Supplementary Material (ESI) for Journal of Materials Chemistry

New electroluminescent bipolar compounds for balanced charge-transport and tuneable colour in organic light emitting diodes: triphenylamine-oxadiazole-fluorene triad molecules

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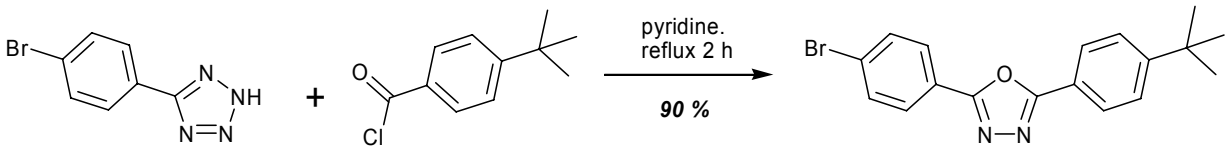
Synthesis of 2-(4-*tert*-butylphenyl)-5-(4-bromophenyl)-1,3,4-oxadiazole 11.[1]



11

An argon purged flask was charged with 5-(4-bromophenyl)-*2H*-tetrazole (6.65 g, 29.5 mmol) and pyridine (60 cm^3). 4-*tert*-butyl benzoyl chloride (8.0 cm^3, 37.6 mmol) was added and the solution was refluxed until the emission of nitrogen stopped (~ 2 h). The solution was cooled and poured into water to precipitate the product, which was filtered and recrystallised from ethanol to yield shiny white needles (9.59 g, 90 %); mp: 145.5 – 146.9 °C; Anal. Calcd. for $C_{18}H_{17}BrN_2O$: C, 60.52; H, 4.80; N, 7.84, Found: C, 60.46; H, 4.81; N 7.96; ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 9H), 7.58 (m, 2H), 7.68 (m, 2H), 8.02 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 31.11, 35.12, 120.92, 123.01, 126.09, 126.82, 128.29, 132.41, 155.56, 163.66, 164.87; MS (EI): m/z 356 (M^+).

[1] For conversions of tetrazoles into oxadiazoles see, for example: J. Ding, M. Day, G. Robertson and J. Roovers, *Macromolecules* 2002, **35**, 3474-3483.

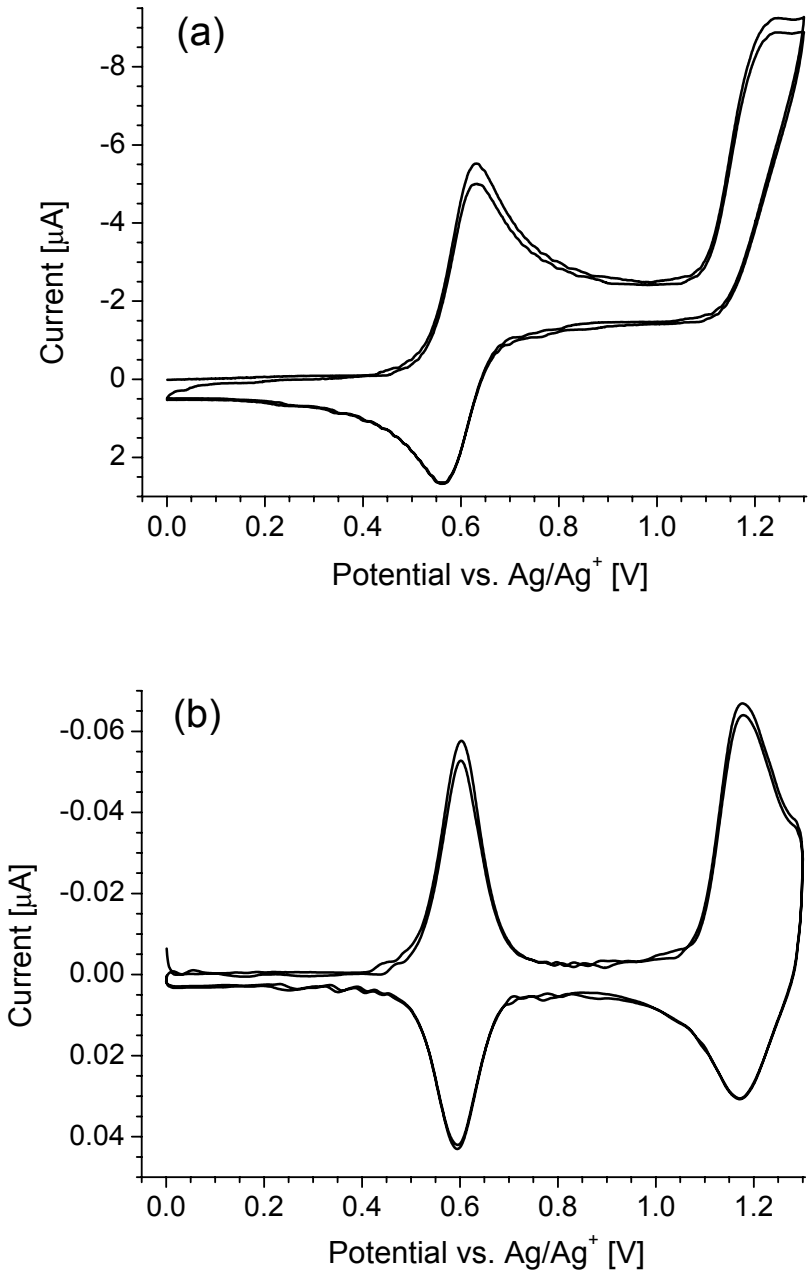


Figure S1. Cyclic voltammogram of compound **14** in benzonitrile, 0.1 M Bu_4NPF_6 at scan rate 100 mV/s; (a) two consecutive scans ($E_{1/2}^{ox1}$ = +0.600 V, ΔE_{pa-pc}^{ox1} = 60 mV, E_{pa}^{ox2} = +1.244 V) and (b) its deconvoluted CV ($E_{1/2}^{ox1}$ = 0.60 V, $E_{1/2}^{ox2}$ = 1.176 V).

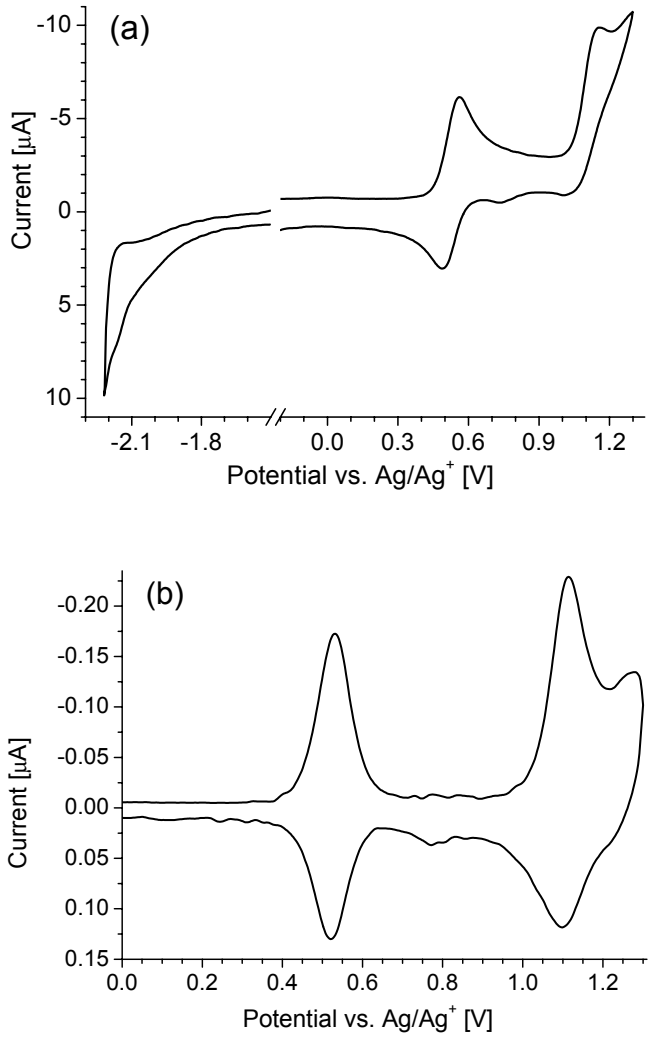


Figure S2. (a) Cyclic voltammogram of compound **16** in benzonitrile, 0.1 M Bu_4NPF_6, at scan rate 100 mV s^{-1}. Reversible oxidation and irreversible reduction have been shown. (b) Deconvoluted CV for the oxidation process.

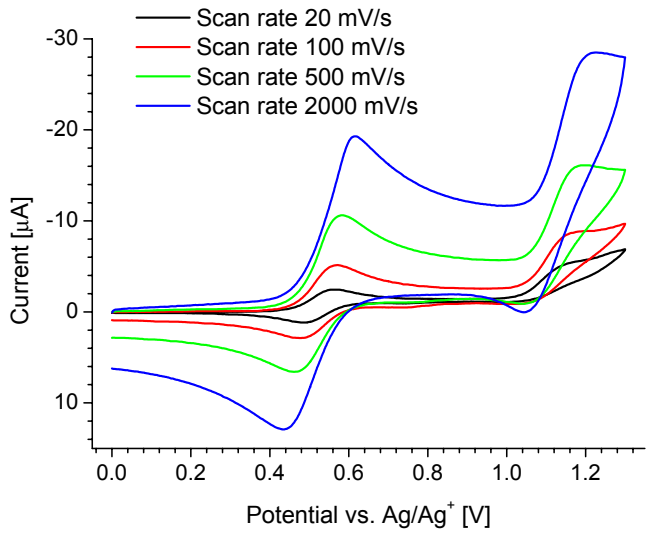


Figure S3. Cyclic voltammograms of compound **16** in benzonitrile, 0.1 M Bu_4NPF_6, at different scan rates. Potentials at scan rate 100 mV/s: $E_{1/2}^{ox1}$ = +0.53 V, ΔE_{pa-pc}^{ox1} = 81 mV, E_{pa}^{ox2} = +1.18 V.

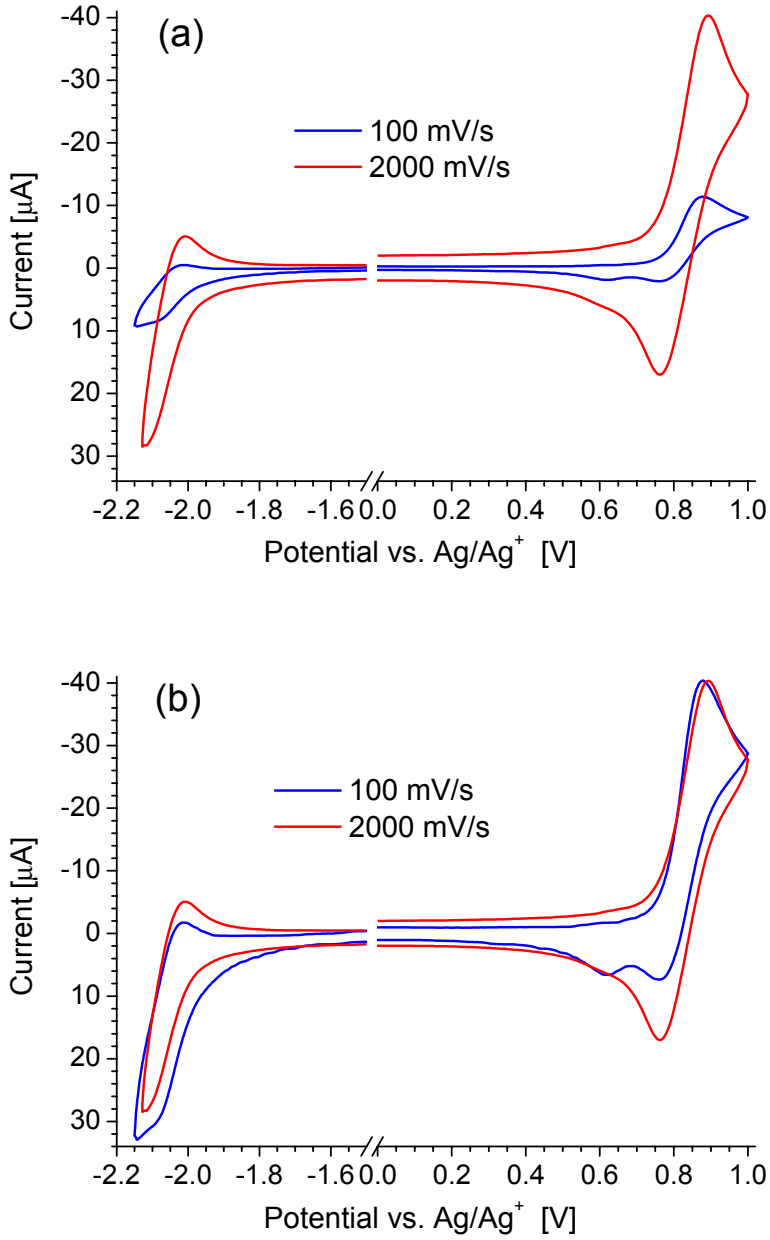


Figure S4. Cyclic voltammograms of compound **7** in benzonitrile, 0.1 M Bu_4NPF_6 at different scan rates. (a) Original CVs. (b) Normalised CV: E_{pa} for CV at 100 mV/s has been multiplied by ×3.53.

