SUPPORTING INFORMATION

New Journal of Chemistry

Synthesis of Benzothiadiazole-based molecules *via* direct arylation: an eco-friendly way of obtaining small semi-conducting organic molecules

Chunxiang Chen,[1,2] Daniel Hernández Maldonado,[1,2] Damien Le Borgne,[1,2] Fabienne Alary,[3] Barbara Lonetti,[4] Benoît Heinrich,[5] Bertrand Donnio,[5] Kathleen I. Moineau-Chane Ching.[1,2*]

[1]CNRS; LCC (Laboratoire de Chimie de Coordination) ; 205, route de Narbonne, F-31077 Toulouse, France.
[2]Université de Toulouse; UPS, INP; LCC; F-31077 Toulouse, France.
[3]CNRS, IRSAMC, Laboratoire de chimie et physique quantiques, 118 route de Narbonne, F-31062 Toulouse, France.
[4]Université de Toulouse; UPS/CNRS; IMRCP UMR 5623, 118 route de Narbonne, F-31062, Toulouse Cedex 9, France.
[5]Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS−Université de Strasbourg, UMR 7504, 67034 Strasbourg cedex 2, France.

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1. Synthesis

Table S1 Yields for molecule **5** obtained from different **Route c** conditions

r	palladium acetate	Yield of reaction
2.2	0.5%	71%
0.9	0.5%	100%
0.5	0.25%	100%

2. ^{1}H NMR spectra:

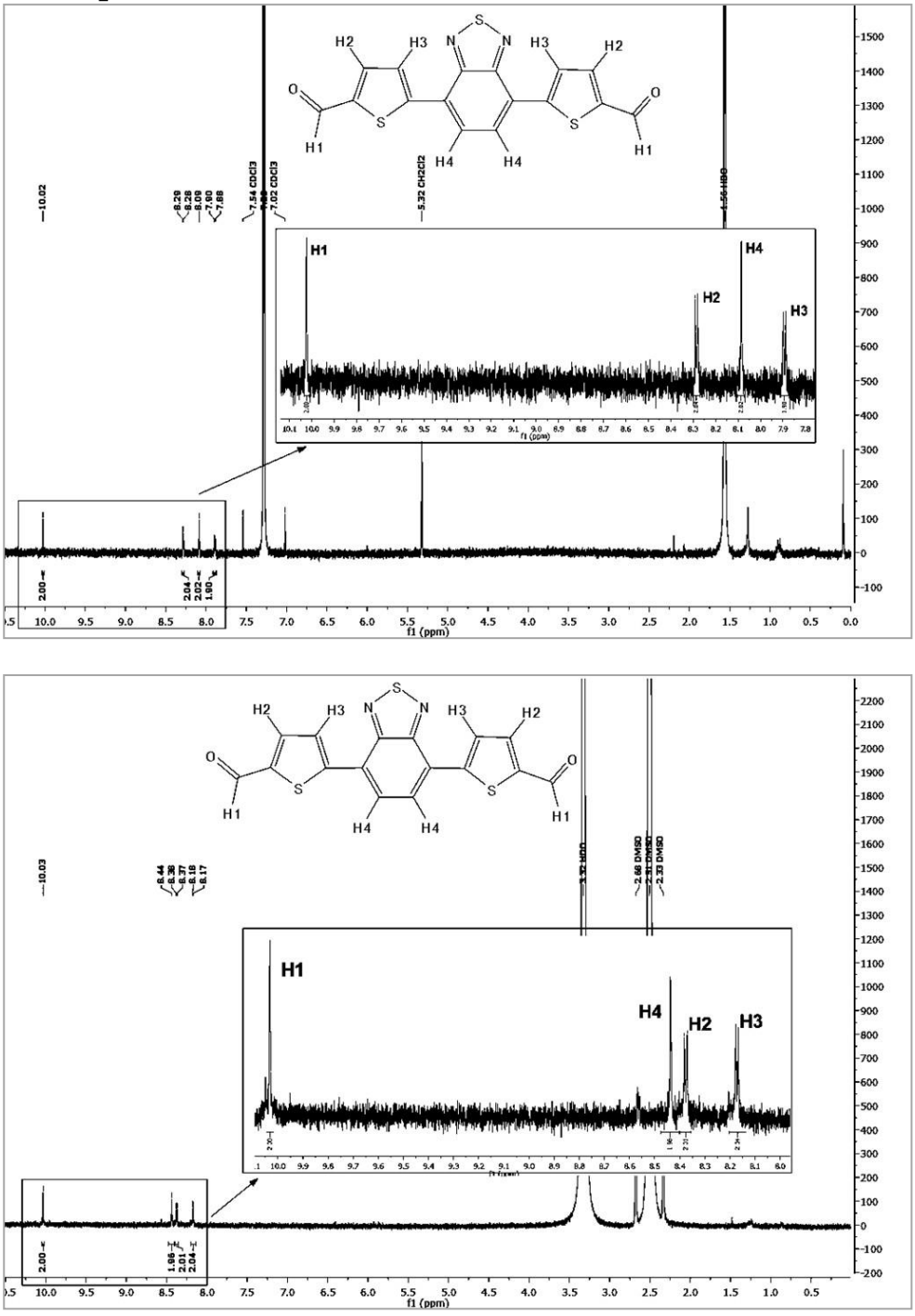


Figure S1: ^{1}H NMR spectrum of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis-(2-thiophenecarboxaldehyde) (molecule 5) in $CDCl_3$ (top) and ^{6}d DMSO (down)

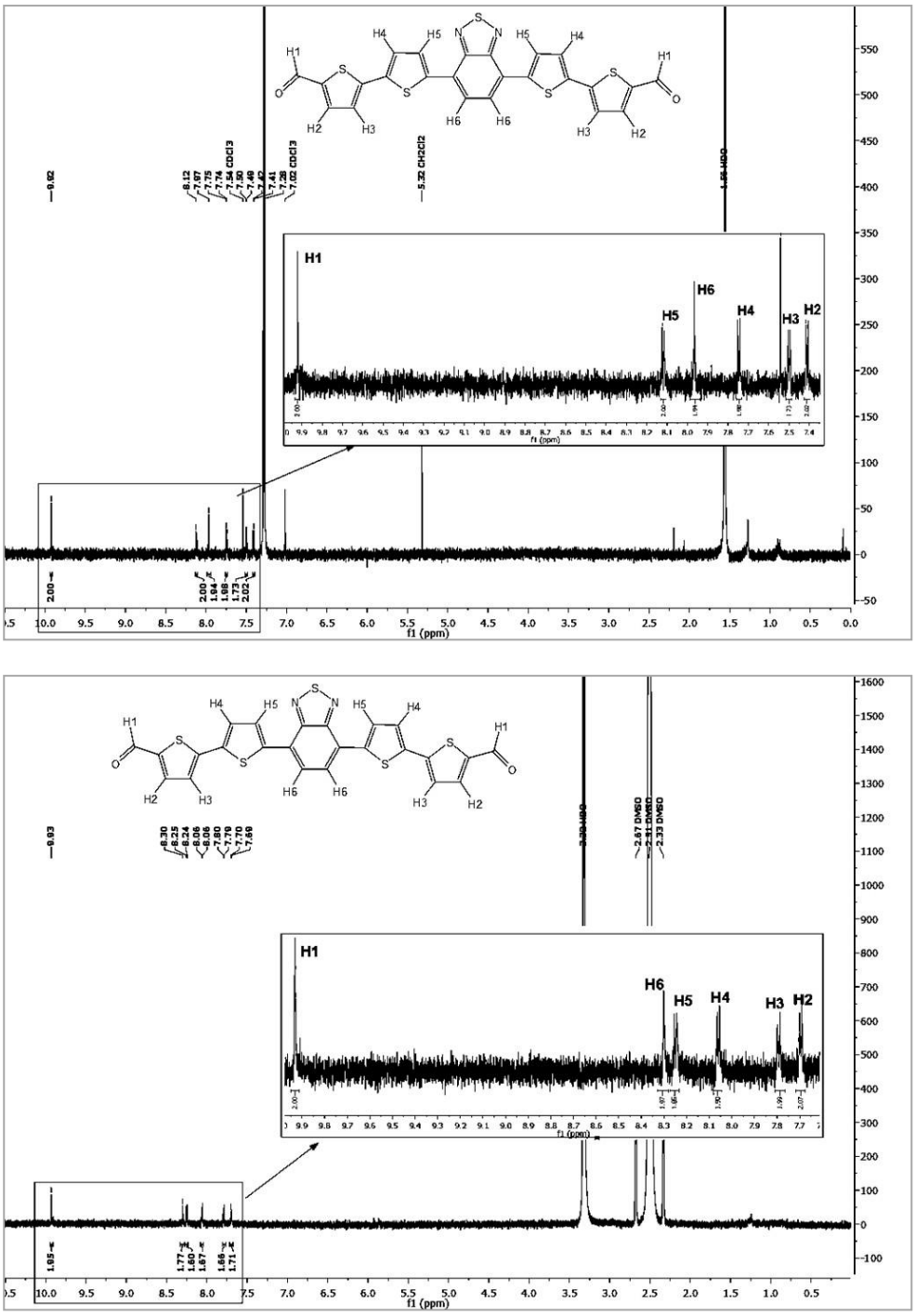


Figure S2: ^{1}H NMR spectrum of 5',5'''-(2,1,3-benzothiadiazole-4,7-diyl)bis-[(2,2'-bithiophene)-5-carboxaldehyde] (molecule 7) in $CDCl_3$ (top) and ^{6}d DMSO (down)

