Supplementary Material (ESI) for *Journal of Materials Chemistry*

1,3,5-Triazine Derivatives as New Electron Transport–Type Host Materials for Highly Efficient Green Phosphorescent OLEDs

Hsiao-Fan Chen[a], Shang-Jung Yang[a], Zhen-Han Tsai[b], Wen-Yi Hung*[b], Ting-Chih Wang[a], Ken-Tsung Wong*[a]

[a] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan. Fax 886 2 33661667; Tel: 886 2 33661665; E-mail: kenwong@ntu.edu.tw*

[b] *Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 202, Fax: 886 2 24634360; Tel: 886 2 24622192 ext. 6718; E-mail:wenhung@mail.ntou.edu.tw*

Supporting Information

Synthesis:

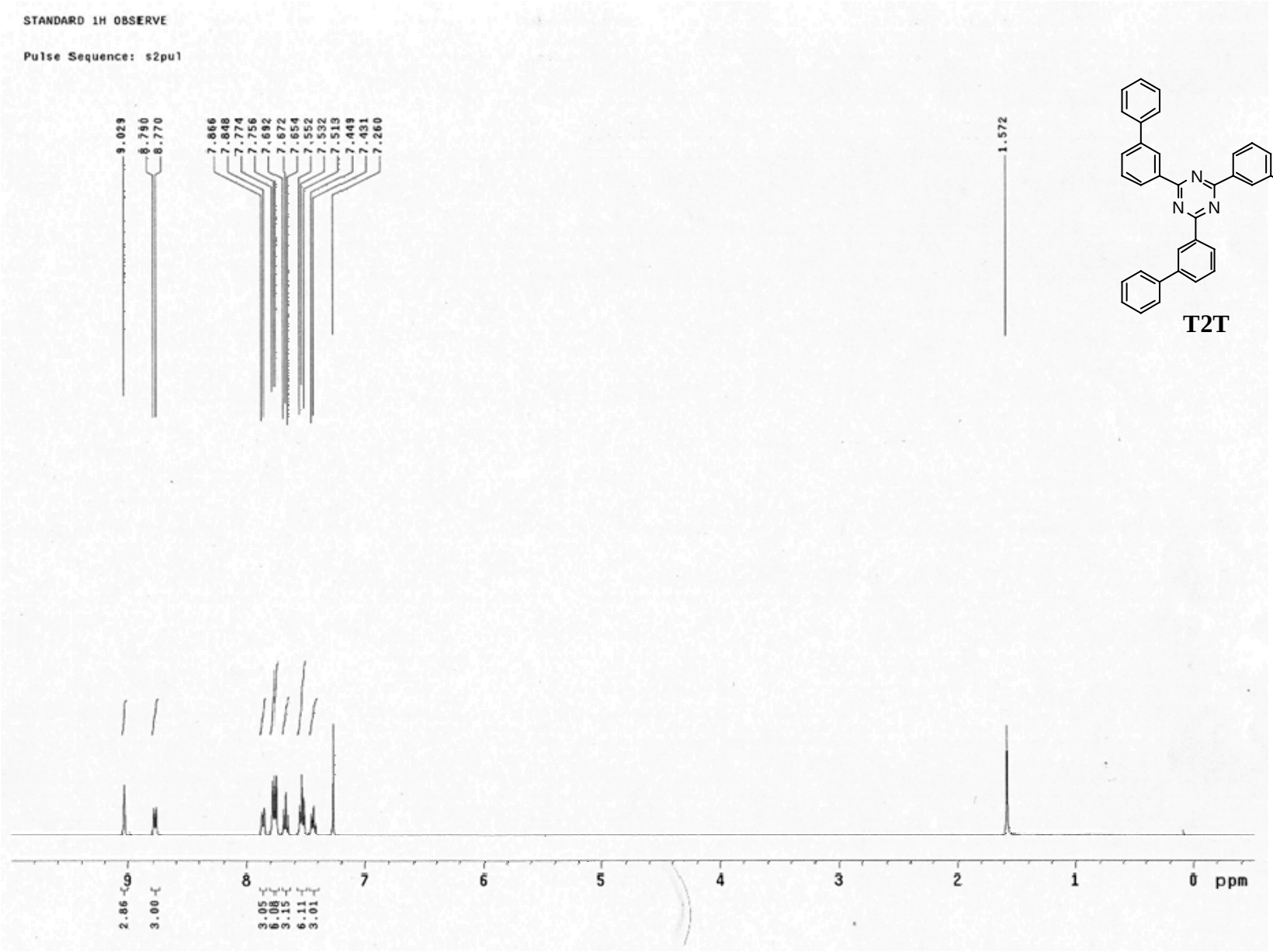
Tris(2-bromophenyl)triazine. Trifluoromethane sulfonic acid (5.00 mL, 56.3 mmol) was added to a solution of 3-bromobenzonitrile (5.00 g, 27.5 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred for 12 h at room temperature and then quenched through the addition of $NaHCO_{3(aq)}$. The aqueous phase was extracted with CH_2Cl_2, dried ($MgSO_4$), and washed with hexane to afford the title compound (3.1 g, 67%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ8.83 (d, J = 2.0 Hz, 3H), 8.67 (d, J = 8.0 Hz, 3H), 7.75 (d, J = 8.0 Hz, 3H), 7.46 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 137.5, 135.6, 131.7, 130.2, 127.5, 122.9; HRMS (*m*/*z*, ESI$^+$) calcd for $C_{21}H_{12}{}^{79}Br_3N_3$ 542.8581, found 542.8580; calcd for $C_{21}H_{12}{}^{79}Br_2{}^{81}BrN_3$ 544.8561, found 544.8571; calcd for $C_{21}H_{12}{}^{79}Br^{81}Br_2N_3$ 546.8540, found 546.8539.

