Supporting Information

Solution-Processable Ambipolar Host Oligomers with High Triplet Energies for Phosphorescent Green Emitters

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Synthesis of 9. Following the reported procedure,[1] **9** was obtained from its dibromo precursor[2] and isolated as a white solid in 68% yield.

1*H*-Tetrazole precursors. 2-Phenyltetrazole (Aldrich), 2-(4-pyridyl)tetrazole (Aldrich) and 2-(4-*t*-butylphenyl)tetrazole (Apollo Scientific) were used as supplied. 2-(4-*n*-Octyloxyphenyl)tetrazole was synthesized following the reported procedure.[3]

General synthesis of oxadiazole derivatives 10-13. A mixture of 3,5-dibromobenzoic acid (1.73 g, 6.18 mmol) and thionyl chloride (10 mL) was stirred and heating at 85 °C for 4 h. Excess thionyl chloride was removed by evaporation under reduced pressure, and then to the residue was added the corresponding tetrazole derivative (6.8 mmol, 1.1. equiv.) in dry pyridine (20 mL). The mixture was stirred at 120 °C for 18 h. The cooled solution was poured into water, and the crude product was extracted with dichloromethane and washed with water three times. The organic layer was separated, dried ($MgSO_4$) and evaporated to give a white solid which was recrystallized from DCM/hexane to give the desired oxadiazole product.

2-(3,5-Dibromophenyl)-5-phenyl-1,3,4-oxadiazole **10.**[1] Yield: 85%.

2-(3,5-Dibromophenyl)-5-(4-pyridyl)-1,3,4-oxadiazole **11.** Yield: 40%. Mp: 196-197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.88 (1H, s), 7.99 (2H, d, *J* 6.0), 8.24 (2H, s), 8.86 (2H, d, *J* 6.0). ^{13}C NMR (100 MHz, $CDCl_3$): 163.4, 163.0, 151.0, 137.6, 130.5, 128.6, 126.4, 123.9, 120.4. Anal. Calcd. for $C_{13}H_7Br_2N_3O$: C, 40.98; H, 1.85; N, 11.03; Found: C, 40.88; H, 1.82; N, 10.78. MS (EI, 70 eV): *m*/*z* 357 (M^+).

2-(3,5-Dibromophenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole **12.** Yield: 85%. Mp: 145-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 1.38 (9H, s), 7.56 (2H, d, *J* 8.5), 7.84 (1H, t, *J* 1.8), 8.06 (2H, d, *J* 8.4), 8.22 (2H, d, *J* 1.8). ^{13}C NMR (100 MHz, $CDCl_3$): 165.3, 161.9, 155.9, 136.9 128.4,

127.2, 127.0, 126.2, 123.7, 120.6, 35.1, 31.1 Anal. Calcd. for $C_{18}H_{16}Br_2N_2O$: C, 49.57; H, 3.70; N, 6.42; Found: C, 49.61; H, 3.67; N, 6.35. MS (EI, 70 eV): *m*/*z* 421 (M^+).

2-(3,5-Dibromophenyl)-5-(4-n-octyloxyphenyl)-1,3,4-oxadiazole **13.** Yield: 60%. Mp: 81-82 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.20 (2H, d, *J* 1.7), 8.06 (2H, d, *J* 8.9), 7.83 (1H, t, *J* 1.7), 7.02 (2H, d, *J* 9.0), 4.04 (2H, t, *J* 6.5), 1.81 (2H, m), 1.38 (10H, m), 0.88 (3H, t, *J* 6.3). ^{13}C NMR (100 MHz, $CDCl_3$) 165.2, 162.6, 161.6, 136.8, 128.9, 128.3, 127.2, 123.6, 115.5, 115.1, 70.9, 39.4, 30.5, 29.1, 23.9, 23.0, 14.0, 11.1. Anal. Calcd. for $C_{22}H_{24}Br_2N_2O_2$: C, 51.99; H, 4.76; N, 5.51; Found: C, 51.87; H, 4.69; N, 5.39. MS (EI, 70 eV): *m*/*z* 508(M^+).