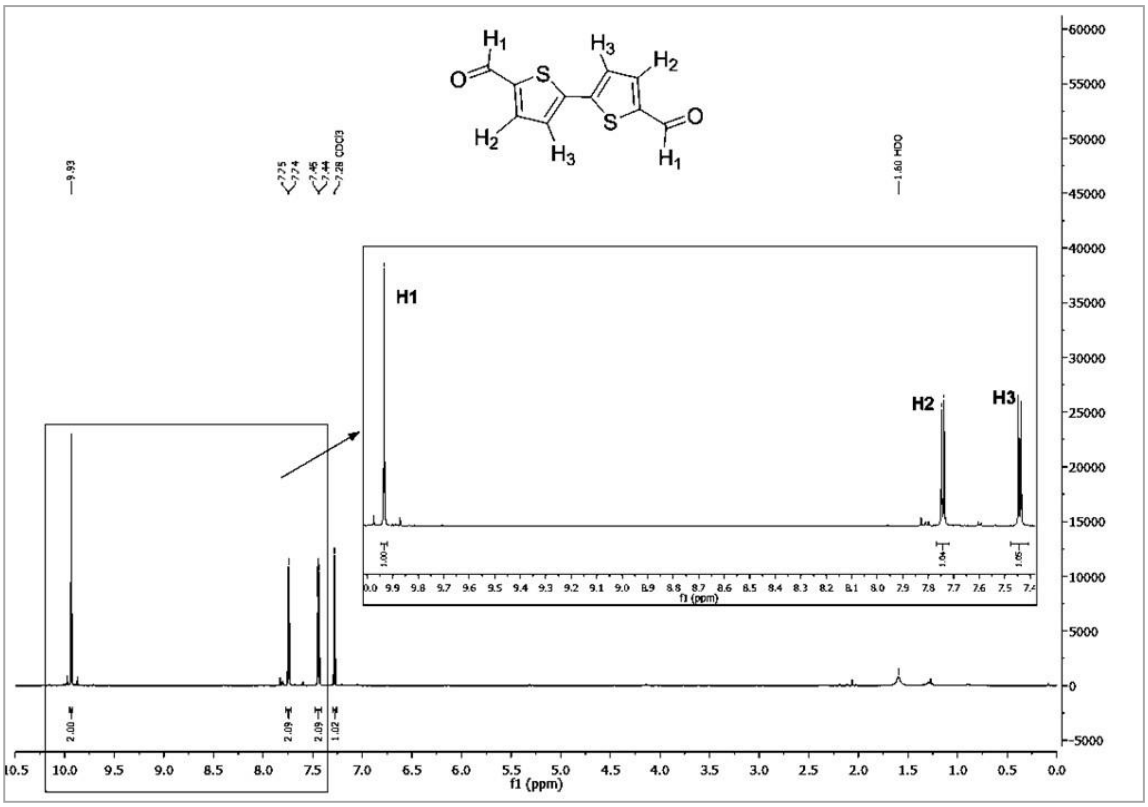


Figure S3: ^{1}H NMR spectrum of Homocoupling product of thiophene carboxhaldehyde in $CDCl_3$. (300 MHz) δ 9.93 (s, 2H), 7.75 (d, *J* = 4.0 Hz, 2H), 7.45 (d, *J* = 4.0 Hz, 2H).

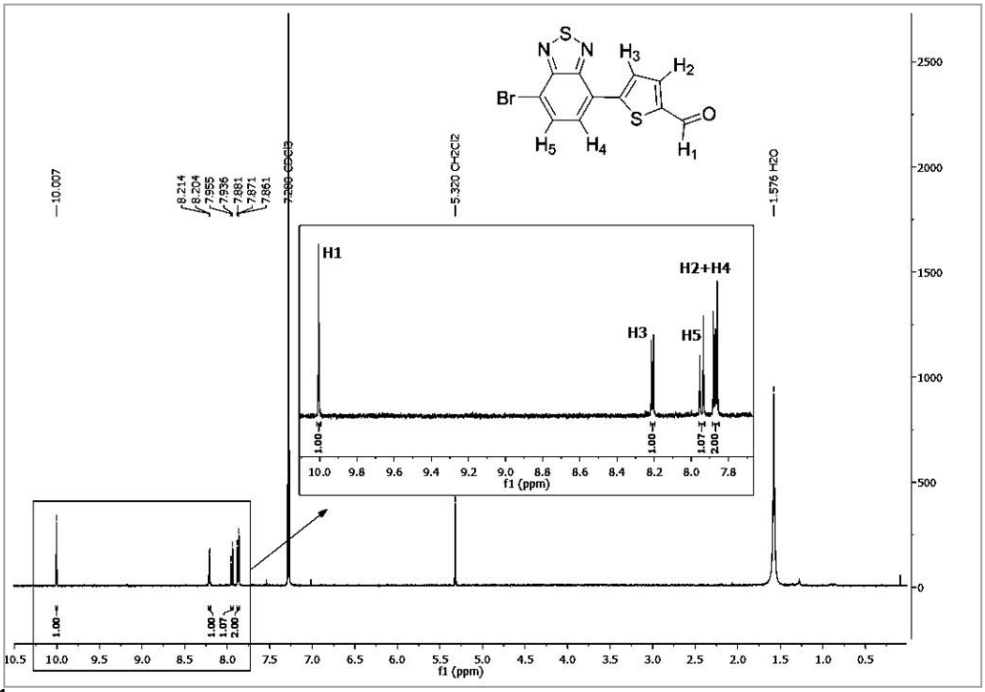


Figure S4: ^{1}H NMR spectrum of Monoarylated product in $CDCl_3$. (300 MHz) δ 10.01 (s, 1H), 8.21 (d, *J* = 4.0 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J*= 8 Hz, 1H), 7.87 (d, *J*= 4 Hz 1H).

