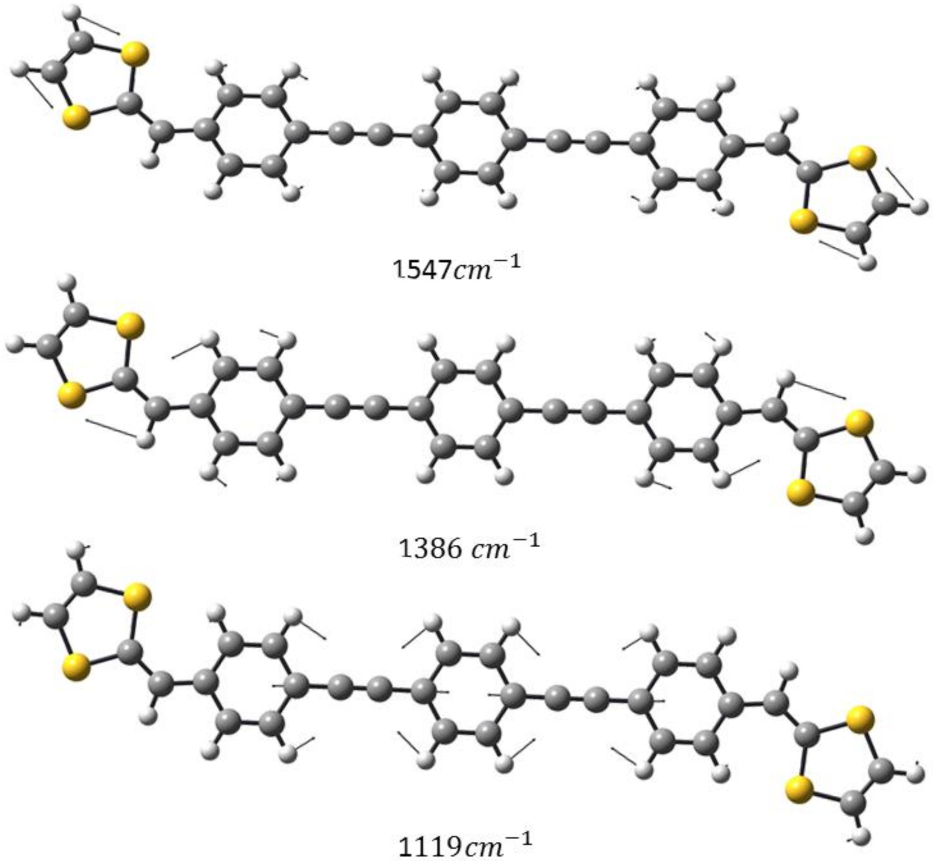


Fig. S-6. Raman active vibrational vectors for compound **1b** in the dication triplet state calculated at the B3LYP/6-31++G(d,p) level.

Table S-9. Raman active vibrational modes for **1b** in the dication singlet state

Entry	**ν_{cal} (cm^{-1})**	**Mode**
1	1119.57	C−H scissoring and C=C benzene ring stretching
2	1547.20	C=C dithiole ring stretching
3	1602.43	C−H scissoring and C=C benzene ring stretching
4	2175.40	C≡C stretching



$1547 cm^{-1}$

$1386\ cm^{-1}$

$1119 cm^{-1}$

Figure S-7. Raman active vibrational vectors for compound **1b** in the dication singlet state calculated at the B3LYP/6-31++G(d,p) level.

3. Raman Spectra of the Oxidized Film of 1a After Two Weeks

The film of **1a** spin-cast on a glass substrate was exposed to iodine vapour in a closed beaker. Raman spectra of the film were taken before and after exposure, as discussed in the paper. The film was then left in open air for two weeks and examined by Raman again.