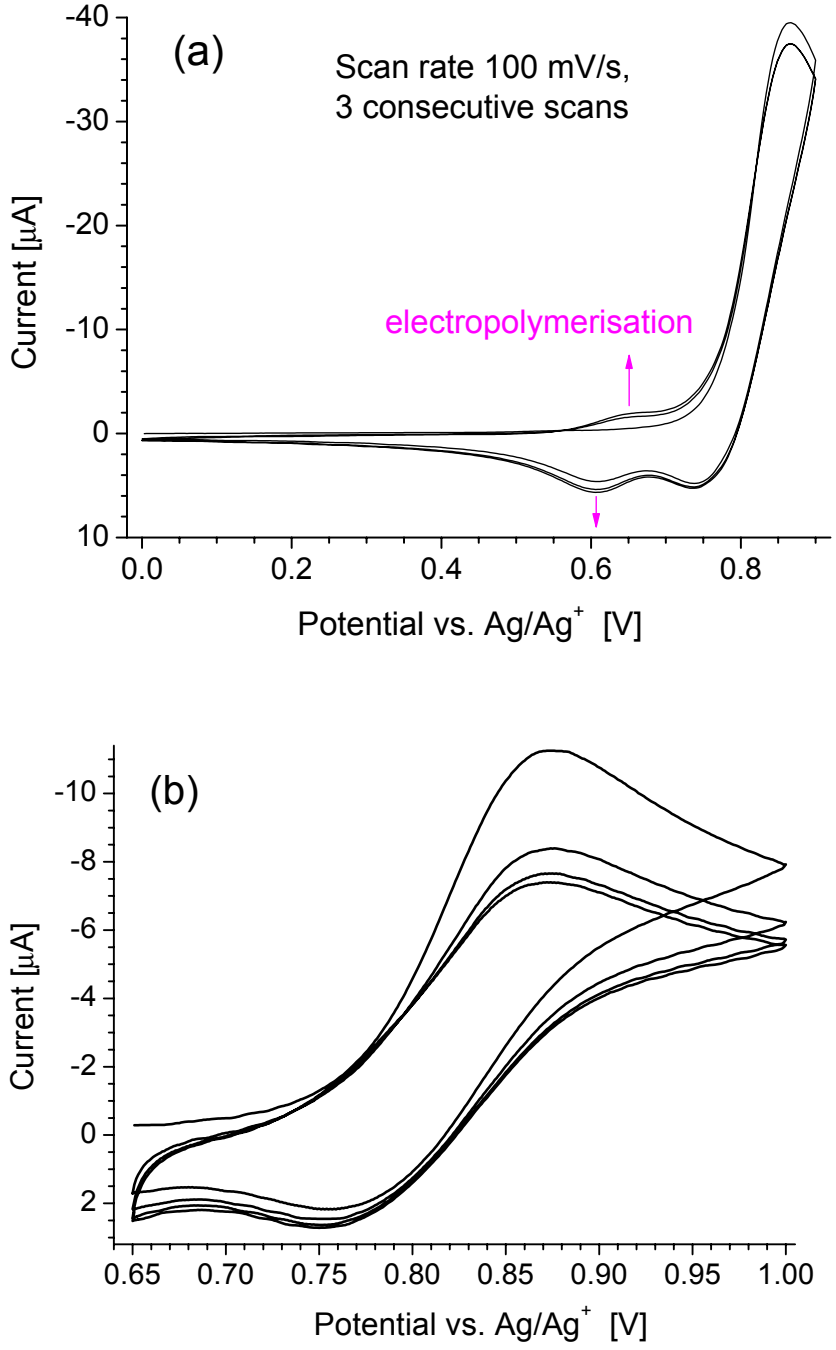


Figure S5. (a) Cyclic voltammogram of compound **7** in benzonitrile, 0.1 M Bu_4NPF_6 at scan rate 100 mV/s, first 3 consecutive scans: electrodeposition of the polymer film started from the 2nd scan (shown by arrows). (b) Four consecutive CV scans of compound **7** between +0.65 V and +1.00 V; benzonitrile, 0.1 M Bu_4NPF_6, scan rate 100 mV/s.

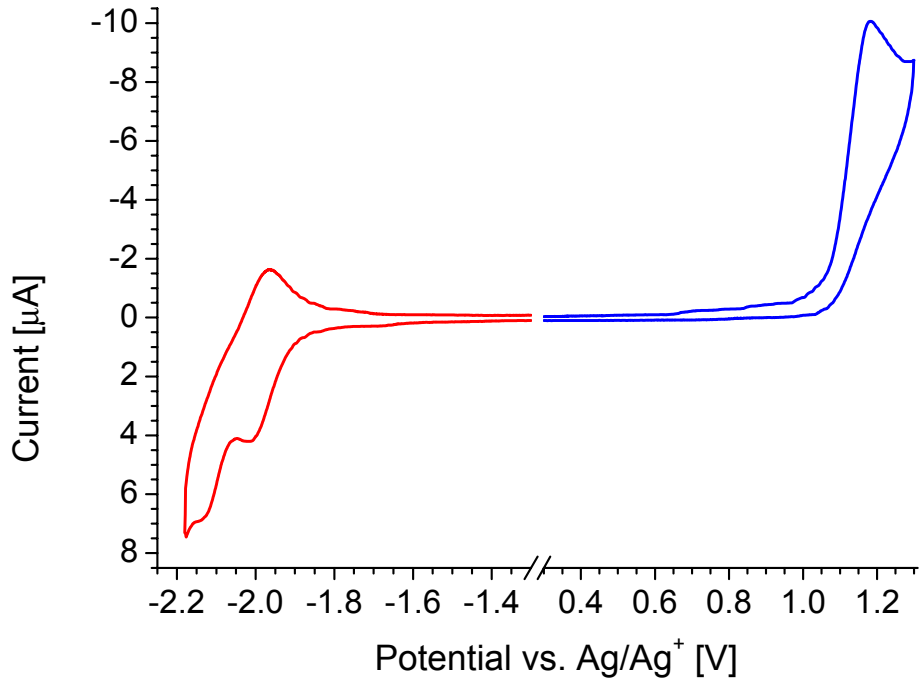


Figure S6. Cyclic voltammogram of compound **8** in benzonitrile, 0.1 M Bu_4NPF_6 at scan rate 100 mV/s.

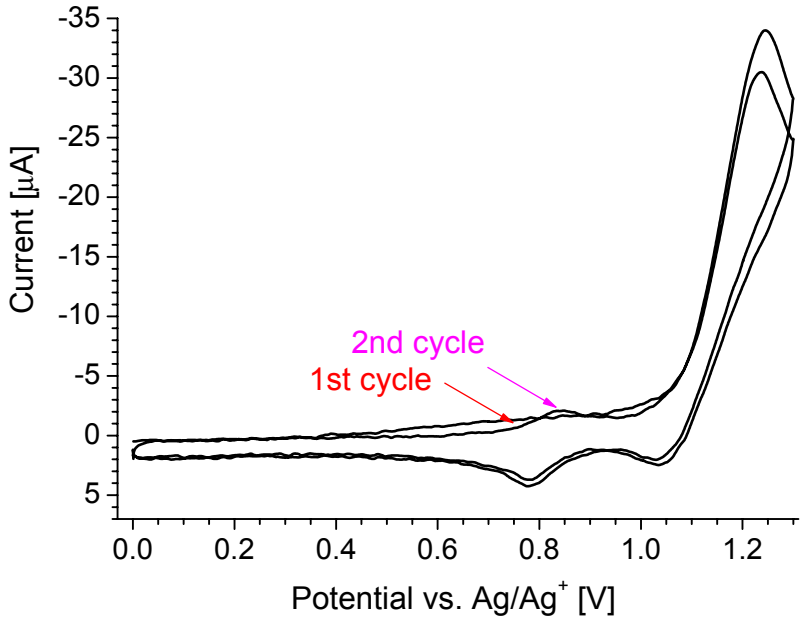


Figure S7. Cyclic voltammogram of compound **8** in benzonitrile, 0.1 M Bu_4NPF_6 at scan rate 2000 mV/s; two consecutive scans in the potential range of 0 V to +1.4 V (electrodeposition of poly(**8**) with response at ~0.75–0.85 V is seen on the second scan).

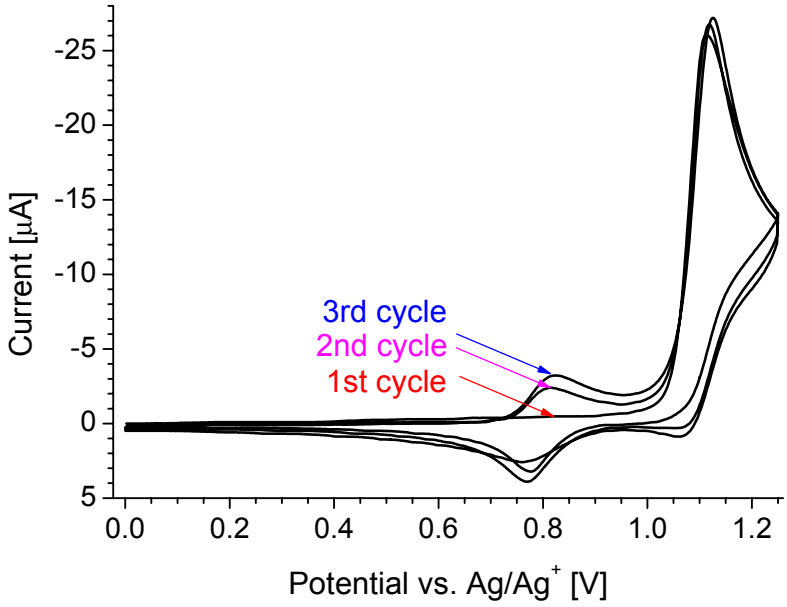


Figure S8. Cyclic voltammogram of compound **8** (increased concentration compared to Fig. S6) in benzonitrile, 0.1 M Bu_4NPF_6 at scan rate 100 mV/s; three consecutive scans in the potential range of 0 V to +1.25 V: electropolymerisation into poly(**8**) after first oxidation scan is clearly seen (growth of a new peak at ~0.8 V).

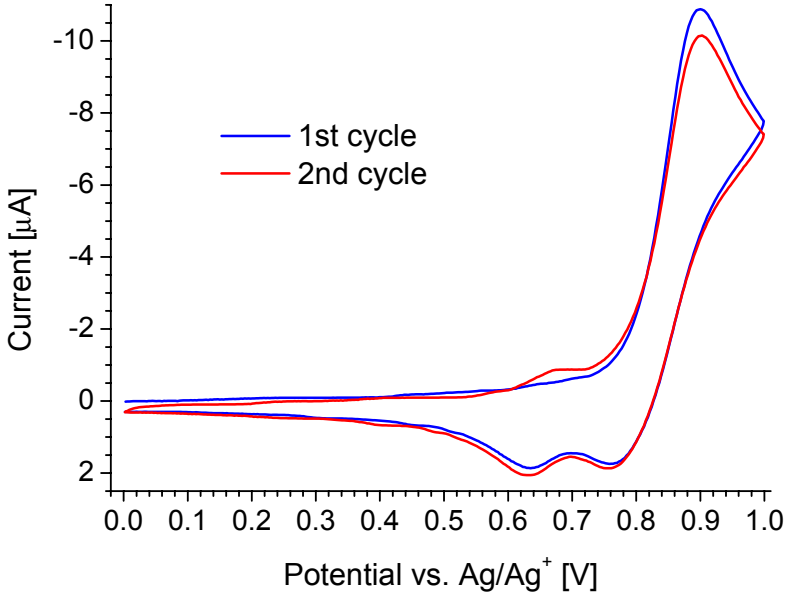


Figure S9. Cyclic voltammogram of compound **20** in benzonitrile, 0.1 M Bu_4NPF_6 at scan rate 100 mV/s; first two cycles of oxidation have been shown: polymerisation starts at the 2nd cycle.