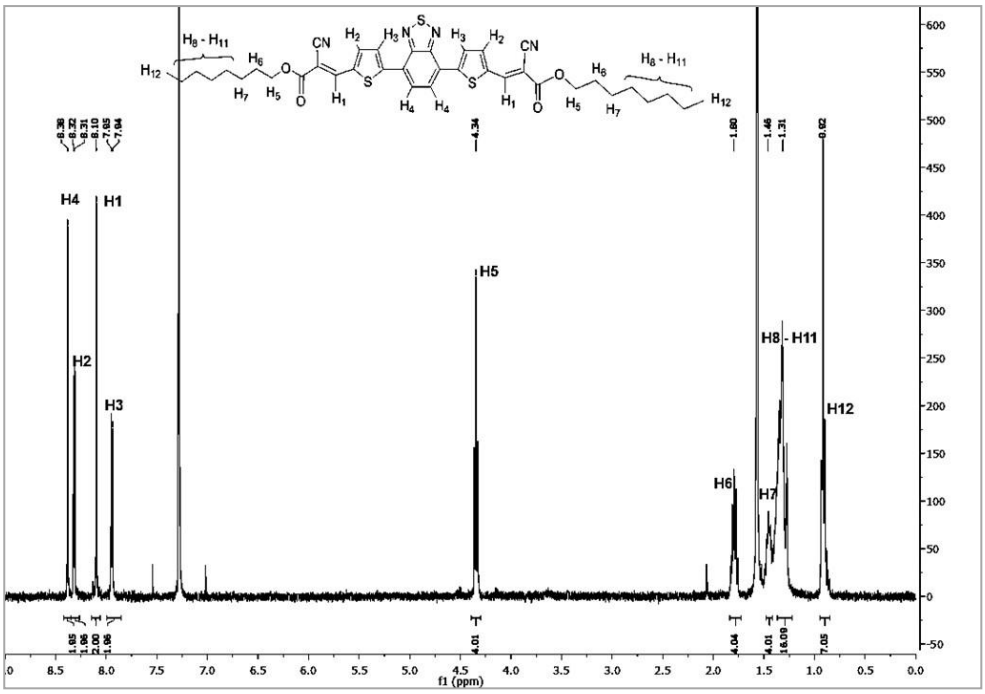


Figure S5: ^{1}H NMR spectrum of Bz(T_1CAO)$_2$

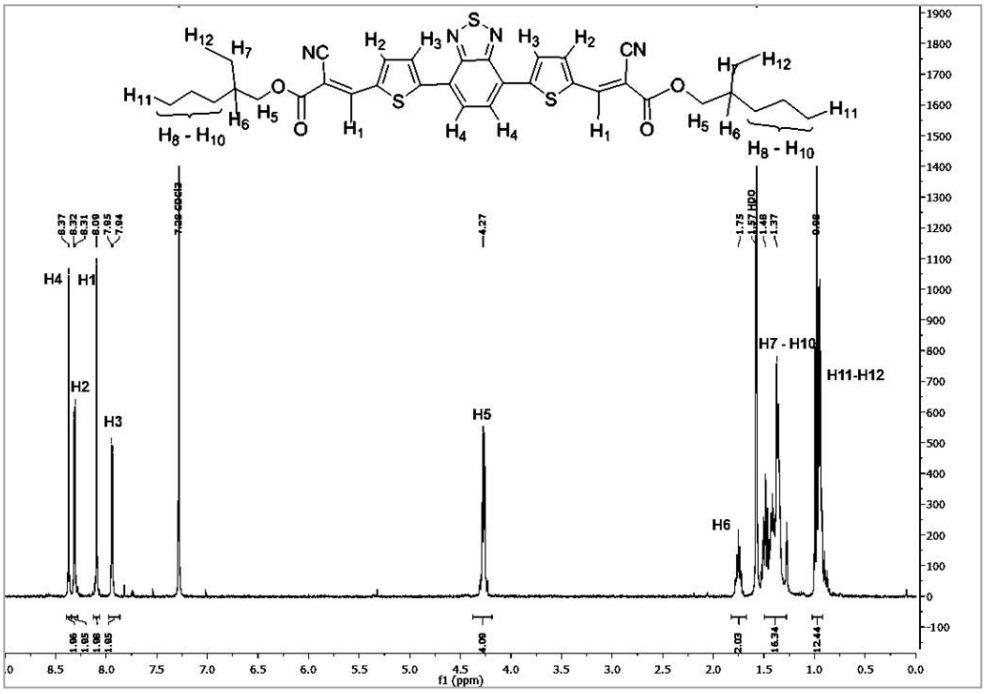


Figure S6: ^{1}H NMR spectrum of Bz(T_1CAEH)$_2$

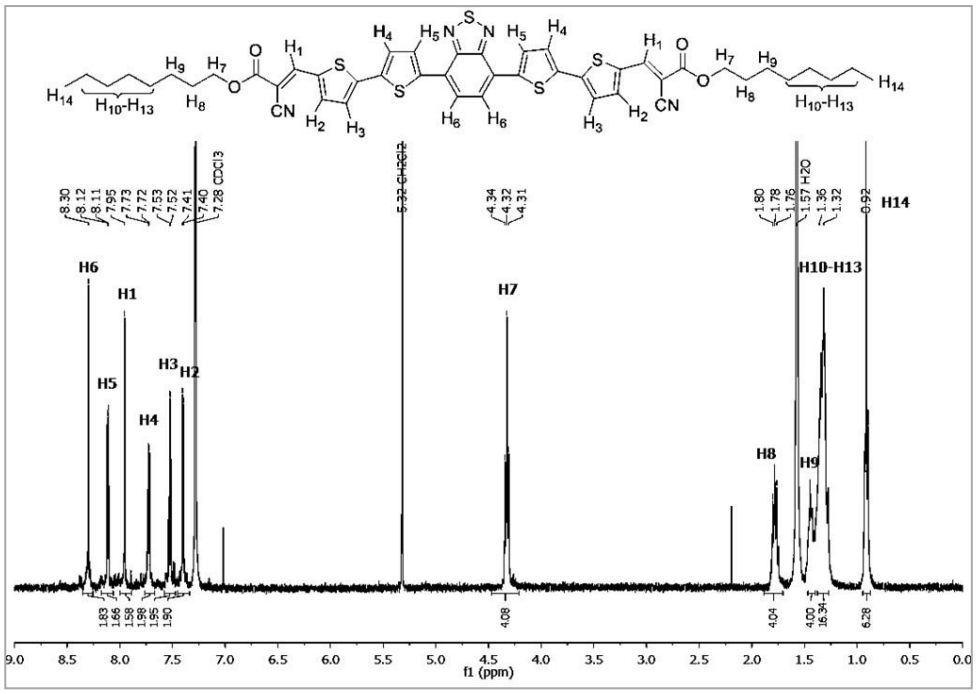


Fig S7: ^{1}H NMR spectrum of Bz(T_2CAO)$_2$

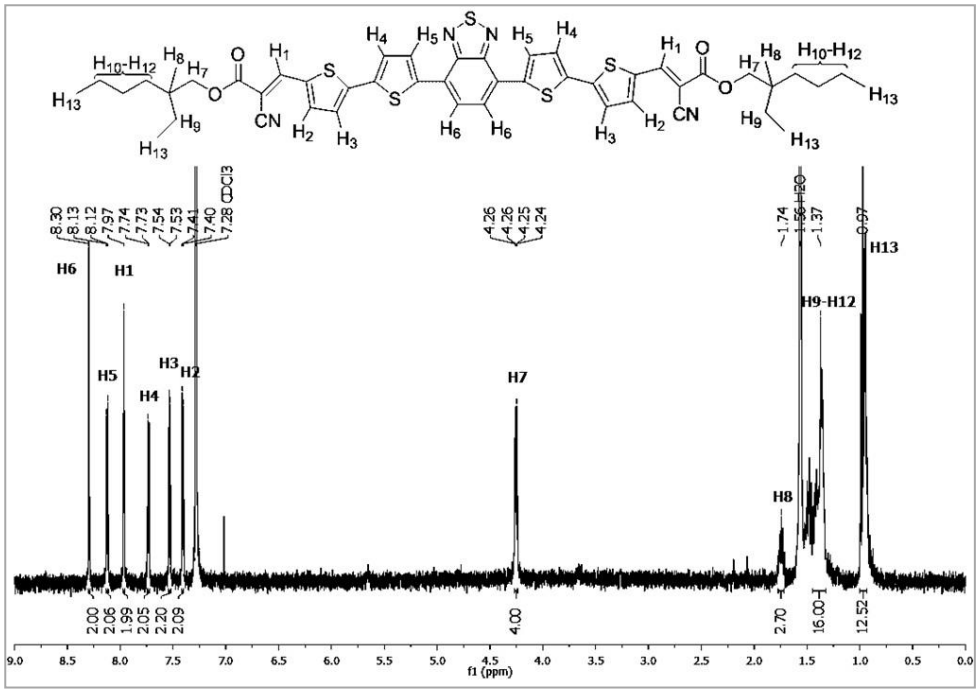


Fig S8: ^{1}H NMR spectrum of Bz(T_2CAEH)$_2$

3. E-factor and costs

Prices are calculated from raw materials purchased from Aldrich unless indicated

Table S2: Molecule 5 obtained *via* route a, b, and c.

reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)	price (€/g or €/mL)	total price (€)
Route a						
2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester)	0.247			0.247	138.000	34.086
5-Bromo-2-thiophenecarboxaldehyde (1.607 g/mL at 25 °C)	0.314			0.314	3.170	0.995
toluene		10	0.865	8.650	0.050	0.500
K_2CO_3 2mol/L (= 280 g/L)		5		1.400	0.140	0.196
H_2O		29	1	29.000		
Aliquat 336		4-5 drops = 0.25	0.884	0.221	0.150	0.033
$Pd(PPh_3)_4$	0.045			0.045	30.000	1.350
ethyl acetate		20	0.902	22.173	0.085	1.700
dichloromethane		20	1.33	26.600	0.059	1.180
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	101.650					
amount of product	0.230					
E-Factor route a	(total masses - amount)/amount					**440.96**
cost (€/g)						175.83
Route b						
reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)		
4,7-Dibromobenzo-2,1,3-thiadiazole [a]	0.100			0.100	6.600	0.660
2-thiophenecarboxaldehyde [b]	0.084			0.084	0.330	0.028
$Pd(OAc)_2$ [c]	0.008			0.008	69.000	0.524
PtBu2Me.HBF4	0.017	5		0.017	63.000	1.065
PivOH	0.035			0.035	0.270	0.009
K_2CO_3	0.141			0.141	0.140	0.020
toluene		4	0.865	3.460	0.050	0.173
H_2O		20	1	20.000		
ethyl acetate		20	0.902	22.173	0.085	1.700
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	59.018					
amount of product	0.119					
E-Factor route b	(total masses - amount)/amount					**494.95**
cost (€/g)						38.48
Route c						
reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)		
4,7-Dibromobenzo-2,1,3-thiadiazole	0.500			0.500	6.600	3.300
2-thiophenecarboxaldehyde	0.419			0.419	0.280	0.117
DMA		6	0.937	5.622	0.040	0.240
KOAc	0.334			0.334	0.300	0.100
Pd(OAc)2	0.002			0.002	63.000	0.120
H_2O		20	1	20.000		
ethyl acetate		20	0.902	22.173	0.085	1.700
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	62.050					
amount of product	0.430					
E-Factor route c	(total masses - amount)/amount					**143.30**
cost (€/g)						13.90

a, b, c: purchased from Interchim, Alfa Aesar, and Strem, respectively

Table S3: Molecule 5 obtained *via* route c and different ratios (r), b, and c.

Route c / **r = 2.2**						
reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)		
4,7-Dibromobenzo-2,1,3-thiadiazole	0.500			0.500	6.600	3.300
2-thiophenecarboxaldehyde	0.419			0.419	0.280	0.117
DMA		6	0.937	5.622	0.040	0.240
KOAc	0.334			0.334	0.300	0.100
Pd(OAc)2	0.002			0.002	63.000	0.120
H_2O		20	1	20.000		
ethyl acetate		20	0.902	22.173	0.085	1.700
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	62.050					
amount of product	0.430					
E-Factor route c	(total masses - amount)/amount					**143.30**
cost (€/g)						13.90
Route c / **r = 0.9**						
reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)		
4,7-Dibromobenzo-2,1,3-thiadiazole	0.500			0.500	6.600	3.300
2-thiophenecarboxaldehyde	0.172			0.172	0.280	0.048
DMA		6	0.937	5.622	0.040	0.240
KOAc	0.334			0.334	0.300	0.100
Pd(OAc)2	0.002			0.002	63.000	0.120
H_2O		20	1	20.000		
ethyl acetate		20	0.902	22.173	0.085	1.700
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	61.803					
amount of product	0.272					
E-Factor route c	(total masses - amount)/amount					**226.22**
cost (€/g)						21.72
Route c / **r = 0.5**						
reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)		
4,7-Dibromobenzo-2,1,3-thiadiazole	0.500			0.500	6.600	3.300
2-thiophenecarboxaldehyde	0.095			0.095	0.280	0.027
DMA		6	0.937	5.622	0.040	0.240
KOAc	0.334			0.334	0.300	0.100
Pd(OAc)2	0.002			0.002	63.000	0.120
H_2O		20	1	20.000		
ethyl acetate		20	0.902	22.173	0.085	1.700
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	61.726					
amount of product	0.151					
E-Factor route c	(total masses - amount)/amount					**407.78**
cost (€/g)						38.98

Table S4: Molecule 7 obtained *via* routes a and c.

reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)	price (€/g or €/mL)	total price (€)
Route a						
2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester)	0.173			0.173	138.000	23.874
5'-Bromo-2,2'-bithiophene-5-carboxaldehyde	0.305			0.305	54.000	16.470
toluene		25	0.865	21.625	0.050	1.250
K_2CO_3 2mol/L (= 280 g/L)		5		1.400	0.140	0.196
H_2O		29	1	29.000		
Aliquat 336		4-5 drops = 0.25	0.884	0.221	0.150	0.033
$Pd(PPh_3)_4$	0.039			0.039	30.000	1.155
ethyl acetate		20	0.902	22.173	0.085	1.700
dichloromethane		20	1.33	26.600	0.059	1.180
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	114.536					
amount of product	0.230					
E-Factor route a	(total masses - amount)/amount					**496.98**
cost (€/g)						201.12
Route c						
reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)		
4,7-Dibromobenzo-2,1,3-thiadiazole	0.500			0.500	6.600	3.300
2,2'-bithiophene-5-carbaldehyde [d]	0.727			0.727	37.000	26.899
DMA		6	0.937	5.622	0.040	0.240
KOAc	0.334			0.334	0.300	0.100
Pd(OAc)2	0.002			0.002	63.000	0.120
H_2O		20	1	20.000		
ethyl acetate		20	0.902	22.173	0.085	1.700
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
total masses	62.358					
amount of product	0.811					
E-Factor route c	(total masses - amount)/amount					**75.89**
cost (€/g)						40.39

d: purchased from TCI Europe

Table S5: $Bz(T_1CAO)_2$

reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)	price (€/g or €/mL)	total price (€)
molecule **5**	0.450			0.450	14.000	6.300
triethylamine	1.680	2.3	0.73	1.680	0.283	0.651
octylcyanoacetate	2.500	2.7	0.924	2.500	3.750	9.375
dichloromethane		30	1.33	39.900	0.059	1.770
water		10	1	10.000		
ethanol		10	1	10.000	0.032	0.320
petroleum ether 40-60°C		30	0.65	19.500	0.020	0.600
ethyl acetate		20	0.902	22.173	0.085	1.700
total masses	106.203					
amount of product	0.460					
E-Factor route c	(total masses - amount)/amount					**229.88**
cost (€/g)						45.03