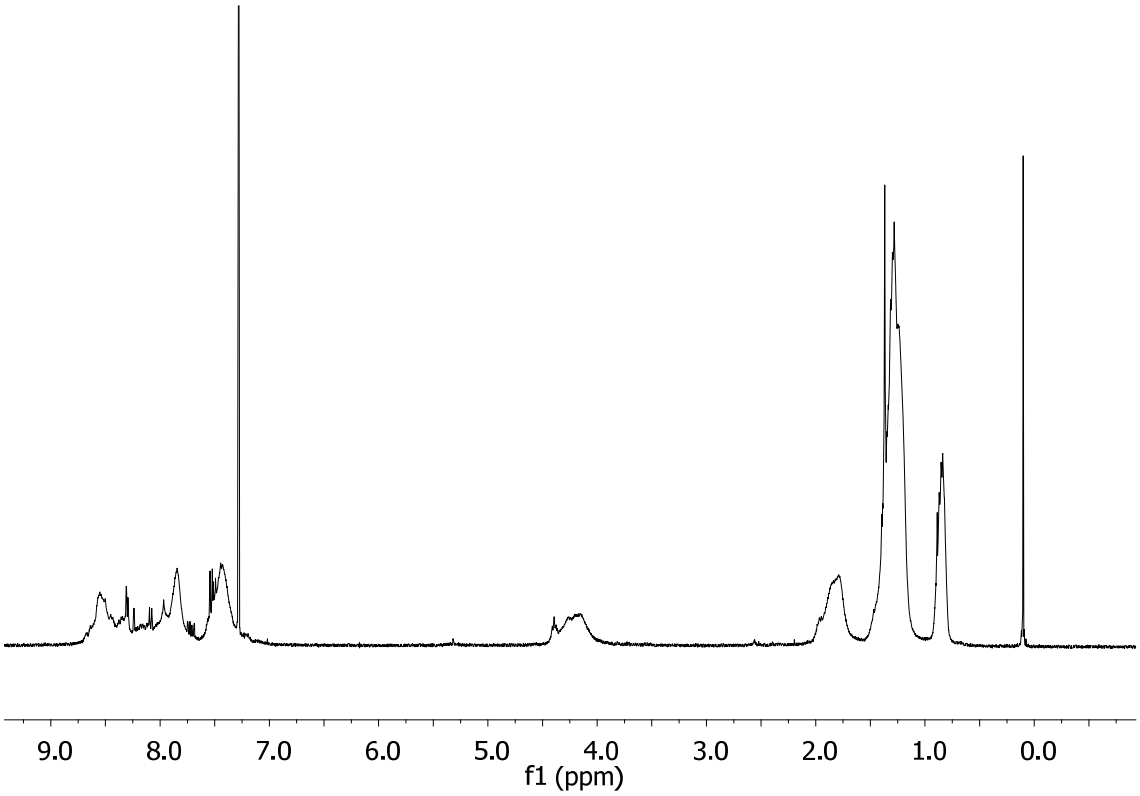


Figure S1. ^{1}H NMR spectrum of oligomer **16**

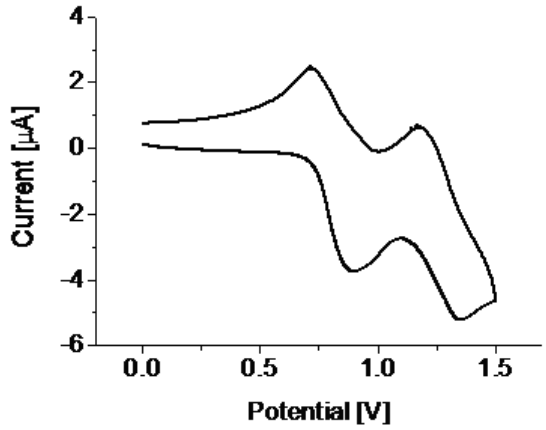


Figure S2. Cyclic voltammogram of oligomer **14**

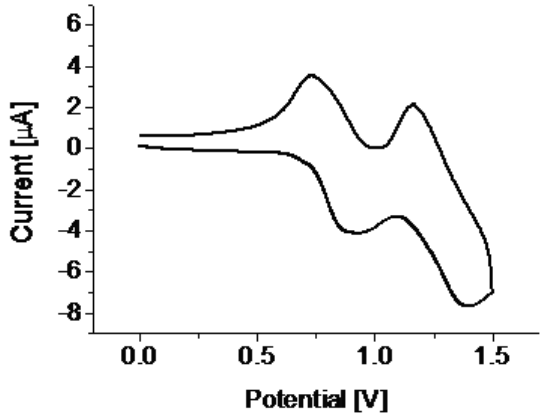


Figure S3. Cyclic voltammogram of oligomer **15**

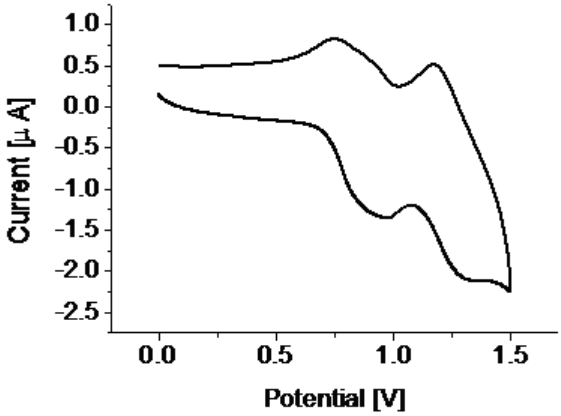


Figure S4. Cyclic voltammogram of oligomer **16**

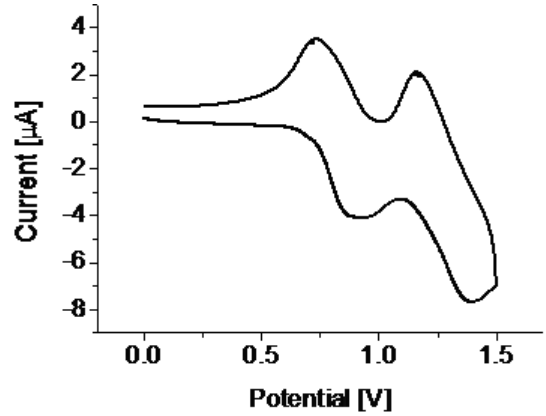
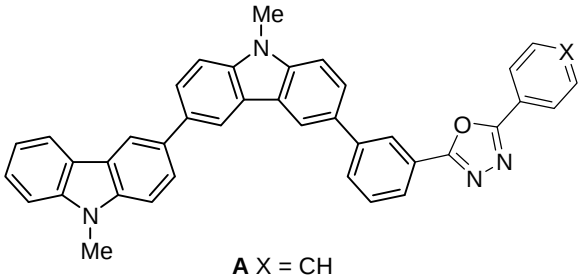


Figure S5. Cyclic voltammogram of oligomer **17**

Computational Data

Model compounds **A** and **B** were computed at the B3LYP/6-31G(d) level. **A** and **B** were chosen as they are the repeat units in oligomers **14** and **15**, respectively, with Me replacing the octyl chains to reduce the computation time. HOMO and LUMO distribution maps of **A** and **B** are shown in Figures S6-S7. For both compounds the HOMO is located on the bicarbazolyl

unit, whereas the LUMO is on the diaryloxadiazole fragment. The HOMO-LUMO gaps are 3.50 eV for **A**, and 3.15 eV for **B**, which demonstrates that the electron-withdrawing pyridyl substituent of **B** reduces the HOMO-LUMO gap.



A X = CH
B X = N

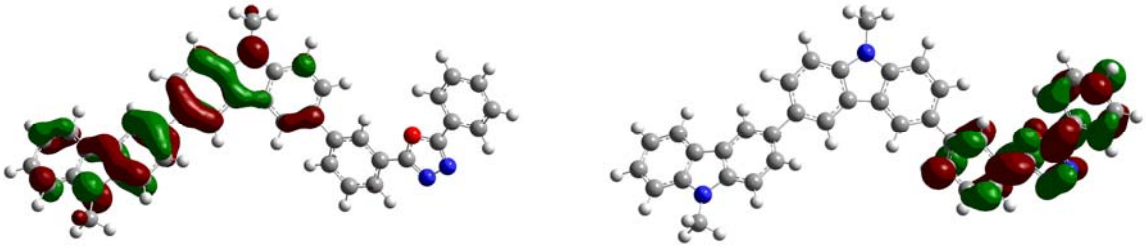


Figure S6. HOMO (left) and LUMO (right) distribution maps for **A**.

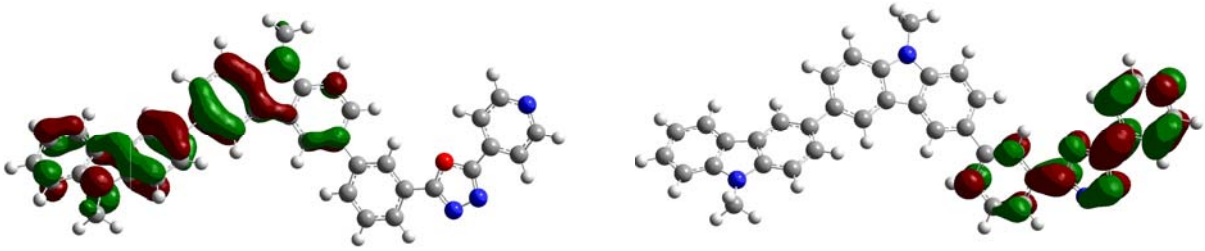


Figure S7. HOMO (left) and LUMO (right) distribution maps for **B**.