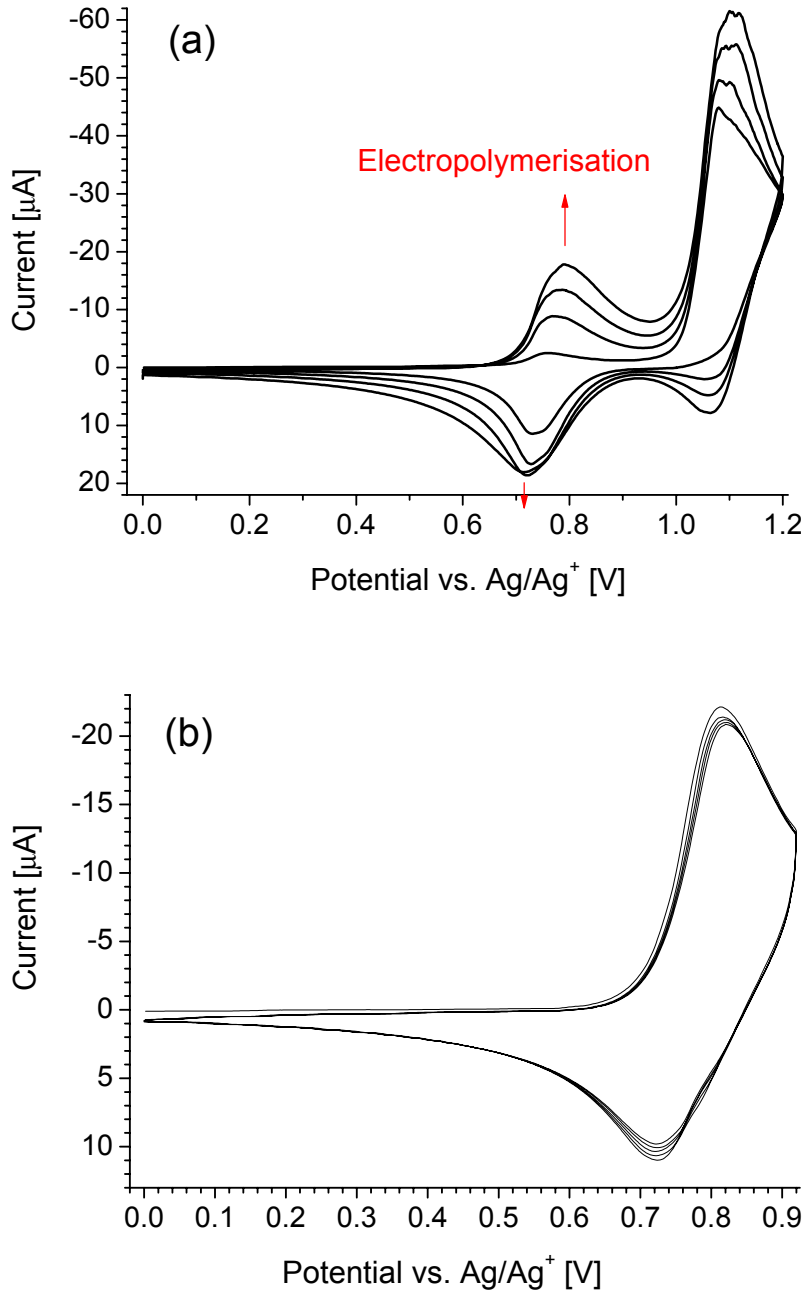


Figure S10.(a) Potentiodynamic electropolymerisation of compound **8** in benzonitrile, 0.1 M Bu_4NPF_6, scan rate 100 mV/s (first four of six ox/red cycles in the potential range of 0 V to +1.2 V are shown); arrows show growth of the polymer film on the Pt electrode. (b) Electrochemical response of poly(**8**), electrodeposited on Pt electrode, in monomer free acetonitrile solution, 0.1 M Bu_4NPF_6, scan rate 100 mV/s, 5 consecutive scans are shown.

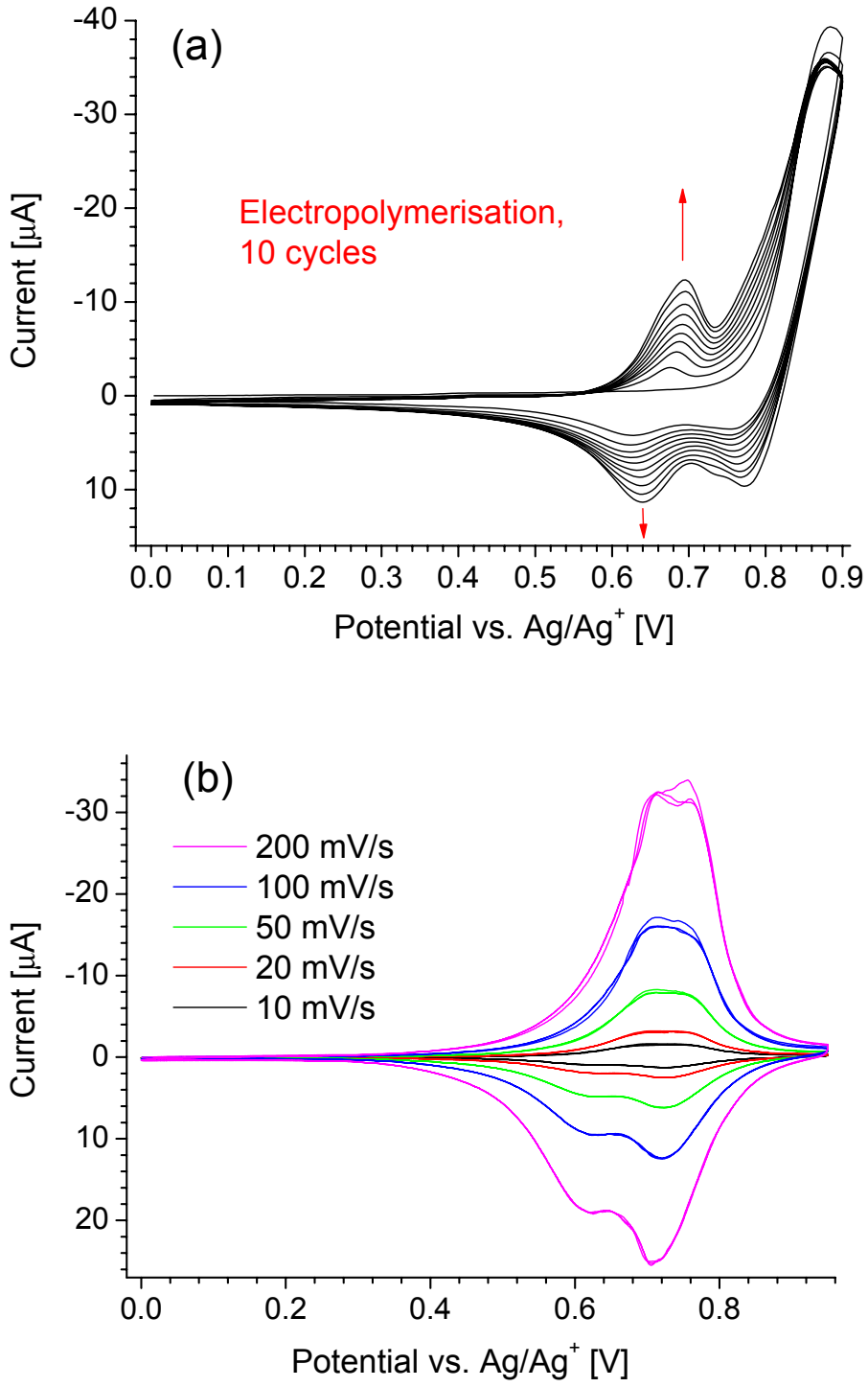


Figure S11.(a) Potentiodynamic electropolymerisation of compound **20** in benzonitrile, 0.1 M Bu_4NPF_6, scan rate 100 mV/s (10 ox/red cycles); arrows show growth of the polymer film on Pt electrode. (b) Electrochemical response of poly(**20**) electrodeposited on Pt electrode in monomer free acetonitrile solution, 0.1 M Bu_4NPF_6, at different scan rates. 3 consecutive scans were performed at each scan rate.

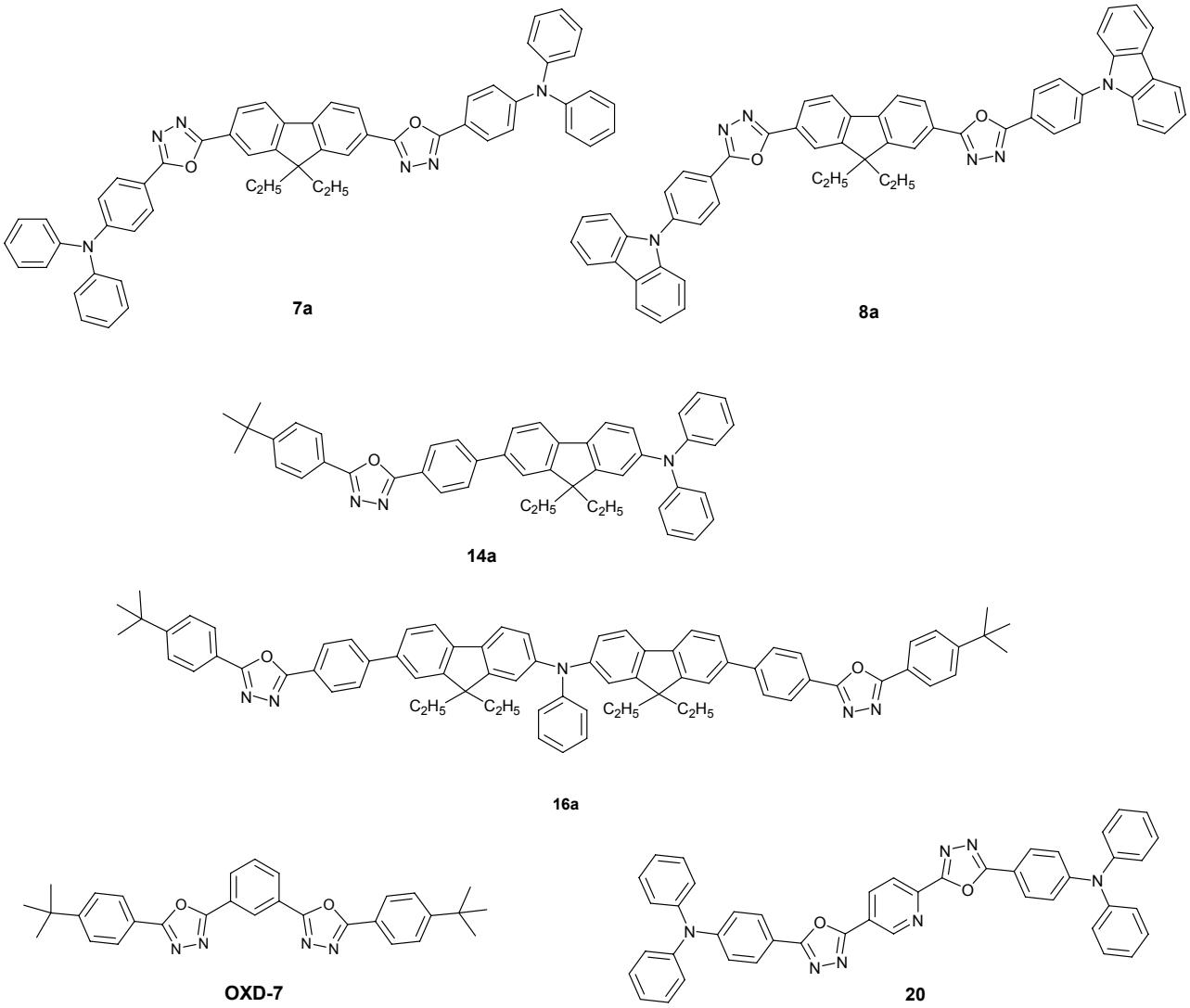


Figure S12. Structures of the compounds used in the DFT calculations.