Table S6: $Bz(T_1CAEH)_2$

reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)	price (€/g or €/mL)	total price (€)
molecule **5**	0.190			0.190	14.000	2.660
triethylamine	0.700	0.96	0.73	0.700	0.283	0.272
2-ethylhexylcyanoacetate [d]	1.050	1.11	0.95	1.050	1.080	1.199
dichloromethane		20	1.33	26.600	0.059	1.180
water		10	1	10.000		
ethanol		10	1	10.000	0.032	0.320
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
ethyl acetate		8	0.902	7.216	0.085	0.680
total masses	68.756					
amount of product	0.180					
E-Factor route c	(total masses - amount)/amount					**380.98**
cost (€/g)						37.28

d: purchased from TCI Europe

Table S7: $Bz(T_2CAO)_2$

reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)	price (€/g or €/mL)	total price (€)
molecule **7**	0.500			0.500	40.000	20.000
triethylamine [d]	1.240	1.7	0.73	1.241	0.283	0.481
octylcyanoacetate	1.850	2	0.924	1.848	3.750	7.500
dichloromethane		40	1.33	53.200	0.059	2.360
ethanol		10	1	10.000	0.032	0.320
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
ethyl acetate		15	0.902	13.530	0.085	1.275
total masses	93.319					
amount of product	0.640					
E-Factor route c	(total masses - amount)/amount					**144.81**
cost (€/g)						50.53

d: purchased from TCI Europe

Table S8: $Bz(T_2CAEH)_2$

reagent	amount (g)	amount (mL)	density (g/mL)	total mass (g)	price (€/g or €/mL)	total price (€)
molecule **7**	0.500			0.500	40.000	20.000
triethylamine [d]	1.240	1.7	0.73	1.241	0.283	0.481
2-ethylhexylcyanoacetate	1.900	2	0.95	1.900	1.080	2.160
dichloromethane		40	1.33	53.200	0.059	2.360
ethanol		10	1	10.000	0.032	0.320
petroleum ether 40-60°C		20	0.65	13.000	0.020	0.400
ethyl acetate		15	0.902	13.530	0.085	1.275
total masses	93.371					
amount of product	0.570					
E-Factor route c	(total masses - amount)/amount					**162.81**
cost (€/g)						47.36

d: purchased from TCI Europe

SAXS analysis

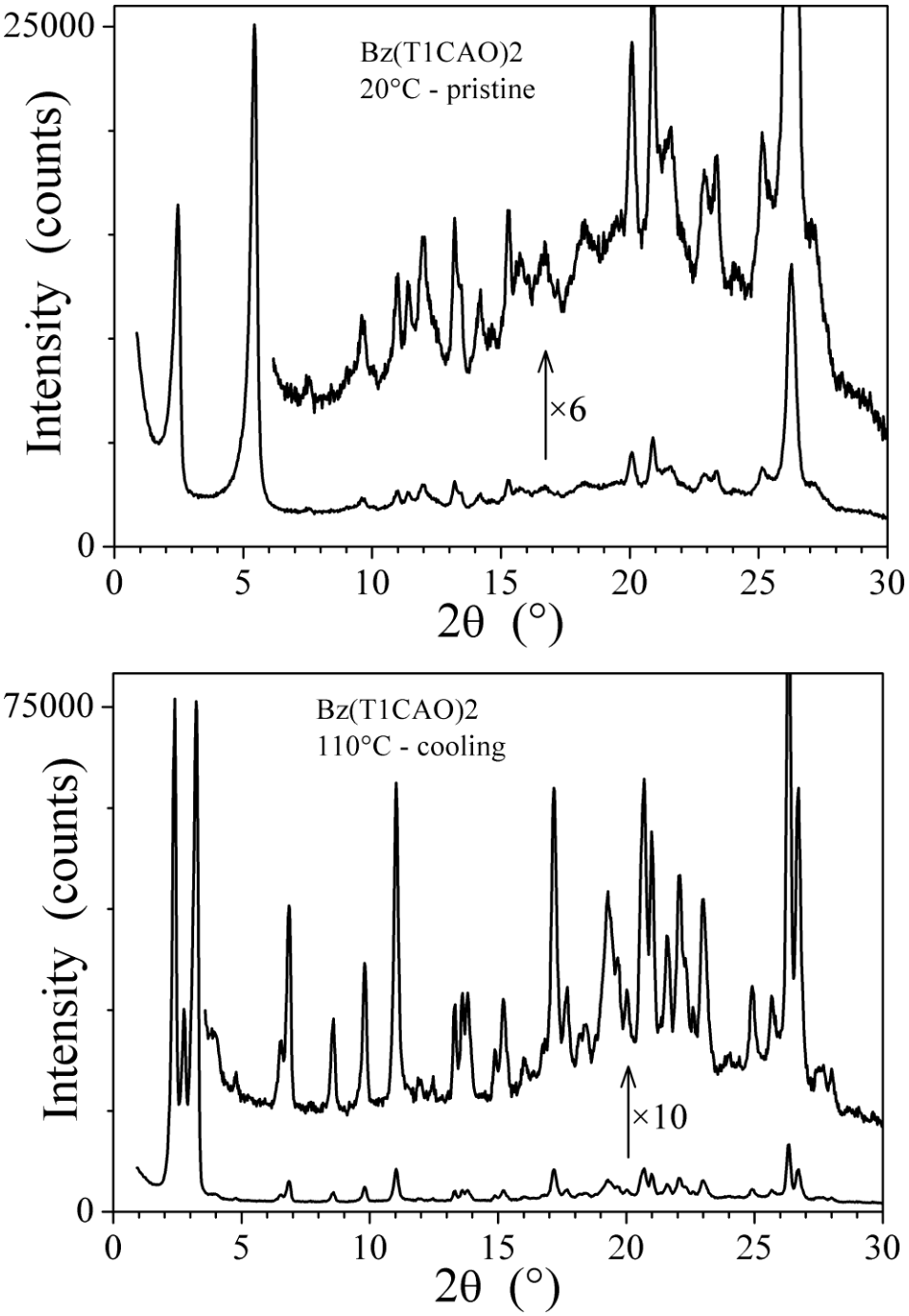


Figure S9: SAXS patterns of **Bz(T$_1$CAO)$_2$** in the pristine state (top) and at 110°C in the crystalline phase obtained on cooling from the smectic A phase (bottom).

Theoretical calculations

Table S9. Ground-state Cartesian coordinates of **BzT1** in CH_2Cl_2

C	3.52188127462369	-3.50865462434769	-0.02312086412719
H	6.05939949349445	0.34079056482612	-0.16504781892921
N	8.34754466317542	-3.61580969983038	-0.39850122729142
S	7.78134230640971	-5.12995119833919	-0.41132145162661
N	6.19618920219010	-4.83712977703144	-0.29639133286658
C	6.03685701268153	-3.51060996373109	-0.24056115463085
C	7.29540800677292	-2.79546367637270	-0.30402323959877
C	4.78835992851491	-2.81384498607865	-0.13664327250968
C	4.88389087188389	-1.43301340167563	-0.13159319269990
C	6.10262632415653	-0.74003211549418	-0.19453001055549
C	7.33712935706796	-1.36252408278048	-0.26993413768217
S	8.56954225326217	1.12263303004226	-0.29344593719670
C	8.57762518478992	-0.61370506658070	-0.30053210408760
C	9.88321744961530	-1.08416482328796	-0.32723821496625
C	10.85023200733237	-0.07280873791571	-0.34172332566478
C	10.31254966787906	1.20514797741097	-0.33005747589957
H	10.11406053777243	-2.13560822455464	-0.33794518110014
H	11.91028457782639	-0.26775026570512	-0.36430544083503
H	3.98084514931512	-0.84213875439689	-0.05211909215821
C	10.91024054080739	2.49624361713146	-0.34754125491095
C	12.22597362628845	2.84551792901466	-0.37544226368309
H	10.23211346392808	3.34239410790516	-0.34899807262004
C	13.25365766837061	1.87128511437694	-0.44599225781470
N	14.07593508392382	1.06407276748994	-0.52184675213081
C	12.52617937758235	4.31799670827946	-0.44366363569693
O	11.69921152568739	5.09793067390376	-0.84241946595305
O	13.73593848469114	4.77769252563035	-0.07832427552227
C	14.62228655700479	4.05698470184201	0.79695399167566
H	15.18272033341919	4.82130202459810	1.33032028348594
H	14.06880680258562	3.45104458856012	1.51314960989640
H	15.30001802495926	3.43020128694078	0.22187604487296
S	2.00966048791308	-2.65601668233909	-0.06791409326934
C	3.29969902312667	-4.86470977431273	0.16077461143412
C	1.95110273866125	-5.20811511097430	0.28054812227799
H	4.10579180022806	-5.57562265383982	0.20879634646427
H	1.60914873140766	-6.21797277178447	0.43685724381129
C	1.09363248732899	-4.12343936431457	0.17869295131518
C	-0.32578079743771	-4.03448690504576	0.22812633866813
C	-1.24307122332730	-5.01685483006144	0.44691508661511
H	-0.75912302713140	-3.05165612662592	0.08016765792875
C	-0.85790637251548	-6.34501901647474	0.75767625068832
N	-0.52905473371920	-7.41781575858922	1.02971138566497
C	-2.68827552642340	-4.60505211956293	0.47144125465656
O	-3.00294546205531	-3.46204849561969	0.68348862096789
O	-3.64948579827646	-5.52730634719019	0.28269727148835
C	-3.43328962670595	-6.77580969871453	-0.40196358392883
H	-4.36826928238882	-6.98741321944136	-0.91549299006198
H	-2.63201635444213	-6.69906220231025	-1.13506158299990
H	-3.21178882225456	-7.56508214262861	0.31208763110612