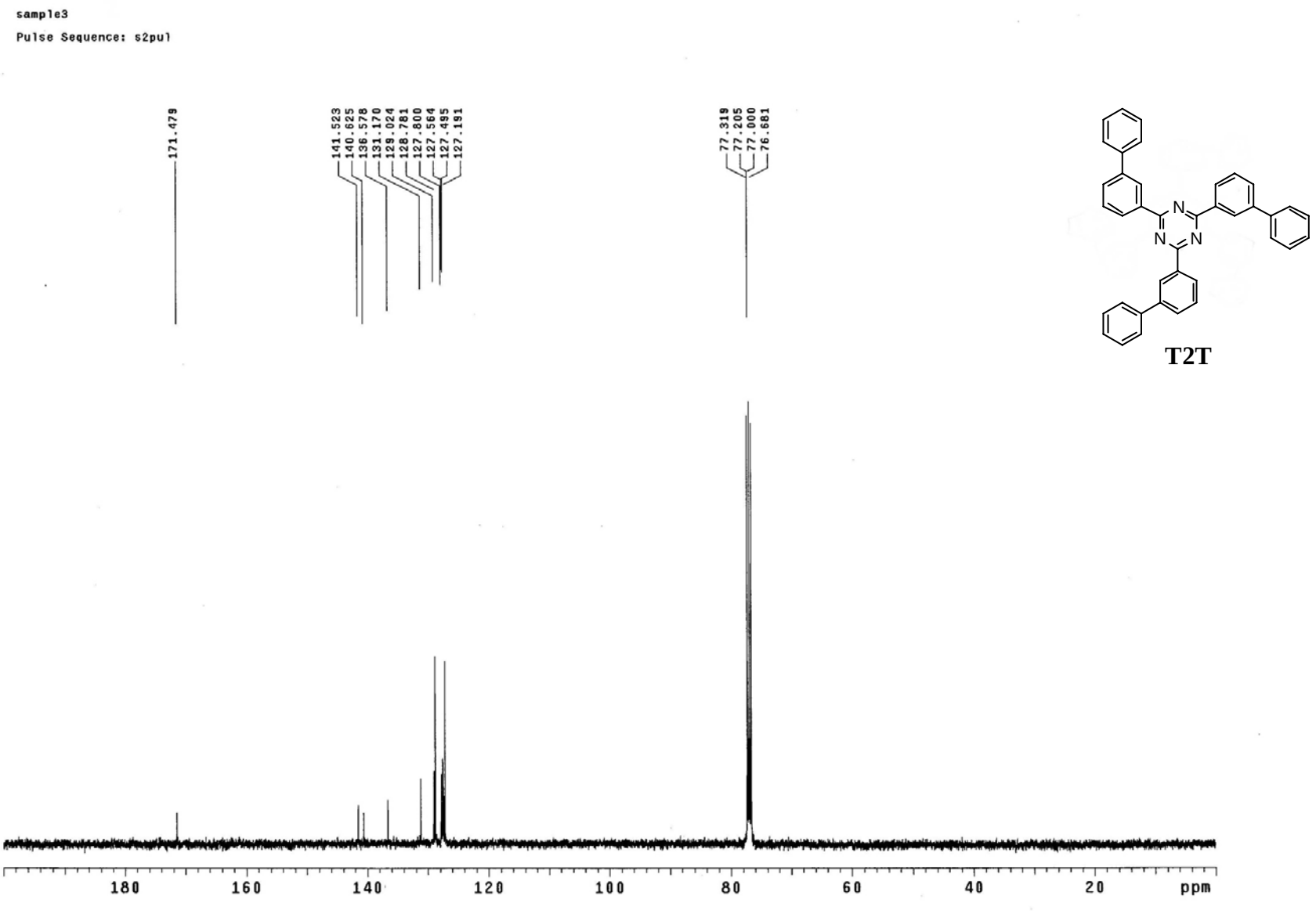
T2T. A mixture of tris(9-bromophenyl)triazine (765 mg, 1.40 mmol), phenylboronic acid (598 mg, 4.90 mmol), $Pd(PPh_3)_4$ (162 mg, 0.14 mmol), $Na_2CO_{3(aq)}$ (14 mL, 28 mmol, 2.0 M), and tri-*tert*-butylphosphine (5.6 mL, 0.28 mmol, 0.05 M in toluene) in toluene (18 mL) was heated under reflux for 24 h. After cooling to room temperature, the reaction was quenched through the addition of water and then the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated under rotary evaporation. The resulting solid residue was washed with hexane to give the title compound (752 mg, 99 %) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.03 (s, 3H), 8.78 (d, J = 8.0 Hz, 3H), 7.86 (d, J = 7.2 Hz, 3H), 7.76 (d, J = 7.2 Hz, 6H), 7.67 (t, J = 8.0 Hz, 3H), 7.53 (t, J = 8.0 Hz, 6H), 7.44 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 171.5, 141.5, 140.6, 136.6, 131.2, 129.0, 128.8,