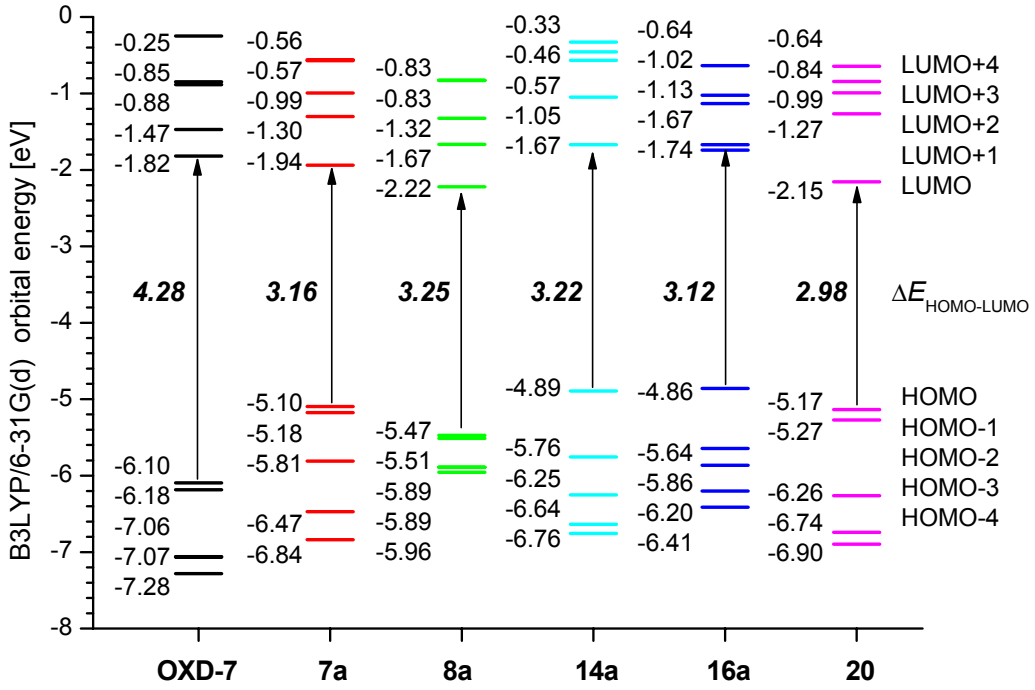


Figure S13. B3LYP/6-31G(d) orbital energy level diagrams for compounds used in OLEDs in the present work (**7a, 8a, 14a, 16a** and **20**) and a comparison with **OXD-7**.

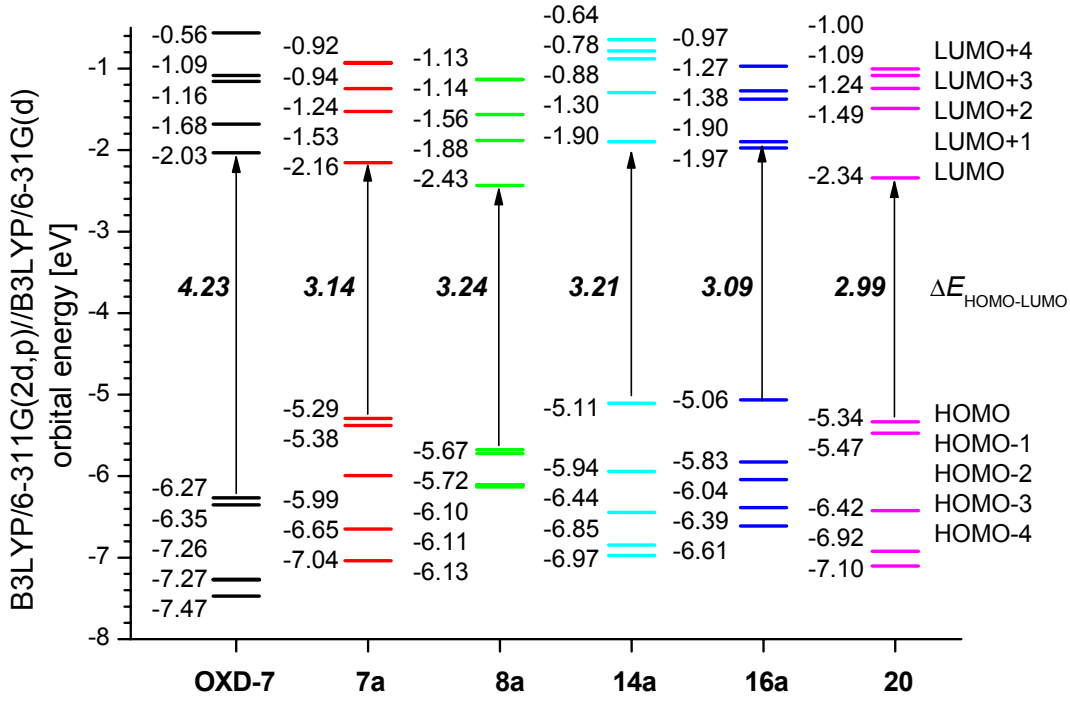


Figure S14. B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) orbital energy level diagrams for compounds used in OLEDs in the present work (**7a, 8a, 14a, 16a** and **20**) and a comparison with **OXD-7**.

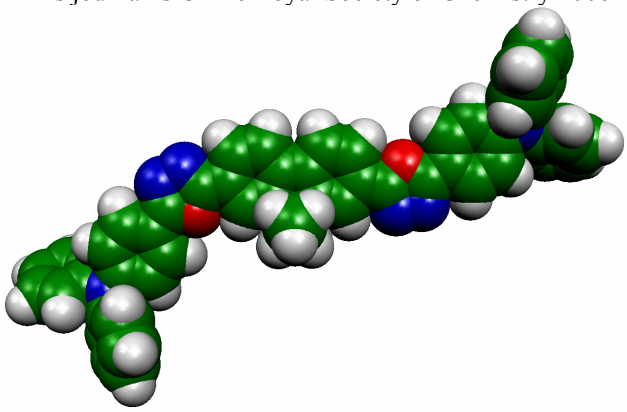


Figure S15. B3LYP/6-31G(d) optimized geometry of compound **7a**.

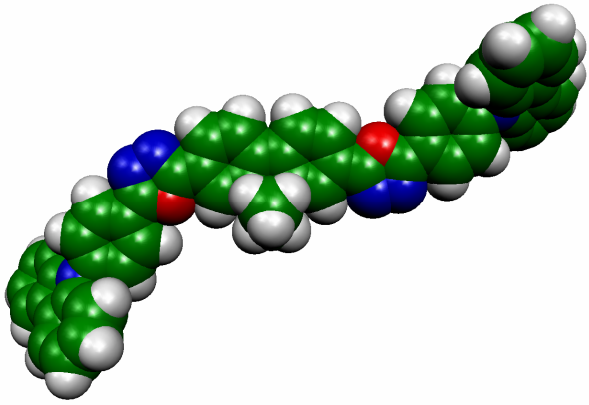


Figure S16. B3LYP/6-31G(d) optimized geometry of compound **8a**.

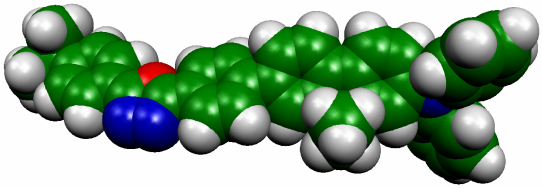


Figure S17. B3LYP/6-31G(d) optimized geometry of compound **14a**.

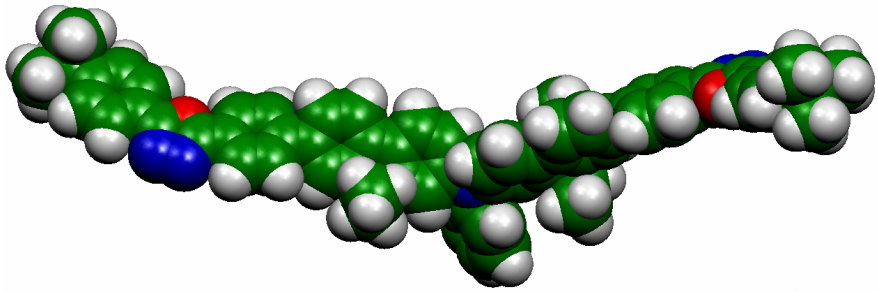


Figure S18. B3LYP/6-31G(d) optimized geometry of compound **16a**.

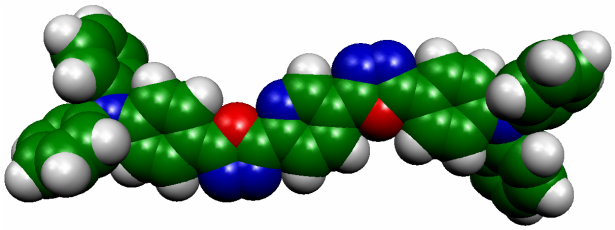
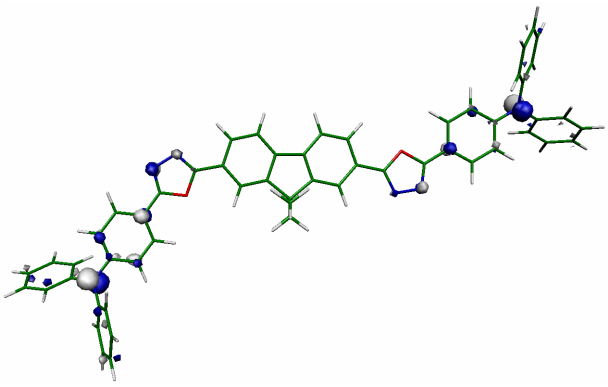
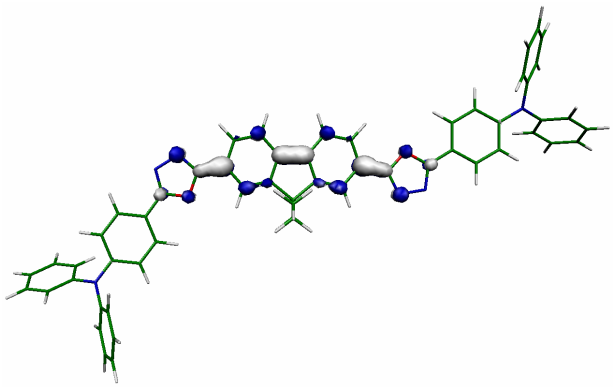


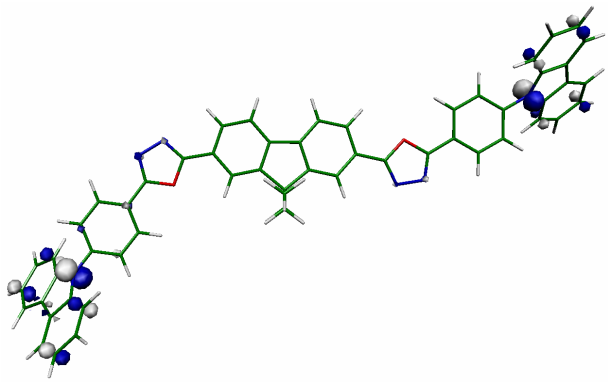
Figure S19. B3LYP/6-31G(d) optimized geometry of compound **20**.