Table S10. Ground-state Cartesian coordinates of **BzT2** in CH_2Cl_2

C	3.34397615474397	-3.36444939449446	0.32636020626414
H	5.71170221841585	0.59725040409583	0.33604861771635
N	8.17006785306471	-3.23946094206575	-0.03554584845209
S	7.67530567705331	-4.77716374647891	-0.10650983001549
N	6.07714047453702	-4.56190121214709	0.01497562164131
C	5.85610735592532	-3.24724074003635	0.11809057044102
C	7.08159697655619	-2.47377458384515	0.08702339206960
C	4.57650542985758	-2.61115745483943	0.24297622512345
C	4.61525246756855	-1.22758313993114	0.29615897962728
C	5.80285693937480	-0.47922823528582	0.26694904662554
C	7.06417900642246	-1.04262597888611	0.17737173493329
S	8.20689171411887	1.49325753420363	0.26011223202984
C	8.27618377204463	-0.25390806920209	0.18646048265958
C	9.59292075747857	-0.67333201426819	0.15872968030302
C	10.52110049668406	0.37790340196747	0.19873446970869
C	9.94218639973843	1.62725227549200	0.25851277277009
H	9.86536054995040	-1.71332442056120	0.11047916562074
H	11.59144275058109	0.22643970952988	0.18502190472244
H	3.68730321007410	-0.67809032859434	0.38555380708297
C	13.43990941708773	5.57048047468734	0.31578361541561
C	14.77032782397694	5.27507408948561	0.27481763868192
H	13.21641479628499	6.63171533160719	0.32853753976167
C	15.23455713908139	3.93997737312530	0.17830111862692
N	15.60082764514565	2.84933609206961	0.07444803203303
C	15.70960220292820	6.44115946507010	0.19850330813517
O	15.33137381308462	7.50990204172196	-0.20926187518677
O	16.99664382438647	6.30063069584158	0.56663560698190
C	17.47137530548624	5.23783657076521	1.41113172980852
H	18.30078524215240	5.66713313719825	1.96860270079816
H	16.70455562011443	4.90336073507709	2.10833956307816
H	17.81751112257238	4.40013982076536	0.80997031680404
S	1.79641541514106	-2.55735446447629	0.43271380503160
C	3.16573924608899	-4.73363217317148	0.37035412753538
C	1.82426635480318	-5.12606442582424	0.49137816733082
H	3.99188952785725	-5.42099923780805	0.31849002741412
H	1.50946398875822	-6.15853894909413	0.54110191086338
C	0.93803258868694	-4.07027191816624	0.53938186949476
C	-4.11888827127637	-5.51826120757370	1.02001685365769
C	-4.43228552599023	-6.84051102983293	1.12427285908194
H	-4.97437436571082	-4.85164533506268	1.03346465476218
C	-3.42613756945301	-7.83575358813215	1.20476979437528
N	-2.59766368464667	-8.63623522357434	1.28970428077655
C	-5.88732329620406	-7.18103013107218	1.26243908937701
O	-6.68179563059622	-6.36663242922519	1.65951633293394
O	-6.31949202870346	-8.41964690203890	0.95644379872917
C	-5.60464428095372	-9.30620867626890	0.07775189926335
H	-6.37036890289432	-9.89076106764908	-0.42725464393152
H	-5.02637887369920	-8.75459230476138	-0.66199768091196
H	-4.95026428432677	-9.96115771552098	0.64876157171191
C	-0.48959367210441	-4.11809784434672	0.65851645597074
C	-1.39658717366572	-3.06937534472384	0.65222623953923
C	-2.72125058022714	-3.49263528908532	0.78181104250788
C	-2.86528133476066	-4.86863193742348	0.89620926289836
S	-1.29962235030570	-5.64455037526270	0.84119794860914
H	-1.10048602394481	-2.03578862440196	0.55040263589144
H	-3.57322494054688	-2.82782806479728	0.79160160722822
C	10.59698983512611	2.89946833105371	0.30479440724380
C	10.03748937027617	4.16470205524521	0.38335695884938
C	10.99353816252661	5.18311180587623	0.39569035719274
C	12.30364276096685	4.72621212041563	0.33085552723408
S	12.32959386042040	2.97972766140094	0.25400939896717
H	8.97180456852473	4.33737539311894	0.42776438459249
H	10.75552695434228	6.23637500011609	0.44913652996973

Table S11: Ground-state Cartesian coordinates of the oxidized form of **BzT2** in CH_2Cl_2 and its SOMO

C	3.33671792757404	-3.30059305982861	0.39114359685763
H	5.64840368976492	0.66388324131837	0.37444214119899
N	8.15081500512980	-3.17737119824655	0.07029275484481
S	7.67109453674612	-4.71979250559196	0.00388316830933
N	6.07198745069536	-4.50731469209620	0.11164340929084
C	5.84419067805861	-3.19707408279657	0.20621859841632
C	7.05980027657614	-2.42013381356566	0.18077595131835
C	4.55104793513201	-2.56379814781528	0.31210803302313
C	4.58056190166238	-1.15729285172429	0.34628067013296
C	5.74726804847273	-0.41281890424129	0.32370893829720
C	7.03298184869401	-0.97849658502586	0.25814507621848
S	8.14641583833998	1.56909958156015	0.32527815906977
C	8.21346255546345	-0.18592301294641	0.27241350396583
C	9.55098243281038	-0.60823269071627	0.25729966386809
C	10.46540820643730	0.42742439936936	0.28383800519813
C	9.87884116408878	1.69388879793314	0.32179679627597
H	9.82903981614142	-1.64777928842230	0.22804246720034
H	11.53529827992181	0.27275445000185	0.27913154205099
H	3.64826986195373	-0.61217722487027	0.41333502606814
C	13.47266743224797	5.54196900129400	0.27338999191996
C	14.79356801103553	5.21638398287138	0.17973873667706
H	13.26402834976570	6.60540098557652	0.30966848070580
C	15.23500872503406	3.87399816024423	0.05615588405826
N	15.58730804787895	2.78190795917506	-0.07506435852326
C	15.77220022527028	6.35153296594781	0.07372406867797
O	15.42606434722655	7.41873625337077	-0.38065525164538
O	17.04460236253065	6.19221426554201	0.44919424268413
C	17.50835650046780	5.14854890296886	1.34210194539574
H	18.30726452639465	5.60636222654416	1.91927226994220
H	16.71909399250280	4.82016952045407	2.01471763754764
H	17.89459276800478	4.31538602053937	0.76062413969671
S	1.77432263918056	-2.50622974381978	0.46253500954627
C	3.16502154200480	-4.69071339837521	0.45238860524511
C	1.84557438511921	-5.08899139730241	0.55876273749105
H	3.99530298936181	-5.37505442176528	0.42495110068935
H	1.54205167621454	-6.12422485627459	0.62122769988280
C	0.93810083039681	-4.02675237397898	0.57655824809700
C	-4.09154687801179	-5.57682302592942	0.95993992502733
C	-4.40354827483153	-6.89903933070771	1.07138459682644
H	-4.94434603641970	-4.90745885161013	0.94201463257166
C	-3.40265785903024	-7.89808209036161	1.18533128113320
N	-2.57913705418001	-8.69869881250359	1.30626667705839
C	-5.86200384675508	-7.24650556482607	1.18726392493458
O	-6.65618917172524	-6.43689158081757	1.61133730130236
O	-6.30368037688369	-8.46085225919447	0.84561121731872
C	-5.58887393571605	-9.36513894264461	-0.03320888891006
H	-6.36168934332649	-9.92394459598497	-0.55409161024597
H	-4.98825973683260	-8.81693467372442	-0.75569039155671
H	-4.97194163524490	-10.04015382695236	0.55447294346059
C	-0.48044469748910	-4.10773905425685	0.67042760998330
C	-1.41420800933187	-3.07509195807345	0.65571068841694
C	-2.72574241836834	-3.52744729364600	0.75482458208817
C	-2.83736672124867	-4.91285188219065	0.85689494936751
S	-1.26416292317516	-5.65704663729099	0.82440607591467
H	-1.14495617339902	-2.03213706139874	0.56887190810596
H	-3.59210333612016	-2.88154915860793	0.75305222150126
C	10.55731470334350	2.94453917556990	0.34554156083234
C	10.03312583976361	4.23117722875742	0.42159259513404
C	11.01482620368357	5.21827943040310	0.41073062995646
C	12.31361456875667	4.71919347981185	0.32207442354456
S	12.29568557055873	2.98013323266671	0.25956560168408
H	8.97444125331409	4.44057184443479	0.48526277644889
H	10.80682748436899	6.27797274377046	0.46353807840767

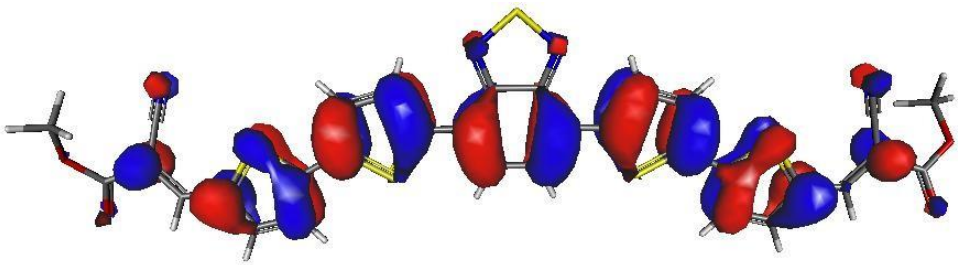


Figure S10:.SOMO of the oxidized form of **BzT2**

Table S12: Ground-state Cartesian coordinates of the reduced form of **BzT2** in CH_2Cl_2 and its SOMO