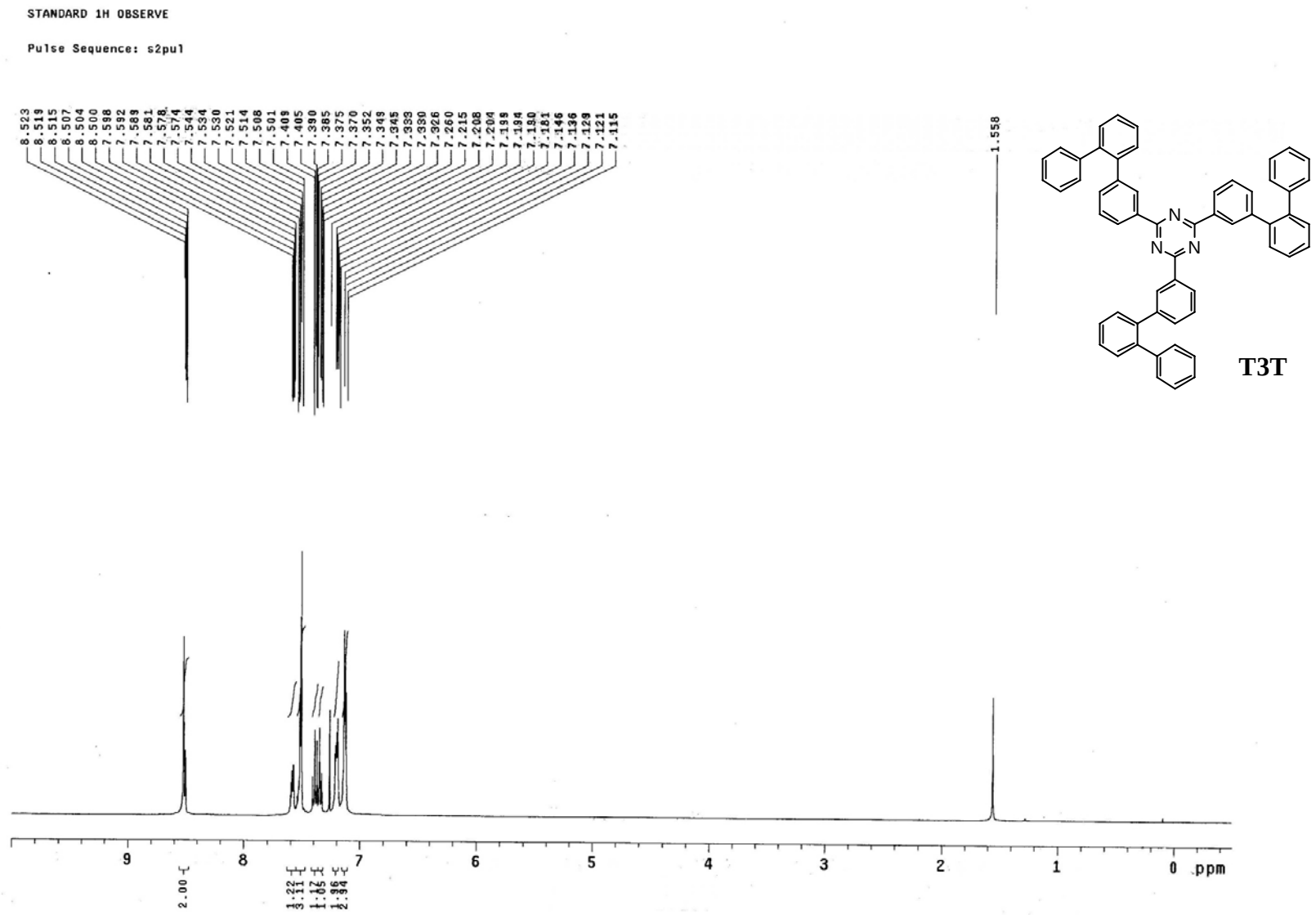
127.8, 127.6, 127.5, 127.2; HRMS (*m*/*z*, ESI^+) calcd for $C_{39}H_{27}N_3$ 537.2205, found 537.2218.