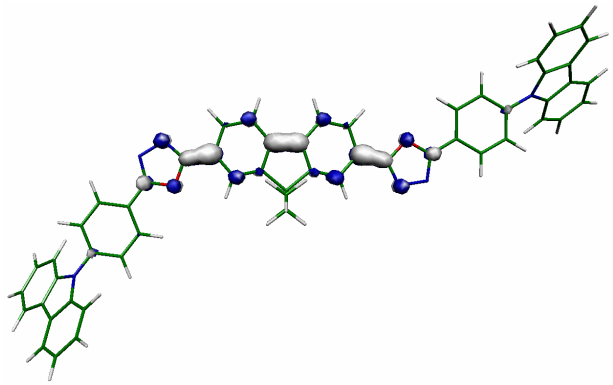
7a, HOMO = –5.29 eV



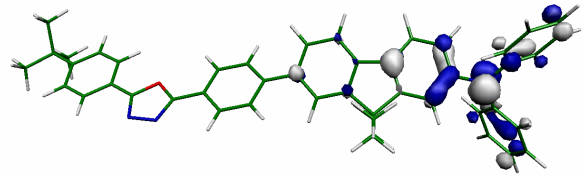
7a, LUMO = –2.16 eV



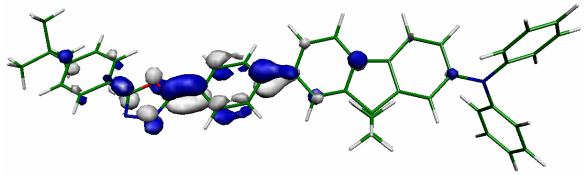
8a, HOMO = –5.67 eV



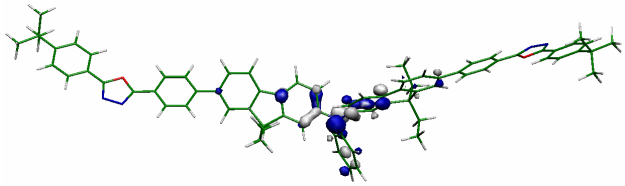
8a, LUMO = –2.43 eV



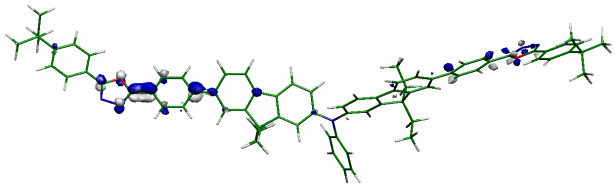
14a, HOMO = –5.11 eV



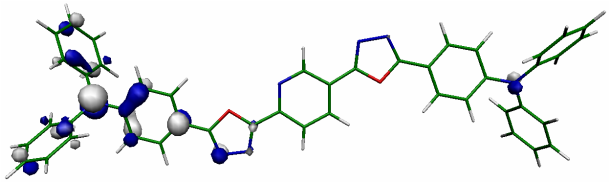
14a, LUMO = –1.90 eV



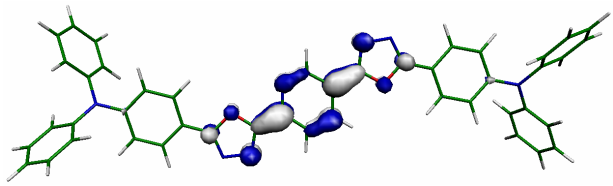
16a, HOMO = –5.06 eV



16a, LUMO = –1.97 eV



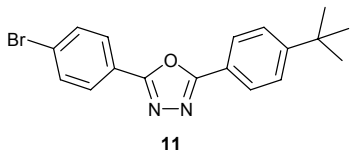
20, HOMO = –5.34 eV



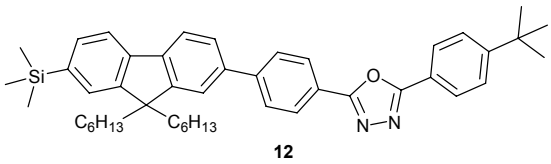
20, LUMO = –2.34 eV

Figure S20. B3LYP/6-311G(2d,p)//B3LYP6031G(d) frontier orbitals of compounds **7a, 8a, 14a, 16a** and **20**.

X-Ray Crystal Structures of 11, **12**, **13** and **20**.



11



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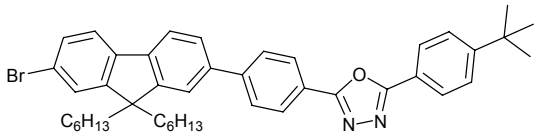

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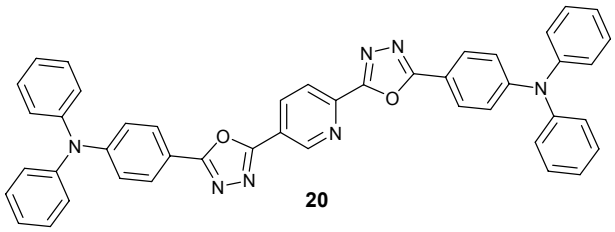

20

X-Ray diffraction experiments were carried out on 3-circle Bruker AXS diffractometers equipped with CCD area detectors APEX (**11**), SMART 6K (**12**, **13**), SMART 1K (**20**). Graphite-monochromated Mo-K_α radiation ($\overline{\lambda}$ =0.71073 Å) from a sealed tube or (for **11**) a 60W microfocus Bede Microsource® with glass polycapillary optics was used. The crystals were cooled using Cryostream open-flow N_2 cryostats (Oxford Cryosystems). Absorption corrections were performed for **13** and **20** by numerical integration (based on crystal face-indexing), for **11** by semi-empirical method based on Laue equivalents.[1] The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[2] Crystals of **11** showed signs of semi-merohedral twinning, which resulted in an imperfect overlap of reflections with h=4n and h=5n. A corresponding correction of intensities reduced $R(F)$ from 9.2 to 6.7%; nevertheless the residual electron density map remained untidy. Crystal data and experimental details are listed in Table S1.

Molecules of **11**, **12** and **13** have no crystallographic symmetry (Figure S21). In **13**, the *tert*-butyl group is disordered between two orientations which differ by a rotation of *ca*. 170° around the C(benzene)−CMe_3 bond and a tilt of this bond by *ca*. 19° (obviously, the tilt may involve the benzene ring also, but that was too small to resolve). The terminal methyl group of one of the *n*-hexyl chains is also disordered between two positions, which form short intermolecular contacts with the disordered *t*-Bu group, hence both disorders must be correlated. The refinement of occupancy factors converged at 82.0(2)% and 18.0(2)% for the major and minor orientations, respectively. In both **12** and **13** the fluorene system is planar. The dihedral angles between adjacent rings are listed in Table S2.

Molecule **20** (Figure S22) lies at a crystallographic inversion centre, hence in the central pyridine ring the nitrogen atom is equally distributed between two positions. The pyridine, oxadiazole and benzene rings (i) are nearly coplanar (as in **11** and **12**, see Table S2) due to the absence in the oxadiazole moiety of sterically hindering peri-hydrogen atoms. The N(4) atom has planar-trigonal geometry, but all three adjacent benzene rings are substantially inclined to its plane (NC_3), in a propeller-like fashion. One molecule of deuteriochloroform occupies a general position in the lattice, another molecule is disordered between two positions related *via* a twofold axis. Thus the asymmetric unit comprises half of the **20**·3$CDCl_3$ formula unit.

References

1. G. M. Sheldrick, SADABS v. 2.03, Bruker AXS, Madison, Wisconsin, USA, 2001.
2. SHELXTL v. 6.12, Bruker AXS, Madison, Wisconsin, USA, 2001.

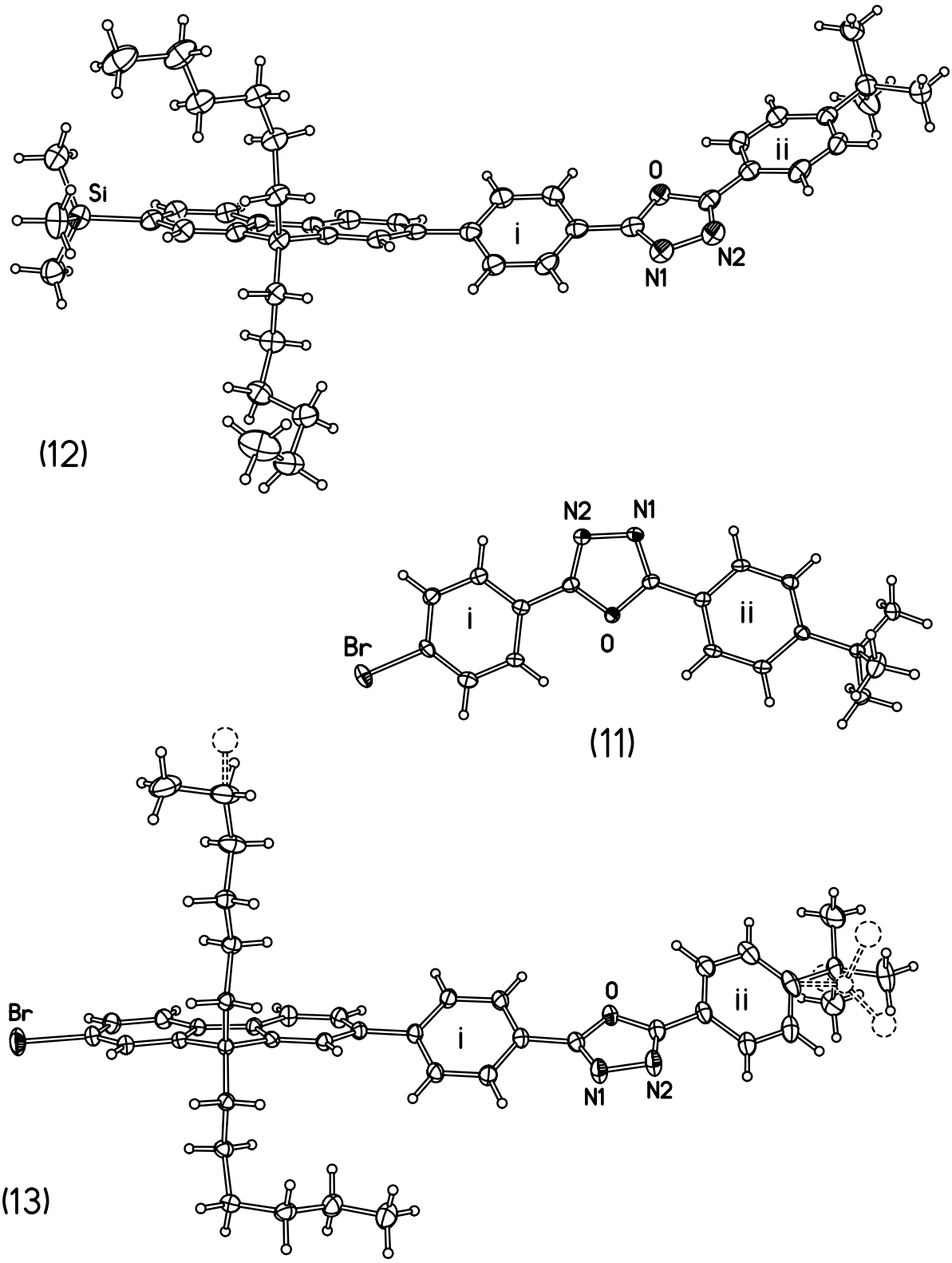

Figure S21. Molecular structures of **11**, **12** and **13** (50% thermal ellipsoids), showing the disorder in the latter.