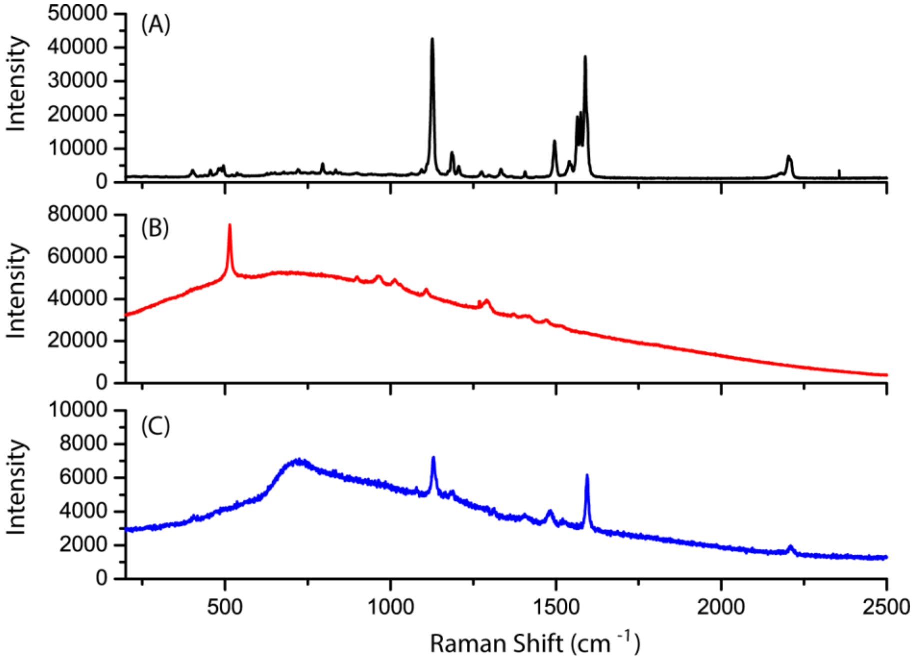


Fig. S-8. Raman spectra of the solid thin film of **1a** on a glass substrate measured (A) before exposure to iodine vapour, (B) after exposure to iodine vapour for 65 min, and (C) after being left in open air for two weeks.

4. Coordinates of Optimized Geometries and Energies

Cartesian coordinates of compound **1b** in the neutral state (sum of electronic and thermal Energies = -2746.293943 Hartree, zero-point correction = 0.377252 Hartree)

S1	-12.4576790000	0.9190120000	0.0000060000
S2	-10.7696220000	-1.5257330000	-0.0000270000
S3	10.7696220000	1.5257320000	-0.0000840000
S4	12.4576790000	-0.9190130000	0.0000540000
C5	12.5177050000	1.7358970000	-0.0000840000
C6	13.2769750000	0.6319700000	-0.0000210000
C7	10.7958610000	-0.2556240000	0.0000140000
C8	-13.2769750000	-0.6319710000	-0.0000130000
C9	-12.5177040000	-1.7358980000	-0.0000280000
C10	-10.7958610000	0.2556240000	-0.0000030000
C11	-9.7283030000	1.0968130000	0.0000080000
C12	9.7283030000	-1.0968140000	0.0000590000
C13	4.0399850000	-0.3993650000	0.0000120000
C14	2.8263910000	-0.2786040000	0.0000070000
C15	-2.8263910000	0.2786050000	-0.0000040000
C16	-4.0399850000	0.3993660000	-0.0000030000
C17	-8.2960250000	0.8389260000	0.0000040000
C18	-7.4317420000	1.9608190000	0.0000200000
C19	-6.0524420000	1.8263660000	0.0000180000
C20	-5.4541230000	0.5467470000	-0.0000020000
C21	-6.3043230000	-0.5785580000	-0.0000180000
C22	-7.6868800000	-0.4368530000	-0.0000160000
C23	5.4541230000	-0.5467460000	0.0000200000
C24	6.3043230000	0.5785590000	-0.0000520000
C25	7.6868800000	0.4368540000	-0.0000420000
C26	8.2960250000	-0.8389260000	0.0000410000
C27	7.4317420000	-1.9608180000	0.0001110000
C28	6.0524420000	-1.8263650000	0.0001010000
C29	-1.4111210000	0.1387910000	-0.0000030000
C30	-0.5718940000	1.2750420000	-0.0000310000
C31	0.8095140000	1.1392190000	-0.0000290000
C32	1.4111210000	-0.1387900000	0.0000020000
C33	0.5718930000	-1.2750410000	0.0000300000
C34	-0.8095140000	-1.1392180000	0.0000280000
H35	9.9833390000	-2.1550070000	0.0001210000
H36	12.8951780000	2.7513060000	-0.0001360000
H37	14.3603320000	0.6262360000	-0.0000150000
H38	-14.3603320000	-0.6262370000	-0.0000120000
H39	-12.8951770000	-2.7513070000	-0.0000410000
H40	-9.9833390000	2.1550070000	0.0000230000
H41	-7.8645880000	2.9577470000	0.0000360000