TABLE S1. Computational details for **A**

---
opt b3lyp/6-31g(d) geom=connectivity

1/14=-1,18=20,19=15,26=3,38=1,57=2/1,3;
2/9=110,12=2,17=6,18=5,40=1/2;
3/5=1,6=6,7=1,11=2,16=1,25=1,30=1,71=1,74=-5/1,2,3;
4//1;
5/5=2,38=5/2;
6/7=2,8=2,9=2,10=2,28=1/1;
7//1,2,3,16;
1/14=-1,18=20,19=15/3(2);
2/9=110/2;
99//99;
2/9=110/2;
3/5=1,6=6,7=1,11=2,16=1,25=1,30=1,71=1,74=-5/1,2,3;
4/5=5,16=3/1;
5/5=2,38=5/2;
7//1,2,3,16;
1/14=-1,18=20,19=15/3(-5);
2/9=110/2;
6/7=2,8=2,9=2,10=2,19=2,28=1/1;
99/9=1/99;

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Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

C	0.81909	-1.28205	0.
C	2.21425	-1.28205	0.
C	2.91179	-0.0743	0.
C	2.21413	1.13421	-0.0012
C	0.81931	1.13413	-0.00168
C	0.12171	-0.07408	-0.00068
H	0.26933	-2.23437	0.00045
H	4.01147	-0.07422	0.00063
H	2.76433	2.08635	-0.00126
H	0.26919	2.08641	-0.00263
C	2.9838	-2.61599	0.00184
O	3.27083	-3.11863	-1.26772
C	3.96172	-4.31571	-1.07473
C	4.3717	-5.03182	-2.375
C	5.60423	-4.75278	-2.96617
C	3.51093	-5.95944	-2.96163
C	5.97553	-5.40078	-4.14407
H	6.28229	-4.02085	-2.50385
C	3.88262	-6.60844	-4.13936
H	2.53954	-6.17961	-2.49573
C	5.11463	-6.32918	-4.7307
H	6.94674	-5.18043	-4.61044
H	3.20391	-7.34009	-4.60145
H	5.40763	-6.84002	-5.65941
N	3.47618	-3.46543	0.97116
N	4.10916	-4.56549	0.27402
C	-1.41829	-0.07382	-0.00093
C	-2.1101	-1.0289	-0.73989
C	-2.10433	0.89328	0.74683
C	-3.51282	-1.04966	-0.75652
H	-1.55388	-1.77974	-1.32034
C	-3.4891	0.88034	0.73624
H	-1.55148	1.64443	1.32818
C	-4.19867	-0.10065	-0.02285
H	-4.04857	-1.8084	-1.34369
C	-4.46529	1.74061	1.40101
C	-5.77463	1.28814	1.05038
C	-4.30008	2.82829	2.24217
C	-6.89368	1.92958	1.54592
C	-5.44194	3.47188	2.73923
H	-3.29645	3.18233	2.51642
C	-6.71674	3.03038	2.39753
H	-7.90503	1.58989	1.28269
H	-7.60065	3.54843	2.79805
C	-5.27678	4.68316	3.67577
C	-4.00801	5.05131	4.11339
C	-6.41249	5.40089	4.07593
C	-3.83124	6.15065	4.96692
H	-3.12885	4.47558	3.78831
C	-6.24742	6.48754	4.91842
H	-7.41139	5.10455	3.72631
C	-4.94429	6.86484	5.36735
H	-2.8247	6.43216	5.30626
C	-7.2182	7.41363	5.49709
C	-6.51151	8.35994	6.30154
C	-8.59612	7.48398	5.37751
C	-7.19331	9.35812	6.97092
C	-9.27808	8.50041	6.06081
H	-9.14678	6.7599	4.76082
C	-8.58905	9.42182	6.84378
H	-6.65972	10.09086	7.5921

H	-10.37267	8.56687	5.97395
H	-9.14199	10.21252	7.37212
N	-5.6811	0.10067	0.13206
N	-5.03657	8.06767	6.26557
C	-5.91877	-0.0545	-1.31027
H	-5.76532	-1.07605	-1.58917
H	-6.92455	0.23036	-1.53869
H	-5.23946	0.56926	-1.85283
C	-3.65476	7.58395	6.39792
H	-3.66364	6.55434	6.68899
H	-3.15009	7.68506	5.45985
H	-3.14476	8.16035	7.14126