Table S1. Crystal Data

Compound	**11**	**12**	**13**	**20**
Formula	$C_{18}H_{17}BrN_2O$	$C_{46}H_{58}N_2OSi$	$C_{43}H_{49}BrN_2O$	$C_{45}H_{31}N_7O_2$ 3 $CDCl_3$
M	357.25	683.03	689.75	1062.89
Temp., K	120	120	120	120
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$ (#14)	$C2/c$ (#15)	$P\bar{1}$ (#2)	$I2/a$ (#15)
a, Å	7.357(1)	14.695(2)	10.945(5)	21.462(6)
b, Å	6.139(1)	13.330(1)	12.714(3)	9.581(3)
c, Å	34.909(6)	41.182(5)	13.128(4)	23.428(6)
α, °	90	90	96.10(1)	90
β, °	91.43(2)	94.32(1)	93.84(1)	96.48(2)
γ, °	90	90	94.38(1)	90
V, Å^3	1576.2(4)	8044(2)	1806(1)	4787(2)
Z	4	8	2	4
D_{calc} (g/cm^3)	1.505	1.128	1.268	1.475
μ, mm^{-1}	2.61	0.09	1.17	0.58
Reflections total	14799	34477	32533	21479
-- unique	3504	7093	10531	4224
-- , with $I \geq 2\sigma(I)$	3114	4312	7932	3572
R_{int}, %	6.7	7.8	4.2	3.1
Refined parameters	203	467	447	320
$R(F)$, $I \geq 2\sigma(I)$, %	7.6	4.5	3.5	5.5
w$R(F^2)$, all data, %	17.1	11.8	9.4	16.6

Table S2. Dihedral angles (°) between planar fragments

Angle	**11**	**12**	**13**	**20**
fluorene / benzene i	-	37.3	40.1	-
benzene i / oxadiazole	5.7	6.7	13.8	3.5
oxadiazole / benzene ii	7.4	7.5	28.9	-
pyridine / oxadiazole				7.2
benzene i / N(4)C(14)C(21)C(31)				27.6
N(4)C(14)C(21)C(31) / phenyl ii				54.1
N(4)C(14)C(21)C(31) / phenyl iii				32.4

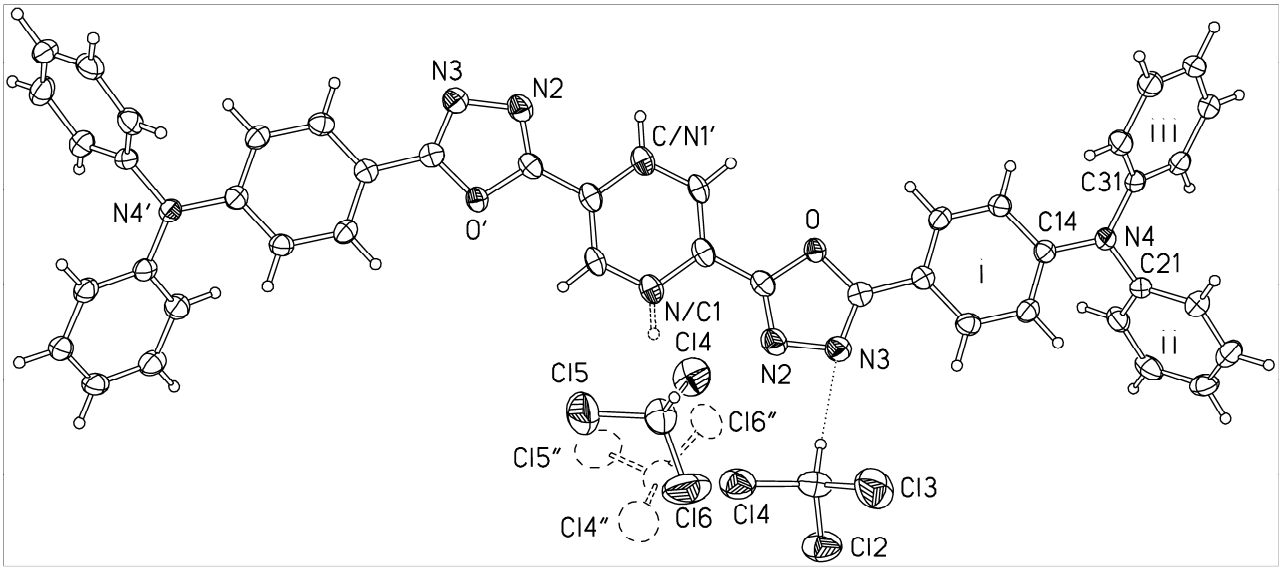

Figure S22. Molecules in the structure of **20**·3CDCl$_3$, showing the disorder. Atoms generated by an inversion centre are primed, those generated by a twofold axis are double-primed. Thermal ellipsoids are drawn at the 50% probability level.

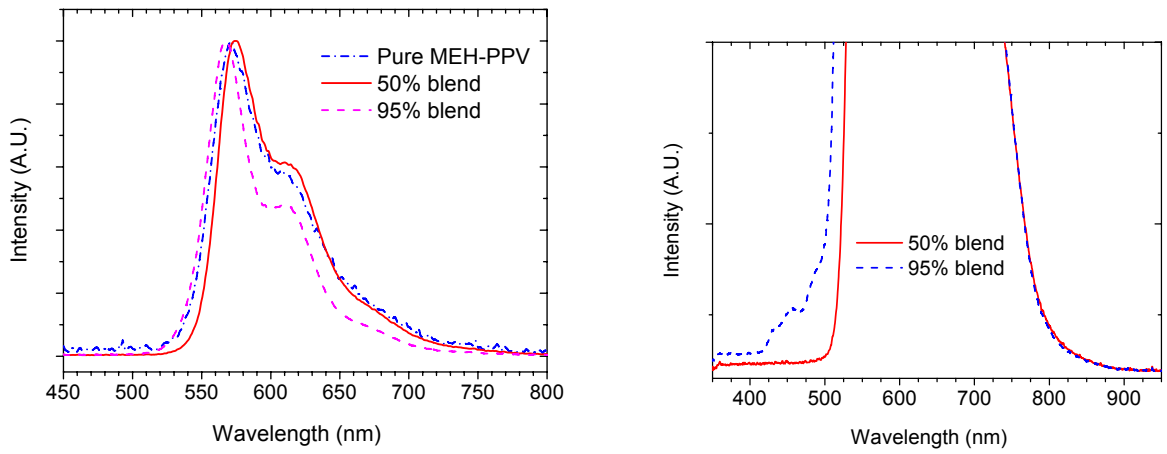

Figure S23. The EL spectra of a pure MEH-PPV OLED and blended-layer devices incorporating MEH-PPV and compound **7** (50% and 95% by weight of **7**). Device structure: ITO/PEDOT/MEH-PPV (blend)/Al.

Table S3. B3LYP/6-31G(d) optimised geometry of compound **7a**
Stoichiometry $C_{57}H_{44}N_6O_2$ E_{total} = –2677.5371608 Hartree
Dipole moment (field-independent basis, Debye): X= -1.2937 Y= 1.2235 Z= -0.1014 Tot= 1.7835

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.788908	-1.474254	-0.066103
2	6	0	0.581124	-1.988881	-0.076692
3	6	0	1.470385	-0.895909	-0.011781
4	6	0	0.708871	0.427559	0.050815
5	6	0	-0.737089	-0.064687	0.008191
6	6	0	-1.904435	0.679201	0.034839
7	6	0	-3.146413	0.013242	-0.012718
8	6	0	-3.192567	-1.390477	-0.087519
9	6	0	-2.017550	-2.137409	-0.114054
10	6	0	1.068042	-3.299112	-0.135720
11	6	0	2.441452	-3.512935	-0.129874
12	6	0	3.334394	-2.425292	-0.067212
13	6	0	2.841200	-1.107739	-0.008507
14	6	0	1.043575	1.351027	-1.157758
15	6	0	1.014302	1.212676	1.361011
16	6	0	0.752169	0.462772	2.670589
17	6	0	0.809595	0.751645	-2.547760
18	6	0	-4.367972	0.802787	0.019550
19	6	0	4.764719	-2.691929	-0.061262
20	8	0	-5.583864	0.175916	-0.024309
21	6	0	-6.467802	1.219732	0.028801
22	7	0	-5.854117	2.369142	0.096918
23	7	0	-4.494734	2.097772	0.091614
24	8	0	5.649087	-1.647164	-0.033752
25	6	0	6.864812	-2.276270	-0.035529
26	7	0	6.736526	-3.574497	-0.061625
27	7	0	5.376838	-3.842189	-0.077253
28	6	0	8.082994	-1.487150	-0.012436
29	6	0	-7.894732	0.953418	0.008187
30	6	0	-8.802482	2.023555	0.097530
31	6	0	-10.169466	1.795440	0.088724
32	6	0	-10.681454	0.486382	-0.021309
33	6	0	-9.770173	-0.582648	-0.117812
34	6	0	-8.401483	-0.351754	-0.096971
35	6	0	9.329413	-2.136414	0.035249
36	6	0	10.507608	-1.407296	0.059794
37	6	0	10.484687	0.002192	0.025435
38	6	0	9.235296	0.649532	-0.027642
39	6	0	8.056558	-0.083748	-0.039806
40	7	0	11.683081	0.743845	0.044364
41	7	0	-12.071822	0.253221	-0.032363
42	6	0	-12.613364	-0.933803	0.543345
43	6	0	-12.962552	1.205073	-0.611253
44	6	0	11.735843	2.024807	0.669244
45	6	0	12.864365	0.231008	-0.569442
46	6	0	12.357210	3.101525	0.019078
47	6	0	12.426785	4.348771	0.637326
48	6	0	11.866002	4.545633	1.900912
49	6	0	11.241573	3.476547	2.547242
50	6	0	11.182972	2.221356	1.944120
51	6	0	14.094127	0.300686	0.102099
52	6	0	15.252387	-0.182119	-0.504375
53	6	0	15.200223	-0.754501	-1.777062
54	6	0	13.975825	-0.830507	-2.444500
55	6	0	12.815599	-0.333229	-1.853314
56	6	0	-13.595730	-1.665105	-0.141010
57	6	0	-14.139893	-2.814153	0.430290
58	6	0	-13.703380	-3.259612	1.679695
59	6	0	-12.721033	-2.536406	2.359747

60	6	0	-12.184326	-1.376249	1.804237
61	6	0	-14.132889	1.578885	0.066007
62	6	0	-15.012321	2.495498	-0.507643
63	6	0	-14.731892	3.063641	-1.752032
64	6	0	-13.564206	2.697331	-2.424934
65	6	0	-12.688169	1.767667	-1.867156
66	1	0	-1.893375	1.763465	0.091927
67	1	0	-4.154606	-1.890696	-0.123916
68	1	0	-2.065596	-3.221493	-0.171183
69	1	0	0.388432	-4.145622	-0.185205
70	1	0	2.847504	-4.517970	-0.173729
71	1	0	3.537851	-0.276187	0.039834
72	1	0	0.450271	2.269105	-1.052195
73	1	0	2.094689	1.656427	-1.064694
74	1	0	2.065826	1.528617	1.325662
75	1	0	0.419646	2.135820	1.344414
76	1	0	0.992567	1.102522	3.526964
77	1	0	-0.298143	0.166715	2.760691
78	1	0	1.365369	-0.441238	2.746504
79	1	0	1.075072	1.479594	-3.322436
80	1	0	1.419214	-0.143753	-2.708577
81	1	0	-0.239889	0.476584	-2.695740
82	1	0	-8.417740	3.033967	0.190427
83	1	0	-10.854313	2.631869	0.174939
84	1	0	-10.143132	-1.596436	-0.213714
85	1	0	-7.717035	-1.190141	-0.177927
86	1	0	9.357144	-3.220723	0.068116
87	1	0	11.458812	-1.925509	0.112239
88	1	0	9.194558	1.732542	-0.065853
89	1	0	7.105038	0.436069	-0.088330
90	1	0	12.783951	2.953336	-0.967905
91	1	0	12.911490	5.173186	0.121114
92	1	0	11.916134	5.520474	2.377448
93	1	0	10.809486	3.613677	3.534973
94	1	0	10.711055	1.388299	2.455758
95	1	0	14.134368	0.734336	1.096343
96	1	0	16.197815	-0.121647	0.028124
97	1	0	16.103591	-1.136359	-2.243971
98	1	0	13.922592	-1.265877	-3.438796
99	1	0	11.868054	-0.379067	-2.381014
100	1	0	-13.928111	-1.326960	-1.117447
101	1	0	-14.900337	-3.369976	-0.111797
102	1	0	-14.124848	-4.159059	2.119324
103	1	0	-12.379218	-2.866478	3.337161
104	1	0	-11.432922	-0.807137	2.342675
105	1	0	-14.346564	1.147410	1.038853
106	1	0	-15.914895	2.775770	0.028888
107	1	0	-15.415895	3.783005	-2.193114
108	1	0	-13.338037	3.125387	-3.397885
109	1	0	-11.789017	1.473073	-2.399291

Table S4. B3LYP/6-31G(d) optimised geometry of compound **8a**
Stoichiometry $C_{57}H_{40}N_6O_2$ E_{total} = –2675.1805199 Hartree
Dipole moment (field-independent basis, Debye): X= 0.9469 Y= -0.1675 Z= 0.0060 Tot= 0.9616

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.801151	1.473699	-0.059162
2	6	0	-0.563346	2.002316	-0.080307
3	6	0	-1.463837	0.919105	-0.006060
4	6	0	-0.716583	-0.411242	0.075380
5	6	0	0.734298	0.065554	0.028123
6	6	0	1.894145	-0.689928	0.059923
7	6	0	3.142184	-0.036174	0.005712