H42	-5.4195930000	2.7080680000	0.0000310000
H43	-5.8662570000	-1.5715650000	-0.0000340000
H44	-8.2871220000	-1.3378710000	-0.0000300000
H45	5.8662580000	1.5715660000	-0.0001160000
H46	8.2871220000	1.3378720000	-0.0001010000
H47	7.8645870000	-2.9577470000	0.0001760000
H48	5.4195920000	-2.7080670000	0.0001570000
H49	-1.0200770000	2.2633200000	-0.0000550000
H50	1.4418520000	2.0211410000	-0.0000510000
H51	1.0200770000	-2.2633190000	0.0000550000
H52	-1.4418520000	-2.0211400000	0.0000500000

Cartesian coordinates of compound **1b** in the radical cation state (Sum of electronic and thermal Energies = -2746.077723 Hartree, zero-point correction = 0.378033 Hartree)

S1	12.3950320000	0.9228740000	0.0000920000
S2	10.7515990000	-1.5219580000	-0.0001370000
S3	-10.7515970000	1.5219600000	-0.0000100000
S4	-12.3950330000	-0.9228690000	-0.0000190000
C5	-12.4915310000	1.7209400000	-0.0000270000
C6	-13.2391010000	0.6040150000	-0.0000320000
C7	-10.7630810000	-0.2404600000	-0.0000120000
C8	13.2391020000	-0.6040100000	-0.0000440000
C9	12.4915330000	-1.7209350000	-0.0001480000
C10	10.7630810000	0.2404620000	0.0000250000
C11	9.6787330000	1.0876610000	0.0000970000
C12	-9.6787340000	-1.0876590000	-0.0000200000
C13	-4.0283610000	-0.3929690000	-0.0000030000
C14	-2.8097290000	-0.2721650000	-0.0000030000
C15	2.8097280000	0.2721600000	0.0000160000
C16	4.0283600000	0.3929650000	0.0000250000
C17	8.2647660000	0.8293250000	0.0000700000
C18	7.3987230000	1.9596950000	0.0001570000
C19	6.0260330000	1.8268050000	0.0001420000
C20	5.4283430000	0.5399080000	0.0000380000
C21	6.2793560000	-0.5944640000	-0.0000500000
C22	7.6544680000	-0.4540610000	-0.0000340000
C23	-5.4283430000	-0.5399110000	-0.0000040000
C24	-6.2793560000	0.5944620000	0.0001020000
C25	-7.6544680000	0.4540610000	0.0001000000
C26	-8.2647670000	-0.8293250000	-0.0000080000
C27	-7.3987250000	-1.9596960000	-0.0001050000
C28	-6.0260340000	-1.8268070000	-0.0001060000
C29	1.4073310000	0.1357580000	0.0000090000
C30	0.5704440000	1.2815020000	0.0001050000
C31	-0.8051310000	1.1488400000	0.0001010000