C	3.35895909524314	-3.37164724059587	0.29022931381003
H	5.73541349547162	0.56799075606796	0.22243844999261
N	8.18701116850452	-3.30502626286746	-0.03675564128488
S	7.68568188369451	-4.85590815688089	-0.08130038118649
N	6.07685184633117	-4.61300844285625	0.02208076110208
C	5.86740083934319	-3.29714320499971	0.09637432027708
C	7.10498918784651	-2.53074892664984	0.05964617846440
C	4.58731071258894	-2.64606243358906	0.19815415005969
C	4.63952078144021	-1.23991648876762	0.21931054447602
C	5.81778635180327	-0.51139364321706	0.18411246245531
C	7.09705949960382	-1.09259726235016	0.11908006368127
S	8.23045142478012	1.44703422906438	0.18468612131428
C	8.29413942674155	-0.31174499055040	0.12245549041981
C	9.62917259128030	-0.72274993859803	0.09522910783444
C	10.55000281356521	0.31937499642416	0.12615108393080
C	9.98006219411350	1.58636110819332	0.17865214523154
H	9.90810379511618	-1.76199101431194	0.05563882475298
H	11.62023583240350	0.15999283294871	0.11233138189950
H	3.71348800806978	-0.68238580830790	0.28440855706167
C	13.43244048174864	5.56816362210001	0.31664661325832
C	14.80160407940782	5.33389368875389	0.33094108093965
H	13.16590144683315	6.61889013692220	0.35103684214115
C	15.33056190825830	4.03051074343705	0.20325980657642
N	15.74719799073552	2.95849027201528	0.06701038801340
C	15.67927981058541	6.52037572763876	0.34144775997717
O	15.28063012619659	7.62180370360900	0.00613341750629
O	16.97833881239366	6.42306838416633	0.70466022824209
C	17.50383022758477	5.36913706282680	1.54101097810199
H	18.29824454874847	5.83452133104758	2.12034890383726
H	16.74340552371990	4.98107543737790	2.21602535204497
H	17.91066638430890	4.56832161925982	0.92799696078296
S	1.80639107780418	-2.54739215729235	0.38300661744709
C	3.15107285517194	-4.75066668477514	0.35357573503387
C	1.81863807236999	-5.12512807926553	0.48092821791760
H	3.96608593861396	-5.45259888834614	0.31344282460768
H	1.50130822824963	-6.15685169106719	0.54852373581769
C	0.92331915053963	-4.06062934333361	0.51576136976472
C	-4.12191108571751	-5.49822377651214	1.04850944665940
C	-4.46737492650425	-6.83885200304498	1.15528710882607
H	-4.96757302688397	-4.81938048292557	1.06576450924957
C	-3.48946261511562	-7.85572391218218	1.23637856029514
N	-2.68535705521120	-8.68372233727379	1.33158026303652
C	-5.89879046849519	-7.16086410514386	1.31430922826040
O	-6.71424323390643	-6.34025466019162	1.69632322830673
O	-6.35157606224516	-8.41163497809232	1.06508568863206
C	-5.71187145382249	-9.31643256937167	0.13803191535565
H	-6.52116180562327	-9.86526092708895	-0.33866730773163
H	-5.14870095509862	-8.77200792740208	-0.61738111053521
H	-5.06155314376547	-10.00376828070193	0.67413509508489
C	-0.48439035766207	-4.11060884756480	0.64504575569410
C	-1.41027683705442	-3.05855002487043	0.65555776845411
C	-2.72199906518843	-3.47668680203439	0.79628624648173
C	-2.88390991419423	-4.86518046592501	0.90997883894359
S	-1.30638920639706	-5.64501268110584	0.82810751056555
H	-1.11890644174052	-2.02247957081382	0.55640140750385
H	-3.57040726821134	-2.80607443118679	0.81770566787584
C	10.63082213871279	2.84003049823419	0.22256915467928
C	10.06390592353170	4.11944344323369	0.27597306449804
C	10.99914367659964	5.13798219871979	0.30576247725508
C	12.33445078592207	4.70651862145570	0.28010269452097
S	12.37637496883122	2.94475239265120	0.21395982966100
H	8.99577700999226	4.28654598833022	0.29171829579334
H	10.74351680803598	6.18840764757638	0.34898889633153

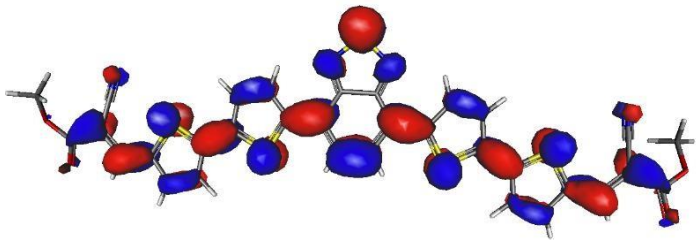
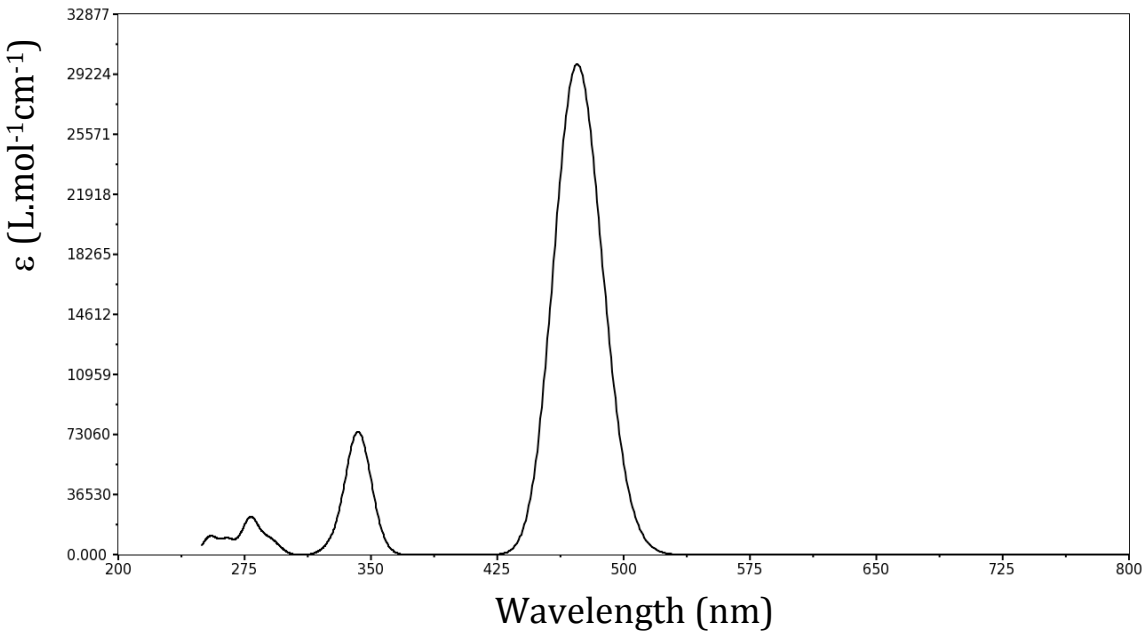
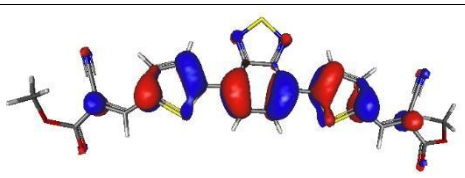
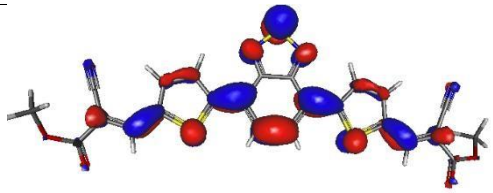
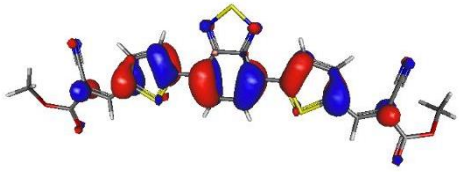
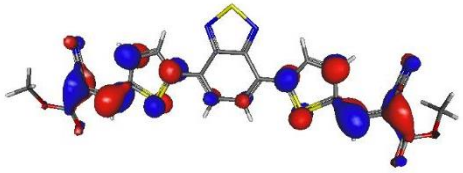
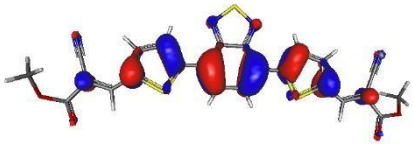
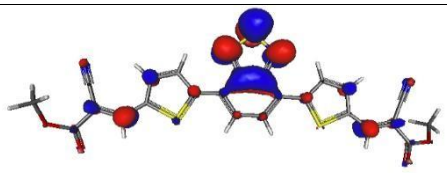
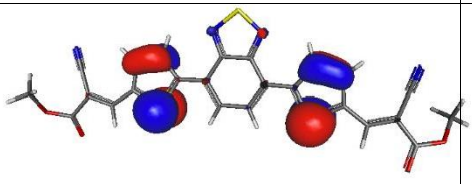
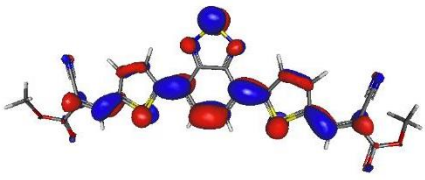
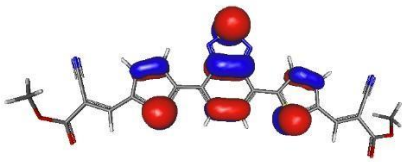
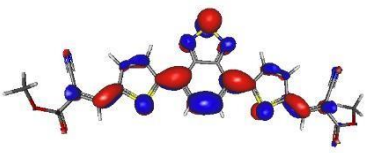
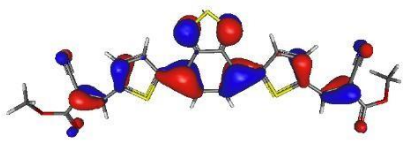
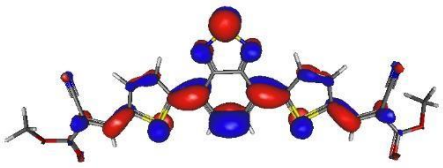
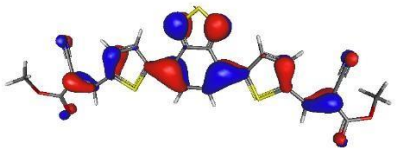
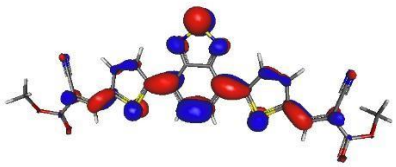
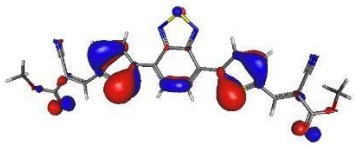
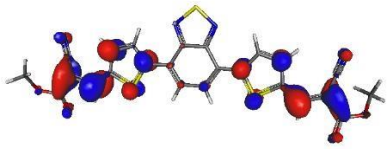
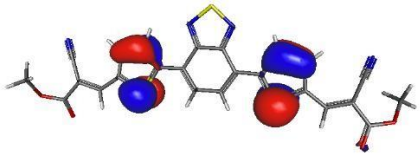
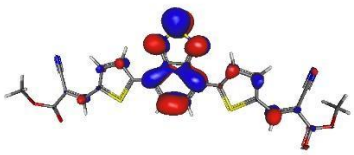
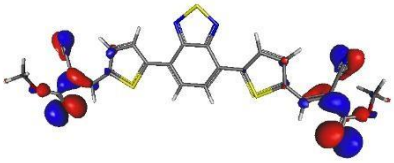
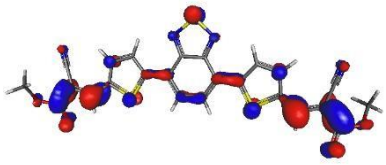
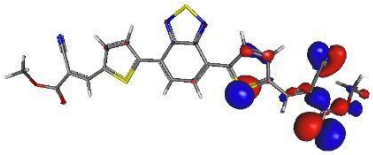
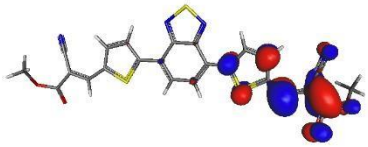
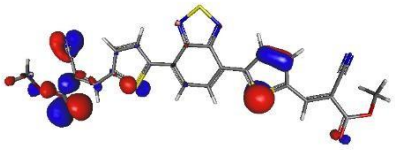
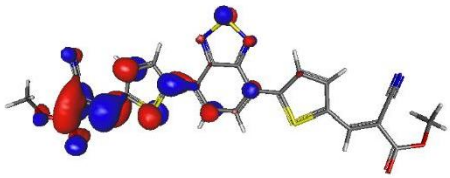
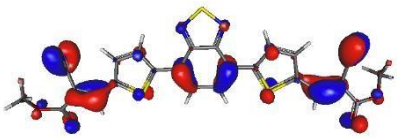
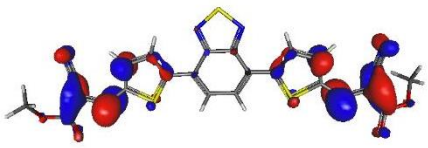