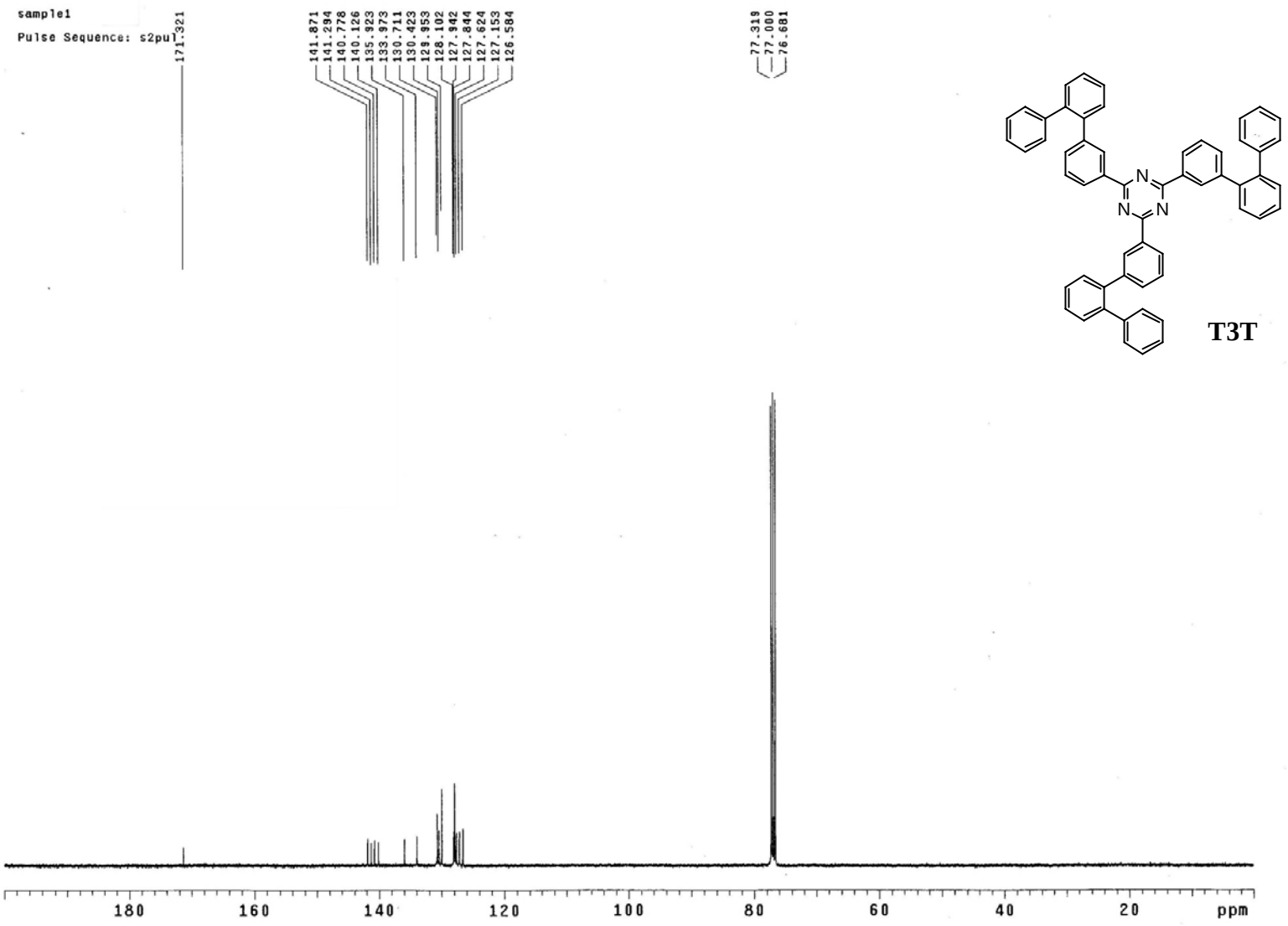
T3T. A mixture of tris(9-bromophenyl)triazine (1.58 g, 2.89 mmol), biphenyl-2-boronic acid (2.00 g, 1.10 mmol), $Pd(PPh_3)_4$ (332 mg, 0.300 mmol), $Na_2CO_{3(aq)}$ (2.0 M, 28.8 mL, 57.8 mmol), and tri-*tert*-butylphosphine (11.5 mL, 0.60 mmol, 0.05 M in toluene) in toluene (60 mL) was heated under reflux for 24 h. After cooling to room temperature, the reaction was quenched through the addition of water and then the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and concentrated under rotary evaporation. The resulting solid residue was washed with hexane to give the title compound (2.17 g, 98%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.51 (d, *J* = 0.2 Hz, 1H), 8.50 (s, 1H), 7.57–7.59 (m, 1H), 7.53–7.50 (m, 3H), 7.40–7.32 (m, 2H), 7.21–7.17 (m, 2H), 7.13–7.12 (m, 3H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 171.3, 141.9, 141.3, 140.8, 140.1, 135.9, 134.0, 130.7, 130.4, 130.0, 128.1, 127.9, 127.8, 127.6, 127.2, 126.6; HRMS (*m*/*z*, ESI^+) calcd for $C_{57}H_{39}N_2$ 765.3144, found 765.3197.