8	6	0	3.203371	1.366438	-0.078242
9	6	0	2.036119	2.124787	-0.110953
10	6	0	-1.035274	3.316845	-0.159910
11	6	0	-2.406279	3.545049	-0.166602
12	6	0	-3.310268	2.467200	-0.094801
13	6	0	-2.832279	1.145350	-0.013517
14	6	0	-1.060093	-1.347919	-1.120517
15	6	0	-1.031412	-1.174327	1.396687
16	6	0	-0.761414	-0.409428	2.695958
17	6	0	-0.817928	-0.771421	-2.518748
18	6	0	4.355492	-0.838346	0.033938
19	6	0	-4.737384	2.749715	-0.108301
20	8	0	5.577680	-0.223787	0.005013
21	6	0	6.448953	-1.277239	0.040300
22	7	0	5.825251	-2.420410	0.086391
23	7	0	4.469069	-2.136375	0.082631
24	8	0	-5.634616	1.717622	-0.050742
25	6	0	-6.840780	2.361066	-0.088463
26	7	0	-6.697851	3.654288	-0.160786
27	7	0	-5.335894	3.906250	-0.173114
28	6	0	-8.073110	1.588672	-0.050498
29	6	0	7.882146	-1.026846	0.023782
30	6	0	8.771512	-2.114814	0.041100
31	6	0	10.143172	-1.899700	0.033655
32	6	0	10.655961	-0.593346	-0.005968
33	6	0	9.770146	0.493094	-0.030155
34	6	0	8.396362	0.278427	-0.007915
35	6	0	-9.306522	2.261787	-0.077108
36	6	0	-10.496511	1.547798	-0.038784
37	6	0	-10.480544	0.144734	0.011075
38	6	0	-9.251040	-0.528766	0.031539
39	6	0	-8.058752	0.186830	0.009465
40	7	0	-11.694034	-0.582533	0.039063
41	7	0	12.054025	-0.374757	-0.020663
42	6	0	12.763513	0.464129	0.851775
43	6	0	12.967853	-0.960903	-0.909445
44	6	0	-12.036143	-1.576077	0.968696
45	6	0	-12.760994	-0.434002	-0.860152
46	6	0	-13.330906	-2.065087	0.662437
47	6	0	-13.902256	-3.057831	1.466632
48	6	0	-13.187785	-3.540409	2.559226
49	6	0	-11.912790	-3.032073	2.859266
50	6	0	-11.321014	-2.044202	2.074397
51	6	0	-13.791232	-1.339785	-0.503603
52	6	0	-14.961739	-1.390584	-1.269227
53	6	0	-15.086761	-0.552657	-2.373405
54	6	0	-14.048578	0.327094	-2.723189
55	6	0	-12.873283	0.397531	-1.977704
56	6	0	14.140481	0.413052	0.519195
57	6	0	15.059471	1.158364	1.266635
58	6	0	14.601278	1.930811	2.329912
59	6	0	13.235080	1.956547	2.656961
60	6	0	12.299395	1.224465	1.928536
61	6	0	14.270125	-0.491903	-0.604198
62	6	0	15.357285	-0.923991	-1.372361
63	6	0	15.134766	-1.802574	-2.428623
64	6	0	13.835050	-2.244494	-2.728137
65	6	0	12.735624	-1.830120	-1.978771
66	1	0	1.872152	-1.773600	0.124245
67	1	0	4.170209	1.856856	-0.119749
68	1	0	2.094911	3.207711	-0.177417
69	1	0	-0.346461	4.155290	-0.216894
70	1	0	-2.801310	4.553499	-0.228223
71	1	0	-3.537588	0.321502	0.040702
72	1	0	-0.477452	-2.271012	-1.000840
73	1	0	-2.114523	-1.640423	-1.024144

74	1	0	-2.086386	-1.478770	1.364814
75	1	0	-0.447541	-2.104341	1.393000
76	1	0	-1.013266	-1.033210	3.560661
77	1	0	0.292880	-0.127520	2.784981
78	1	0	-1.361349	0.504537	2.757631
79	1	0	-1.091459	-1.507405	-3.282819
80	1	0	-1.416660	0.128696	-2.693703
81	1	0	0.234849	-0.511204	-2.670141
82	1	0	8.371613	-3.122755	0.075709
83	1	0	10.827721	-2.740500	0.074635
84	1	0	10.164086	1.502685	-0.082313
85	1	0	7.718005	1.124900	-0.030293
86	1	0	-9.314825	3.346079	-0.112699
87	1	0	-11.446807	2.071342	-0.031377
88	1	0	-9.236249	-1.613481	0.047081
89	1	0	-7.111991	-0.343009	0.021383
90	1	0	-14.894046	-3.441961	1.242874
91	1	0	-13.620157	-4.311973	3.189758
92	1	0	-11.374776	-3.412146	3.723410
93	1	0	-10.342093	-1.648866	2.323860
94	1	0	-15.759933	-2.079844	-1.006433
95	1	0	-15.991148	-0.581589	-2.974307
96	1	0	-14.159268	0.965931	-3.595101
97	1	0	-12.073013	1.071238	-2.264766
98	1	0	16.118095	1.128644	1.022313
99	1	0	15.304741	2.514460	2.916701
100	1	0	12.897264	2.556087	3.497868
101	1	0	11.248786	1.240551	2.198288
102	1	0	16.361254	-0.572574	-1.149204
103	1	0	15.970638	-2.146251	-3.031152
104	1	0	13.679220	-2.921684	-3.563452
105	1	0	11.734817	-2.167447	-2.226592

Table S5. B3LYP/6-31G(d) optimised geometry of compound **14a**
Stoichiometry $C_{47}H_{43}N_3O$ E_{total} = –2056.4182449 Hartree
Dipole moment (field-independent basis, Debye): X= -1.2512 Y= -1.3679 Z= -3.2685 Tot= 3.7576

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.933220	-1.052700	-0.343107
2	6	0	-2.478181	-1.068112	-0.180196
3	6	0	-2.080618	0.147303	0.415322
4	6	0	-3.287822	1.051526	0.667273
5	6	0	-4.426203	0.175499	0.143182
6	6	0	-5.784615	0.453572	0.119598
7	6	0	-6.680028	-0.495564	-0.413120
8	6	0	-6.180222	-1.716197	-0.906221
9	6	0	-4.817363	-2.000021	-0.864897
10	6	0	-1.521622	-2.031609	-0.507816
11	6	0	-0.177934	-1.773247	-0.242394
12	6	0	0.236652	-0.566337	0.352821
13	6	0	-0.742453	0.394560	0.682346
14	7	0	-8.071839	-0.221363	-0.451790
15	6	0	1.670464	-0.308277	0.624478
16	6	0	2.079065	0.388813	1.778073
17	6	0	3.420009	0.638630	2.034914
18	6	0	4.406448	0.195980	1.137607
19	6	0	4.015000	-0.501468	-0.015405
20	6	0	2.669372	-0.746867	-0.263197
21	6	0	5.806728	0.470722	1.420599
22	7	0	6.324035	1.084374	2.447356
23	7	0	7.697492	1.098239	2.255402
24	6	0	7.925696	0.492123	1.124731
25	8	0	6.767510	0.064022	0.535674

26	6	0	9.199878	0.246416	0.465244
27	6	0	9.270783	-0.410055	-0.772940
28	6	0	10.502170	-0.623808	-1.380784
29	6	0	11.705641	-0.199525	-0.789904
30	6	0	11.614588	0.453454	0.449403
31	6	0	10.388653	0.676151	1.070551
32	6	0	-3.185378	2.391416	-0.119923
33	6	0	-3.457012	1.387639	2.177618
34	6	0	13.044399	-0.457407	-1.503221
35	6	0	13.033890	0.246651	-2.881414
36	6	0	14.247883	0.073762	-0.701707
37	6	0	13.233643	-1.979929	-1.706358
38	6	0	-9.012559	-1.249724	-0.167216
39	6	0	-8.532937	1.077424	-0.804889
40	6	0	-10.166053	-1.398091	-0.953884
41	6	0	-11.090966	-2.399321	-0.663359
42	6	0	-10.876004	-3.278641	0.399925
43	6	0	-9.725186	-3.138685	1.178872
44	6	0	-8.803709	-2.129213	0.907520
45	6	0	-9.589850	1.673164	-0.097979
46	6	0	-10.045693	2.941582	-0.452098
47	6	0	-9.447729	3.644703	-1.500269
48	6	0	-8.391062	3.058056	-2.199846
49	6	0	-7.940635	1.782414	-1.865113
50	6	0	-2.995879	2.265314	-1.634390
51	6	0	-3.594042	0.188076	3.119866
52	1	0	-6.172146	1.391640	0.505867
53	1	0	-6.872530	-2.439416	-1.324360
54	1	0	-4.454644	-2.948534	-1.252978
55	1	0	-1.812951	-2.977370	-0.957772
56	1	0	0.564085	-2.532444	-0.472869
57	1	0	-0.434251	1.342457	1.116768
58	1	0	1.332410	0.715413	2.495798
59	1	0	3.723155	1.169428	2.931477
60	1	0	4.766544	-0.840951	-0.720863
61	1	0	2.383777	-1.262426	-1.175267
62	1	0	8.360636	-0.749385	-1.257098
63	1	0	10.521799	-1.133335	-2.339756
64	1	0	12.511580	0.801018	0.949010
65	1	0	10.339973	1.184802	2.027964
66	1	0	-4.095370	2.971277	0.085787
67	1	0	-2.353873	2.970408	0.304588
68	1	0	-2.595610	1.996105	2.485351
69	1	0	-4.337853	2.035700	2.282431
70	1	0	13.981535	0.071668	-3.405228
71	1	0	12.226441	-0.122171	-3.522445
72	1	0	12.903270	1.328795	-2.767999
73	1	0	15.174054	-0.130910	-1.250138
74	1	0	14.189538	1.157019	-0.546398
75	1	0	14.331414	-0.409142	0.278560
76	1	0	14.187178	-2.180408	-2.209736
77	1	0	13.239546	-2.506435	-0.745251
78	1	0	12.436524	-2.412985	-2.319732
79	1	0	-10.331137	-0.725561	-1.789598
80	1	0	-11.978380	-2.499583	-1.282932
81	1	0	-11.595682	-4.062213	0.619069
82	1	0	-9.547761	-3.810137	2.014986
83	1	0	-7.918112	-2.014790	1.524550
84	1	0	-10.048502	1.136126	0.726275
85	1	0	-10.864916	3.387383	0.106053
86	1	0	-9.800902	4.636294	-1.768516
87	1	0	-7.921082	3.589031	-3.023636
88	1	0	-7.129345	1.324571	-2.422255
89	1	0	-2.935688	3.258621	-2.093341
90	1	0	-2.074852	1.726730	-1.880200
91	1	0	-3.831661	1.731795	-2.099387

92	1	0	-3.705690	0.529391	4.155225
93	1	0	-4.471255	-0.418405	2.871333
94	1	0	-2.713073	-0.460895	3.074727

Table S6. B3LYP/6-31G(d) optimised geometry of compound **16a**
Stoichiometry $C_{76}H_{71}N_5O_2$ E_{total} = –3363.1392095 Hartree
Dipole moment (field-independent basis, Debye): X= -0.5873 Y= -0.5366 Z= 0.1126 Tot= 0.8035