Figure S11:.SOMO of the reduced form of **BzT2**



State, f, λ (nm), n	Hole	Electron
S_1, 2.07, 472.7, 0.93		
S_2, 0.088, 343, 0.88		
S_3, 0.422, 342.8, 0.93		
S_6, 0.06, 290.6, 0.84		
S_7, 0.15, 278.7, 0.77		

$S_{8,}$ 0.06, 265.2, 0.83		
$S_{9,}$ 0.07, 255.0, 0.83		
$S_{12,}$ 0.05, 239.8, 0.44		
$S_{12,}$ 0.05, 239.8, 0.29		
$S_{12,}$ 0.05, 239.8, 0.19		
$S_{15,}$ 0.08, 238.2, 0.42		
$S_{15,}$ 0.08, 238.2, 0.34		
$S_{22,}$ 0.05, 219.7, 0.47		

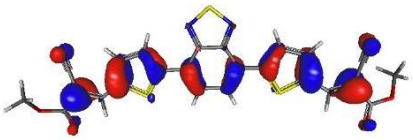
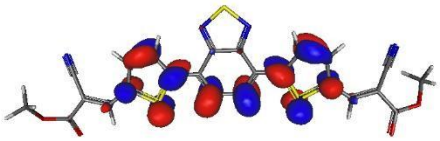
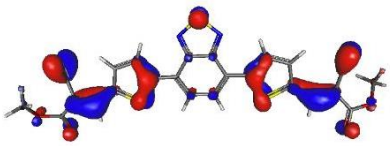
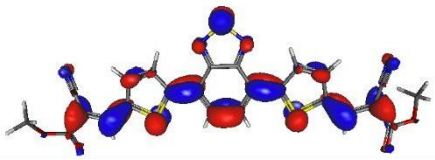
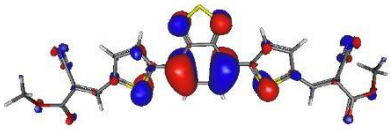
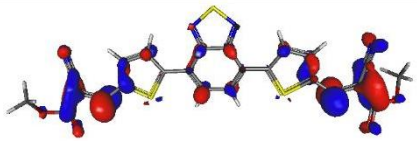
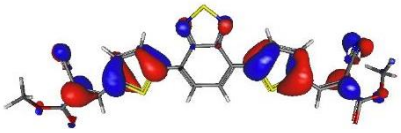
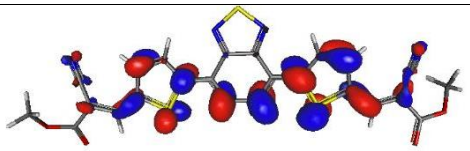
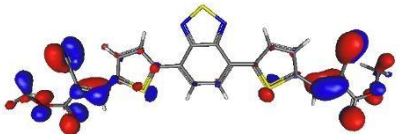
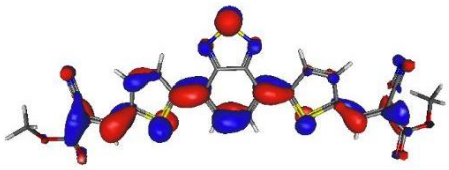
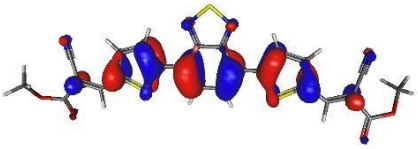
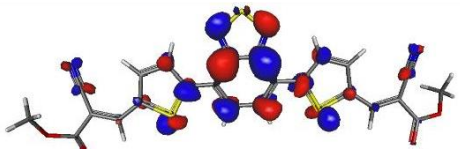
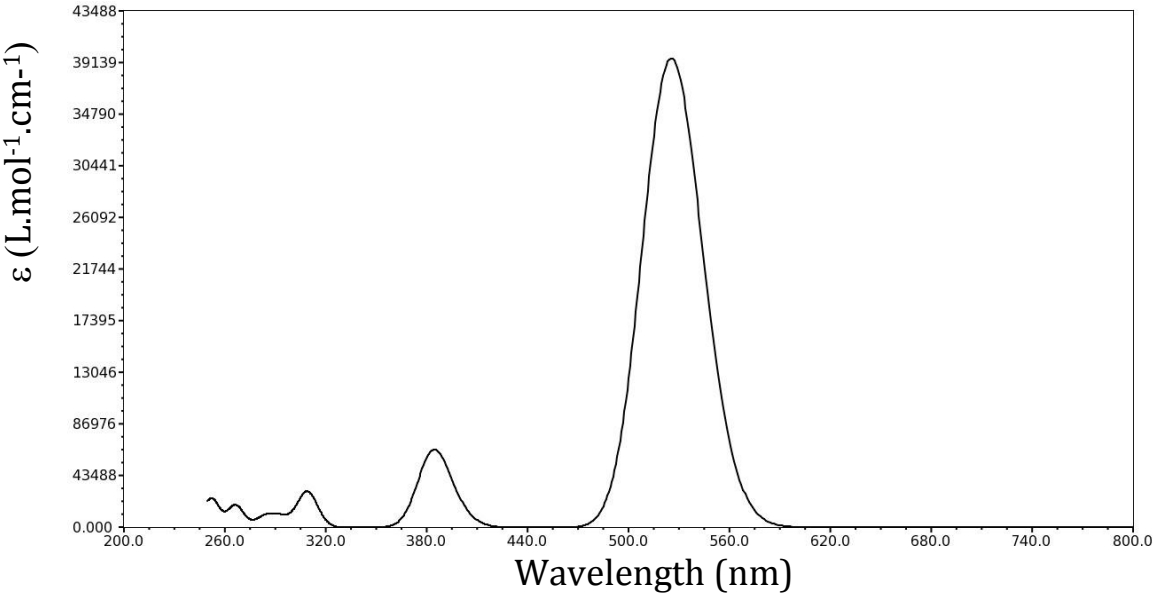
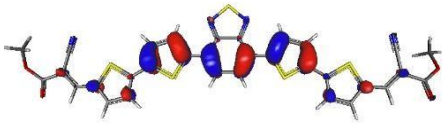
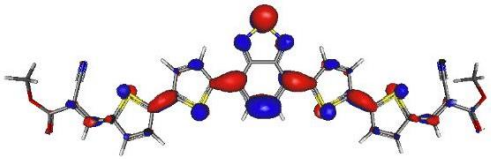
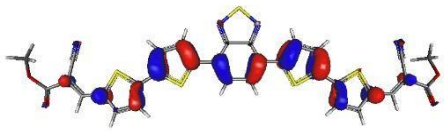
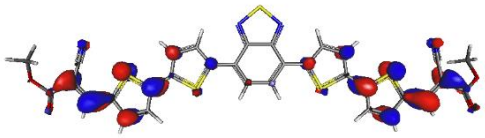
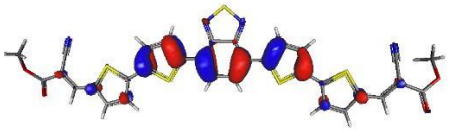
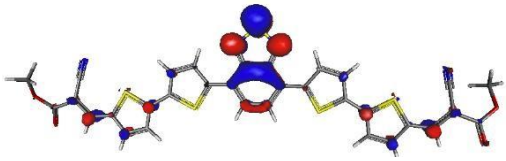
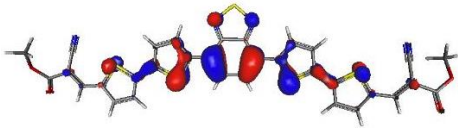
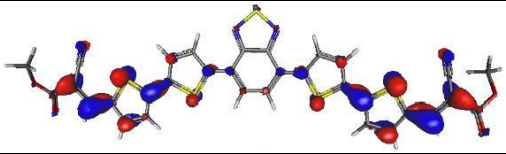
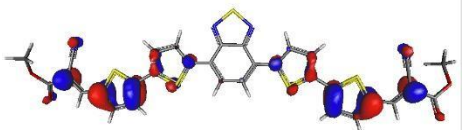
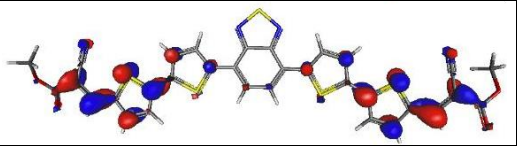
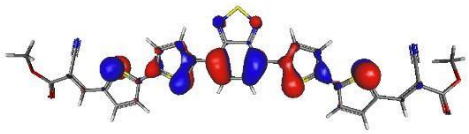
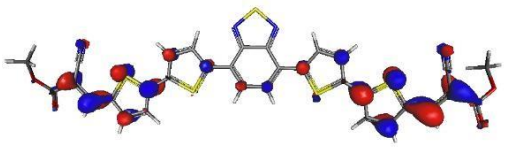
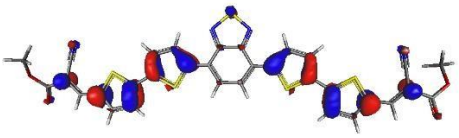
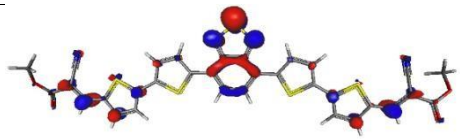
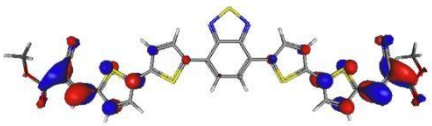
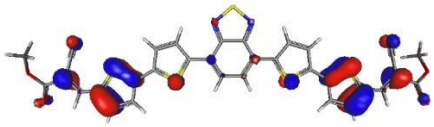
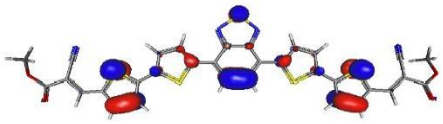
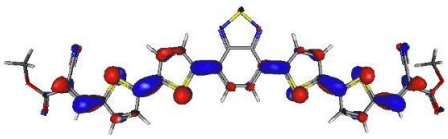
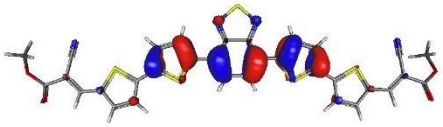
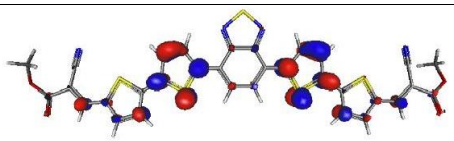
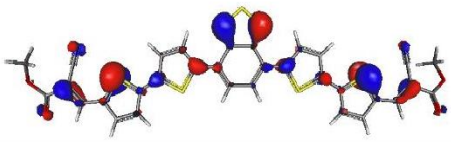
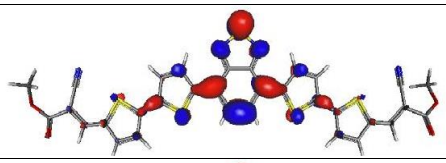
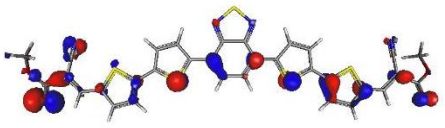
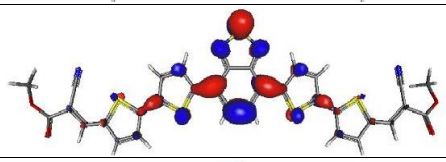
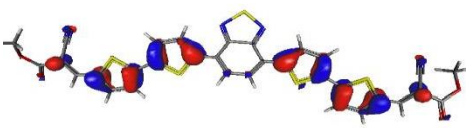
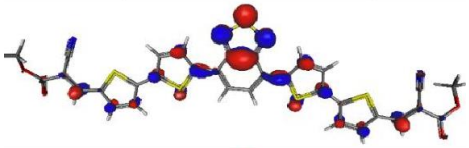
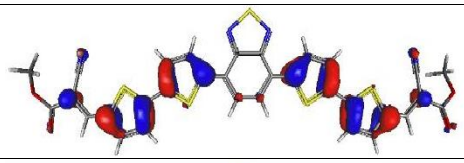
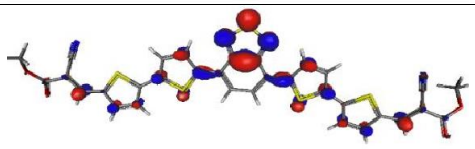
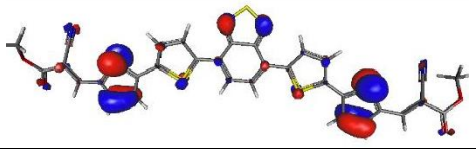
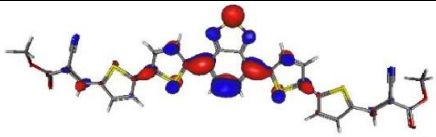
$S_{22,}$ 0.05, 219.7, 0.25		
$S_{22,}$ 0.05, 219.7, 0.17		
$S_{25,}$ 0.07, 209.8, 0.32		
$S_{25,}$ 0.07, 209.8, 0.29		
$S_{25,}$ 0.07, 209.8, 0.24		
$S_{29,}$ 0.13, 206.6, 0.63		