TABLE S2. Computational details for **B**

```
# opt b3lyp/6-31g(d) geom=connectivity
 ---------------------------------------
 1/14=-1,18=20,19=15,26=3,38=1,57=2/1,3;
 2/9=110,12=2,17=6,18=5,40=1/2;
 3/5=1,6=6,7=1,11=2,16=1,25=1,30=1,71=1,74=-5/1,2,3;
 4//1;
 5/5=2,38=5/2;
 6/7=2,8=2,9=2,10=2,28=1/1;
 7//1,2,3,16;
 1/14=-1,18=20,19=15/3(2);
 2/9=110/2;
 99//99;
 2/9=110/2;
 3/5=1,6=6,7=1,11=2,16=1,25=1,30=1,71=1,74=-5/1,2,3;
 4/5=5,16=3/1;
 5/5=2,38=5/2;
 7//1,2,3,16;
 1/14=-1,18=20,19=15/3(-5);
 2/9=110/2;
 6/7=2,8=2,9=2,10=2,19=2,28=1/1;
 99/9=1/99;
 ---------------------
 Title Card Required
 ---------------------
 Symbolic Z-matrix:
 Charge =  0 Multiplicity = 1
 C                  0.81909  -1.28205   0.
 C                  2.21425  -1.28205   0.
 C                  2.91179  -0.0743    0.
 C                  2.21413   1.13421  -0.0012
 C                  0.81931   1.13413  -0.00168
 C                  0.12171  -0.07408  -0.00068
 H                  0.26933  -2.23437   0.00045
 H                  4.01147  -0.07422   0.00063
 H                  2.76433   2.08635  -0.00126
 H                  0.26919   2.08641  -0.00263
 C                  2.9838   -2.61599   0.00184
 O                  3.27083  -3.11863  -1.26772
 C                  3.96172  -4.31571  -1.07473
 C                  4.3717   -5.03182  -2.375
 C                  5.60423  -4.75278  -2.96617
 C                  3.51093  -5.95944  -2.96163
 C                  5.97553  -5.40078  -4.14407
 H                  6.28229  -4.02085  -2.50385
 C                  3.88262  -6.60844  -4.13936
 H                  2.53954  -6.17961  -2.49573
 H                  6.94674  -5.18043  -4.61044
 H                  3.20391  -7.34009  -4.60145
 N                  3.47618  -3.46543   0.97116
```

N	4.10916	-4.56549	0.27402
C	-1.41829	-0.07382	-0.00093
C	-2.1101	-1.0289	-0.73989
C	-2.10433	0.89328	0.74683
C	-3.51282	-1.04966	-0.75652
H	-1.55388	-1.77974	-1.32034
C	-3.4891	0.88034	0.73624
H	-1.55148	1.64443	1.32818
C	-4.19867	-0.10065	-0.02285
H	-4.04857	-1.8084	-1.34369
C	-4.46529	1.74061	1.40101
C	-5.77463	1.28814	1.05038
C	-4.30008	2.82829	2.24217
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C	-5.44194	3.47188	2.73923
H	-3.29645	3.18233	2.51642
C	-6.71674	3.03038	2.39753
H	-7.90503	1.58989	1.28269
H	-7.60065	3.54843	2.79805
C	-5.27678	4.68316	3.67577
C	-4.00801	5.05131	4.11339
C	-6.41249	5.40089	4.07593
C	-3.83124	6.15065	4.96692
H	-3.12885	4.47558	3.78831
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H	-7.41139	5.10455	3.72631
C	-4.94429	6.86484	5.36735
H	-2.8247	6.43216	5.30626
C	-7.2182	7.41363	5.49709
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C	-9.27808	8.50041	6.06081
H	-9.14678	6.7599	4.76082
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C	-3.65476	7.58395	6.39792
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H	-3.14476	8.16035	7.14126
N	5.11463	-6.32918	-4.7307

References for the Supporting Information

(1) Brunner, K.; De Kok-Van Breeman, M. M.; Langeveld, B. M. W.; Kiggen, N. M. M.; Bastiaansen, J. J. A. M; Hofstraat, J. W.; Boerner, H. F.; Schoo, H. F. M. US Patent Application US 2006/0073357.

(2) Brunner, K.; van Dijken, A.; Börner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. *J. Am. Chem. Soc.* **2004**, *126*, 6035-6042.

(3) Gallardo, H.; Magnago, R.; Bortoluzzi, A. J. *Liq. Cryst.* **2001**, *28*, 1343-1352.