C32	-1.4073320000	-0.1357630000	-0.0000010000
C33	-0.5704440000	-1.2815070000	-0.0000990000
C34	0.8051310000	-1.1488450000	-0.0000940000
H35	-9.9371990000	-2.1445240000	-0.0000490000
H36	-12.8788210000	2.7326630000	-0.0000320000
H37	-14.3222890000	0.5819730000	-0.0000430000
H38	14.3222900000	-0.5819660000	-0.0000380000
H39	12.8788250000	-2.7326580000	-0.0002390000
H40	9.9371970000	2.1445260000	0.0001910000
H41	7.8349130000	2.9543820000	0.0002390000
H42	5.3912630000	2.7064330000	0.0002100000
H43	5.8371780000	-1.5851060000	-0.0001300000
H44	8.2551860000	-1.3544190000	-0.0001020000
H45	-5.8371770000	1.5851040000	0.0001900000
H46	-8.2551850000	1.3544190000	0.0001970000
H47	-7.8349160000	-2.9543820000	-0.0001840000
H48	-5.3912660000	-2.7064360000	-0.0001850000
H49	1.0236030000	2.2669970000	0.0001840000
H50	-1.4384530000	2.0294840000	0.0001760000
H51	-1.0236030000	-2.2670020000	-0.0001780000
H52	1.4384520000	-2.0294890000	-0.0001690000

Cartesian coordinates of compound **1b** in the dication triplet state (sum of electronic and thermal Energies = -2745.779398 Hartree, zero-point correction = 0.378547 Hartree)

S1	12.3713100000	0.9400280000	0.0001020000
S2	10.7902440000	-1.5198880000	-0.0001330000
S3	-10.7902320000	1.5199050000	-0.0000050000
S4	-12.3713160000	-0.9399980000	-0.0000110000
C5	-12.5199360000	1.6910050000	0.0000070000
C6	-13.2489430000	0.5528380000	0.0000020000
C7	-10.7735650000	-0.2248890000	-0.0000150000
C8	13.2489480000	-0.5528020000	-0.0000280000
C9	12.5199490000	-1.6909740000	-0.0001360000
C10	10.7735640000	0.2249070000	0.0000260000
C11	9.6629010000	1.0689750000	0.0000950000
C12	-9.6629070000	-1.0689650000	-0.0000370000
C13	-4.0310130000	-0.3703710000	-0.0000150000
C14	-2.8135200000	-0.2546150000	-0.0000120000
C15	2.8135190000	0.2545820000	0.0000130000
C16	4.0310120000	0.3703420000	0.0000220000
C17	8.2617310000	0.8050850000	0.0000680000
C18	7.3959760000	1.9413400000	0.0001550000
C19	6.0250530000	1.8072110000	0.0001390000
C20	5.4318930000	0.5171180000	0.0000360000
C21	6.2816330000	-0.6232870000	-0.0000510000

C22	7.6533550000	-0.4839710000	-0.0000350000
C23	-5.4318960000	-0.5171370000	-0.0000170000
C24	-6.2816280000	0.6232740000	0.0000820000
C25	-7.6533510000	0.4839670000	0.0000790000
C26	-8.2617350000	-0.8050840000	-0.0000230000
C27	-7.3959880000	-1.9413460000	-0.0001140000
C28	-6.0250640000	-1.8072260000	-0.0001140000
C29	1.4028470000	0.1258970000	0.0000050000
C30	0.5805190000	1.2779240000	0.0000970000
C31	-0.7992300000	1.1541350000	0.0000910000
C32	-1.4028480000	-0.1259300000	-0.0000080000
C33	-0.5805200000	-1.2779570000	-0.0001020000
C34	0.7992290000	-1.1541680000	-0.0000950000
H35	-9.9179720000	-2.1268770000	-0.0000760000
H36	-12.9283440000	2.6951400000	0.0000160000
H37	-14.3321270000	0.5082940000	0.0000080000
H38	14.3321320000	-0.5082500000	-0.0000160000
H39	12.9283640000	-2.6951070000	-0.0002240000
H40	9.9179580000	2.1268880000	0.0001870000
H41	7.8323400000	2.9356760000	0.0002360000
H42	5.3886940000	2.6850920000	0.0002060000
H43	5.8366240000	-1.6121660000	-0.0001290000
H44	8.2543510000	-1.3845040000	-0.0001010000
H45	-5.8366120000	1.6121500000	0.0001650000
H46	-8.2543400000	1.3845050000	0.0001680000
H47	-7.8323590000	-2.9356790000	-0.0001880000
H48	-5.3887110000	-2.6851110000	-0.0001880000
H49	1.0393050000	2.2605760000	0.0001740000
H50	-1.4257690000	2.0393530000	0.0001630000
H51	-1.0393070000	-2.2606090000	-0.0001780000
H52	1.4257680000	-2.0393860000	-0.0001670000