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.628292	1.011340	-0.141830
2	6	0	4.992609	0.493571	-0.026636
3	6	0	5.763163	1.418825	0.707993
4	6	0	4.920085	2.627494	1.116641
5	6	0	3.562335	2.255073	0.519025
6	6	0	2.373041	2.966684	0.573928
7	6	0	1.223158	2.449563	-0.056390
8	6	0	1.299195	1.212467	-0.725050
9	6	0	2.489586	0.490834	-0.761254
10	6	0	5.577951	-0.681199	-0.503823
11	6	0	6.926948	-0.920343	-0.248792
12	6	0	7.712687	-0.006645	0.479749
13	6	0	7.104605	1.172676	0.959637
14	7	0	0.002146	3.171423	-0.022190
15	6	0	9.147602	-0.276189	0.733874
16	6	0	9.759284	0.107632	1.943215
17	6	0	11.104249	-0.137481	2.183057
18	6	0	11.889786	-0.783009	1.213343
19	6	0	11.294242	-1.173524	0.004346
20	6	0	9.947167	-0.920949	-0.227180
21	6	0	13.298019	-1.030380	1.481329
22	7	0	13.990137	-0.723986	2.542171
23	7	0	15.285005	-1.166532	2.317047
24	6	0	15.295760	-1.713311	1.134284
25	8	0	14.064113	-1.663346	0.540946
26	6	0	16.409728	-2.329063	0.428066
27	6	0	16.252655	-2.885863	-0.850402
28	6	0	17.336883	-3.466881	-1.497464
29	6	0	18.612681	-3.519084	-0.908247
30	6	0	18.749851	-2.956887	0.370620
31	6	0	17.673688	-2.371659	1.031976
32	6	0	5.472373	3.951989	0.512129
33	6	0	4.851007	2.792350	2.662918
34	6	0	19.783060	-4.171216	-1.664846
35	6	0	20.015581	-3.418743	-2.997171
36	6	0	21.094995	-4.135649	-0.858170
37	6	0	19.440804	-5.650347	-1.964879
38	6	0	0.004299	4.589117	-0.149220
39	6	0	-0.814254	5.375198	0.677498
40	6	0	-0.822755	6.762326	0.544183
41	6	0	-0.005890	7.389850	-0.398806
42	6	0	0.816059	6.610950	-1.216403
43	6	0	0.817807	5.221873	-1.102615
44	6	0	-3.666773	1.121782	0.390291
45	6	0	-5.030304	0.593115	0.311896
46	6	0	-5.735108	1.316060	-0.672988
47	6	0	-4.848963	2.394022	-1.297914
48	6	0	-3.540101	2.174960	-0.538839
49	6	0	-2.336439	2.848187	-0.685974
50	6	0	-1.234813	2.484309	0.112616
51	6	0	-1.369717	1.438886	1.045217
52	6	0	-2.574911	0.753751	1.180580
53	6	0	-5.665767	-0.434434	1.012463
54	6	0	-6.996247	-0.732763	0.723418

55	6	0	-7.713818	-0.024488	-0.259675
56	6	0	-7.057785	1.011654	-0.957017
57	6	0	-9.124921	-0.362944	-0.560374
58	6	0	-9.623700	-0.293422	-1.875755
59	6	0	-10.942959	-0.610865	-2.166674
60	6	0	-11.815948	-1.014245	-1.142302
61	6	0	-11.333965	-1.088370	0.173424
62	6	0	-10.011108	-0.766140	0.454641
63	6	0	-13.194078	-1.346132	-1.469332
64	7	0	-13.780303	-1.321373	-2.632955
65	7	0	-15.091197	-1.724729	-2.429651
66	6	0	-15.216839	-1.968684	-1.155804
67	8	0	-14.048151	-1.748460	-0.479201
68	6	0	-16.394128	-2.423121	-0.430459
69	6	0	-16.367866	-2.634273	0.956506
70	6	0	-17.509263	-3.071623	1.618135
71	6	0	-18.714733	-3.316714	0.936769
72	6	0	-18.721681	-3.098280	-0.449940
73	6	0	-17.587083	-2.659853	-1.126981
74	6	0	-5.421284	3.823679	-1.066897
75	6	0	-4.674385	2.184358	-2.830793
76	6	0	-19.950921	-3.804545	1.712022
77	6	0	-20.326829	-2.760734	2.791042
78	6	0	-21.172810	-4.009434	0.796628
79	6	0	-19.628078	-5.155086	2.395459
80	6	0	-4.110150	0.827171	-3.261543
81	6	0	-5.660151	4.222765	0.392415
82	6	0	4.326163	1.583286	3.443090
83	6	0	5.622928	3.982556	-1.011705
84	1	0	2.311674	3.918238	1.093550
85	1	0	0.415174	0.824076	-1.219696
86	1	0	2.524356	-0.461064	-1.285243
87	1	0	4.994251	-1.409511	-1.061121
88	1	0	7.376266	-1.846354	-0.595855
89	1	0	7.704703	1.899613	1.501317
90	1	0	9.162133	0.582139	2.716235
91	1	0	11.561929	0.155595	3.122254
92	1	0	11.892198	-1.664034	-0.756948
93	1	0	9.512300	-1.203139	-1.181345
94	1	0	15.281335	-2.862706	-1.334168
95	1	0	17.181233	-3.888686	-2.486248
96	1	0	19.711198	-2.969396	0.871199
97	1	0	17.801584	-1.942616	2.020548
98	1	0	4.809451	4.768556	0.828793
99	1	0	6.446577	4.153902	0.977922
100	1	0	5.858217	3.047168	3.020050
101	1	0	4.222910	3.666953	2.880274
102	1	0	20.843365	-3.876751	-3.552017
103	1	0	19.130032	-3.442835	-3.640910
104	1	0	20.268426	-2.368070	-2.815353
105	1	0	21.896239	-4.606874	-1.438070
106	1	0	21.409670	-3.110016	-0.634737
107	1	0	21.008249	-4.681518	0.088157
108	1	0	20.262127	-6.125974	-2.514511
109	1	0	19.281772	-6.212456	-1.037647
110	1	0	18.534982	-5.745524	-2.572805
111	1	0	-1.439846	4.891877	1.421356
112	1	0	-1.462257	7.355545	1.192604
113	1	0	-0.009527	8.471774	-0.495298
114	1	0	1.451329	7.084690	-1.960267
115	1	0	1.446763	4.619280	-1.750300
116	1	0	-2.225769	3.650911	-1.409069
117	1	0	-0.518941	1.170443	1.663193
118	1	0	-2.657264	-0.049955	1.907917
119	1	0	-5.134431	-1.007462	1.768171
120	1	0	-7.481684	-1.551392	1.247077

121	1	0	-7.606466	1.586919	-1.698614
122	1	0	-8.956329	-0.012500	-2.685023
123	1	0	-11.312774	-0.562935	-3.185659
124	1	0	-12.000601	-1.388831	0.975375
125	1	0	-9.664411	-0.801960	1.483141
126	1	0	-15.453284	-2.455265	1.512825
127	1	0	-17.455455	-3.224767	2.692066
128	1	0	-19.624723	-3.271055	-1.024209
129	1	0	-17.613331	-2.497863	-2.199713
130	1	0	-4.731594	4.541041	-1.531962
131	1	0	-6.363818	3.902889	-1.625502
132	1	0	-5.653199	2.339423	-3.304928
133	1	0	-4.025337	2.985750	-3.209276
134	1	0	-21.204377	-3.097993	3.355843
135	1	0	-19.513254	-2.599312	3.506023
136	1	0	-20.567481	-1.793779	2.334904
137	1	0	-22.024979	-4.355827	1.391784
138	1	0	-21.472847	-3.078774	0.301839
139	1	0	-20.982694	-4.762706	0.023735
140	1	0	-20.497894	-5.512365	2.959971
141	1	0	-19.368019	-5.918155	1.653089
142	1	0	-18.789764	-5.070062	3.094887
143	1	0	-4.033948	0.776883	-4.353558
144	1	0	-3.109810	0.659999	-2.848602
145	1	0	-4.751697	0.003065	-2.932270
146	1	0	-6.061221	5.241121	0.446189
147	1	0	-6.377858	3.554394	0.879352
148	1	0	-4.730834	4.198301	0.971199
149	1	0	4.318450	1.798980	4.517483
150	1	0	3.303555	1.328079	3.145960
151	1	0	4.953004	0.699620	3.283720
152	1	0	6.021992	4.950992	-1.333818
153	1	0	6.308615	3.204520	-1.362898
154	1	0	4.660663	3.833895	-1.512962

Table S7. B3LYP/6-31G(d) optimised geometry of compound **20**
Stoichiometry $C_{45}H_{31}N_7O_2$ E_{total} = –2267.1417592 Hartree
Dipole moment (field-independent basis, Debye): X= 2.0338 Y= -0.8912 Z= 0.1562 Tot= 2.2260

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.141779	-1.015266	-0.026996
2	6	0	-0.109104	-1.613081	-0.030901
3	6	0	-1.244942	-0.788170	-0.028982
4	7	0	-1.180561	0.556035	-0.021210
5	6	0	0.024462	1.117412	-0.017999
6	6	0	1.226918	0.385358	-0.021772
7	6	0	-2.571478	-1.397723	-0.038342
8	6	0	2.499609	1.084522	-0.023545
9	8	0	-3.687304	-0.617554	-0.022399
10	6	0	-4.697405	-1.534796	-0.040981
11	7	0	-4.241249	-2.761363	-0.065479
12	7	0	-2.861926	-2.668220	-0.064398
13	7	0	2.721708	2.367413	-0.042174
14	7	0	4.096178	2.535714	-0.039047
15	6	0	4.623405	1.340750	-0.020107
16	8	0	3.663111	0.364710	-0.008704
17	6	0	-6.075153	-1.081425	-0.031739
18	6	0	6.025271	0.968977	-0.011603
19	6	0	6.434231	-0.372630	0.057396
20	6	0	7.781466	-0.704667	0.070816
21	6	0	8.770756	0.296419	0.003277
22	6	0	8.356009	1.642825	-0.072148
23	6	0	7.010086	1.971123	-0.073711

24	6	0	-7.118613	-2.021991	-0.091302
25	6	0	-8.442016	-1.611490	-0.087651
26	6	0	-8.771715	-0.242121	-0.012505
27	6	0	-7.723443	0.696852	0.052114
28	6	0	-6.398833	0.283571	0.036464
29	7	0	-10.117029	0.175111	-0.001829
30	6	0	-10.496352	1.425306	-0.575154
31	6	0	-11.125805	-0.637004	0.596774
32	7	0	10.137889	-0.037139	0.011217
33	6	0	11.101168	0.847591	0.583104
34	6	0	10.591105	-1.272569	-0.541317
35	6	0	12.286447	1.137999	-0.108212
36	6	0	13.237767	1.985356	0.457247
37	6	0	13.015443	2.565779	1.707711
38	6	0	11.833224	2.282019	2.394893
39	6	0	10.884472	1.421552	1.844807
40	6	0	11.495106	-2.072873	0.172337
41	6	0	11.954525	-3.269828	-0.374602
42	6	0	11.509131	-3.692401	-1.628786
43	6	0	10.604876	-2.899153	-2.338522
44	6	0	10.153909	-1.692164	-1.806865
45	6	0	-12.340552	-0.856114	-0.069663
46	6	0	-13.335352	-1.631900	0.522927
47	6	0	-13.129325	-2.211935	1.776403
48	6	0	-11.918189	-1.999874	2.438615
49	6	0	-10.924643	-1.210907	1.861301
50	6	0	-11.354288	2.288636	0.122103
51	6	0	-11.741901	3.500984	-0.445890
52	6	0	-11.269179	3.877013	-1.704898
53	6	0	-10.409928	3.021421	-2.397910
54	6	0	-10.031570	1.799035	-1.845311
55	1	0	2.043871	-1.618273	-0.029312
56	1	0	-0.227734	-2.690768	-0.036435
57	1	0	0.059875	2.203871	-0.012585
58	1	0	5.690469	-1.160788	0.117282
59	1	0	8.076678	-1.745584	0.141127
60	1	0	9.100011	2.428918	-0.136553
61	1	0	6.701698	3.009492	-0.139238
62	1	0	-6.874335	-3.077358	-0.156245
63	1	0	-9.234032	-2.349596	-0.149850
64	1	0	-7.954750	1.753909	0.122088
65	1	0	-5.605664	1.022212	0.093595
66	1	0	12.455522	0.696559	-1.085468
67	1	0	14.151443	2.201679	-0.089885
68	1	0	13.755720	3.231118	2.142632
69	1	0	11.651720	2.720318	3.372589
70	1	0	9.973203	1.190567	2.387746
71	1	0	11.833221	-1.750494	1.152151
72	1	0	12.654822	-3.879896	0.189625
73	1	0	11.863982	-4.628784	-2.049685
74	1	0	10.258207	-3.212005	-3.319824
75	1	0	9.463321	-1.069242	-2.366888
76	1	0	-12.498144	-0.415095	-1.048986
77	1	0	-14.271222	-1.792973	-0.005517
78	1	0	-13.904036	-2.821511	2.232603
79	1	0	-11.747957	-2.438264	3.418345
80	1	0	-9.990207	-1.035357	2.385189
81	1	0	-11.713364	2.002630	1.105699
82	1	0	-12.406977	4.159807	0.106083
83	1	0	-11.567684	4.825643	-2.141807
84	1	0	-10.041582	3.297949	-3.382209
85	1	0	-9.375846	1.128721	-2.392269