Figure S12: Simulated absorption spectrum of **BzT_1** in CH_2Cl_2 and Natural transitions orbital isodensity surface for main transitions (f>0.05) of **BzT_1**.



State, f, λ (nm), n	Hole	Electron
S_1, 2.73, 525.7, 0.90		
S_2, 0.05, 398.1, 0,73		
S_3, 0.43, 384.3, 0,89		
S_5, 0.20, 309.2, 0,54		
S_5, 0.20, 309.2, 0,39		

S_7, 0.05, 293.6, 0.67		
S_7, 0.05, 293.6, 0.20		
S_{13}, 0.11, 266.7,		
S_{15}, 0.14, 255.0, 0.34		
S_{15}, 0.14, 255.0, 0.29		
S_{25} 0.05, 239.8,0.49		
S_{25} 0.05, 239.8, 0.21		
S_{26}, 0.08, 238.2, 0.57		
S_{26}, 0.08, 238.2, 0.17		
S_{28}, 0.05, 219.7, 0.32		

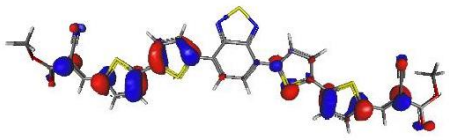
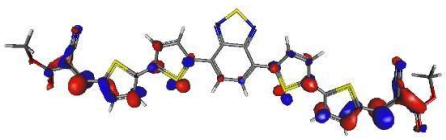
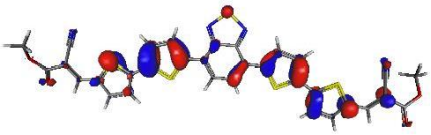
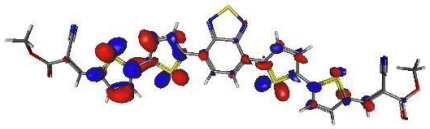
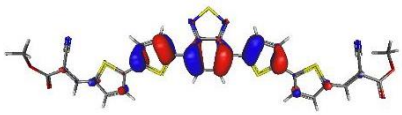
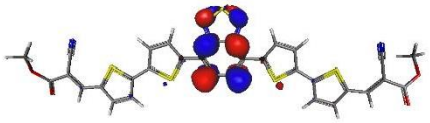
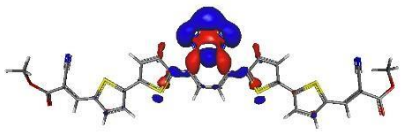
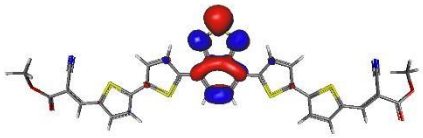
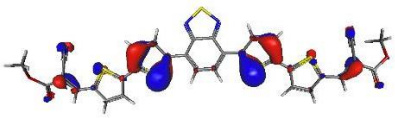
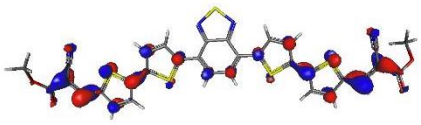
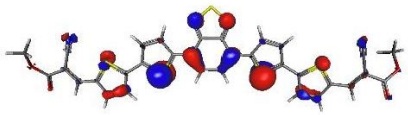
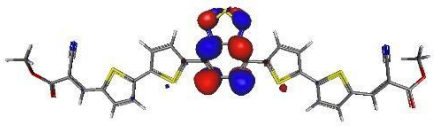
$S_{28,}$ 0.05, 219.7, 0.22		
$S_{28,}$ 0.05, 219.7, 0.14		
$S_{35,}$ 0.07, 209.8, 0,41		
$S_{35,}$ 0.07, 209.8, 0,37		
$S_{38,}$ 0.13, 206.6, 0.43		
$S_{38,}$ 0.13, 206.6, 0.22		

Figure S13: Simulated absorption spectrum of BzT_2 in CH_2Cl_2 and Natural transitions orbital isodensity surface for main transitions (f>0.05) of BzT_2.

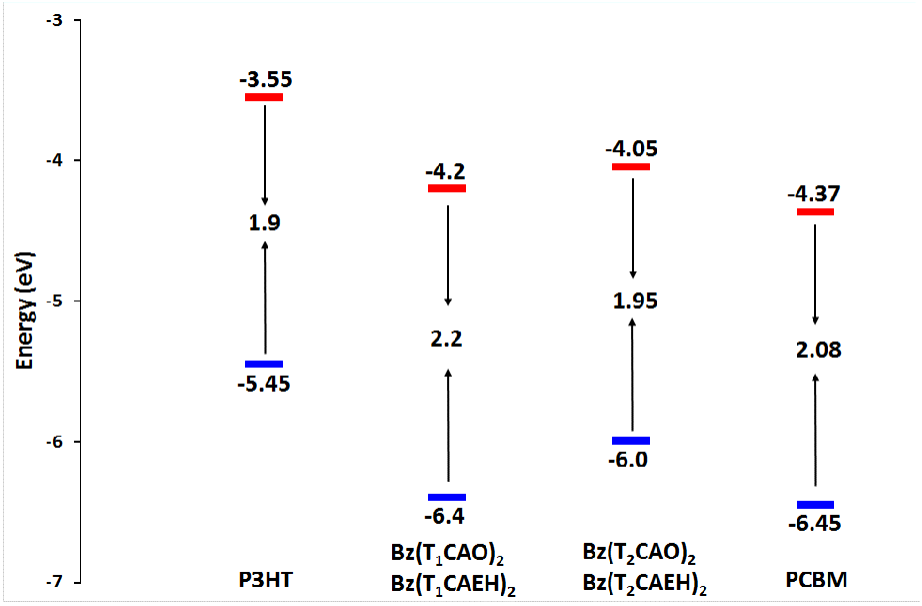


Figure S14: Diagram of the energy levels for the investigated molecules, P3HT and PCBM, estimated *via* electrochemical measurements. (All values have been evaluated from electrochemical measurements made in our laboratory in the same experimental conditions)