Cartesian coordinates of compound **1b** in the dication singlet state (sum of electronic and thermal Energies = -2745.773027 Hartree, zero-point correction = 0.378722 Hartree)

S1	12.3424420000	0.9338140000	0.0000830000
S2	10.7535170000	-1.5189610000	-0.0001030000
S3	-10.7535130000	1.5189670000	0.0000640000
S4	-12.3424440000	-0.9338040000	-0.0000550000
C5	-12.4858980000	1.6987160000	0.0000720000
C6	-13.2171610000	0.5647400000	0.0000170000
C7	-10.7410800000	-0.2261380000	-0.0000210000
C8	13.2171620000	-0.5647290000	-0.0000220000
C9	12.4859020000	-1.6987060000	-0.0001080000
C10	10.7410790000	0.2261440000	0.0000240000
C11	9.6347870000	1.0760170000	0.0000820000

C12	-9.6347890000	-1.0760140000	-0.0000660000
C13	-4.0202980000	-0.3762620000	-0.0000210000
C14	-2.7948240000	-0.2578680000	-0.0000150000
C15	2.7948240000	0.2578570000	0.0000140000
C16	4.0202970000	0.3762530000	0.0000220000
C17	8.2396980000	0.8143950000	0.0000600000
C18	7.3682080000	1.9525190000	0.0001410000
C19	6.0024790000	1.8192910000	0.0001290000
C20	5.4053910000	0.5233750000	0.0000330000
C21	6.2611090000	-0.6196380000	-0.0000490000
C22	7.6284440000	-0.4785560000	-0.0000360000
C23	-5.4053920000	-0.5233810000	-0.0000280000
C24	-6.2611070000	0.6196330000	0.0000570000
C25	-7.6284430000	0.4785550000	0.0000480000
C26	-8.2396990000	-0.8143950000	-0.0000470000
C27	-7.3682120000	-1.9525210000	-0.0001290000
C28	-6.0024830000	-1.8192960000	-0.0001210000
C29	1.4061040000	0.1286620000	0.0000060000
C30	0.5725330000	1.2871470000	0.0000910000
C31	-0.7971180000	1.1618660000	0.0000840000
C32	-1.4061050000	-0.1286730000	-0.0000080000
C33	-0.5725340000	-1.2871580000	-0.0000940000
C34	0.7971180000	-1.1618770000	-0.0000870000
H35	-9.8940380000	-2.1324760000	-0.0001290000
H36	-12.8883010000	2.7050680000	0.0001210000
H37	-14.3002870000	0.5220920000	0.0000140000
H38	14.3002880000	-0.5220780000	-0.0000140000
H39	12.8883080000	-2.7050570000	-0.0001790000
H40	9.8940340000	2.1324800000	0.0001600000
H41	7.8059570000	2.9460310000	0.0002150000
H42	5.3648560000	2.6964360000	0.0001920000
H43	5.8165980000	-1.6089280000	-0.0001220000
H44	8.2313580000	-1.3774020000	-0.0001010000
H45	-5.8165940000	1.6089230000	0.0001310000
H46	-8.2313550000	1.3774020000	0.0001190000
H47	-7.8059630000	-2.9460320000	-0.0002000000
H48	-5.3648620000	-2.6964420000	-0.0001860000
H49	1.0332760000	2.2688150000	0.0001620000
H50	-1.4284690000	2.0435790000	0.0001490000
H51	-1.0332770000	-2.2688260000	-0.0001650000
H52	1.4284690000	-2.0435900000	-0.0001520000