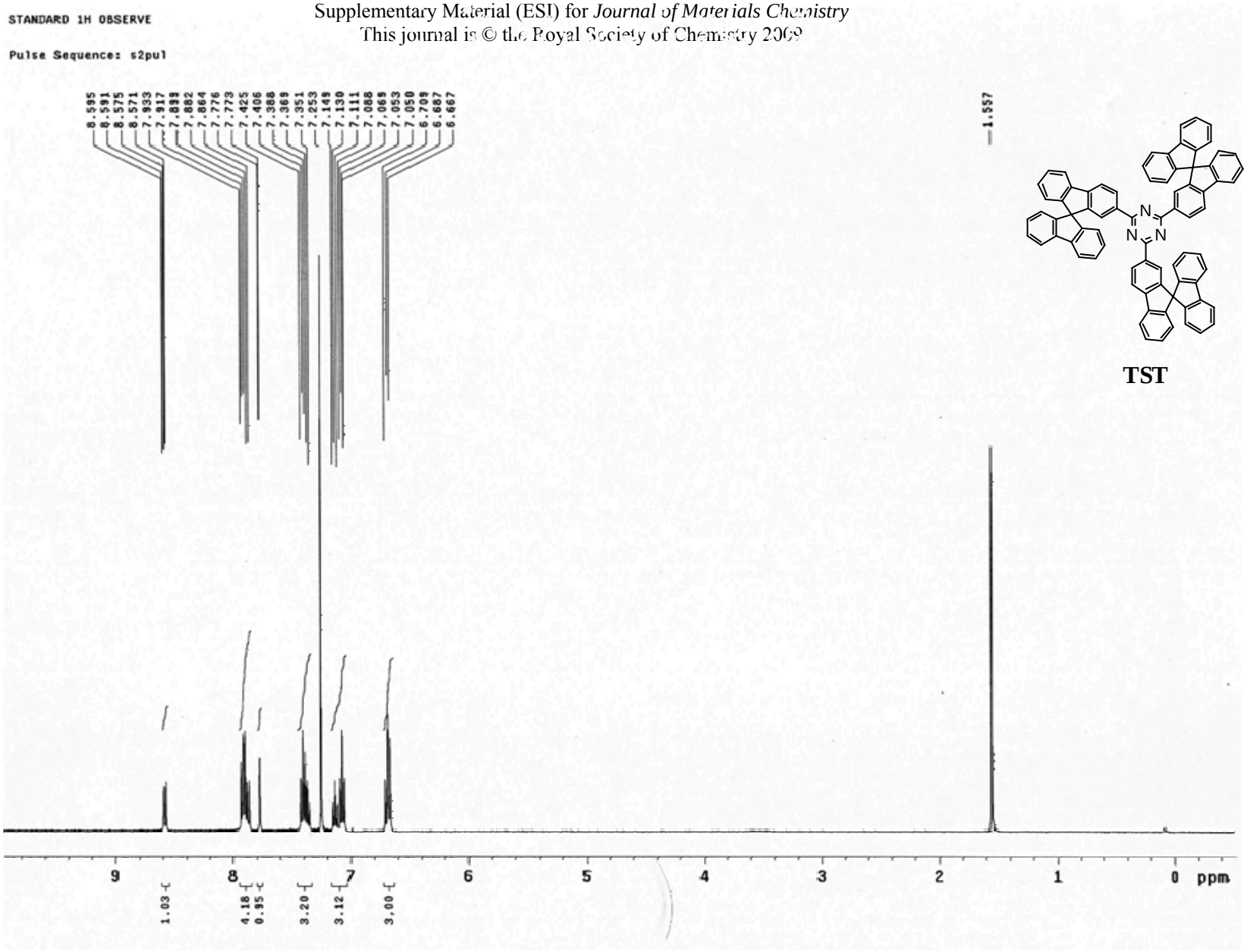
TST. Trifluoromethanesulfonic acid (1.10 mL, 11.7 mmol) was added to a solution of 9,9′-spirobi[fluorene]-2-carbonitrile (2.0 g, 5.87 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred for 12 h at room temperature and then the reaction was quenched through the addition of $NaHCO_{3(aq)}$. The mixture was concentrated through rotary evaporation. The resulting suspension was filtered and the solids washed with CH_2Cl_2 to give the title compound (1.25 g, 63%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.59 (dd, *J* = 1.2, 8.2 Hz, 3H), 7.94–7.87 (m, 12H), 7.78 (s, 3H), 7.43–7.36 (m, 9H), 7.14 (t, *J* = 6.4 Hz, 3H), 7.08 (t, *J* = 7.6 Hz, 6H), 6.69 (t, *J* = 7.6 Hz, 9H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 170.9, 150.0, 148.6, 147.9, 146.0, 141.6, 140.5, 135.6, 129.2, 128.6, 127.8, 127.6, 124.2, 123.9, 120.5, 120.0, 66.0; HRMS (*m*/*z*, ESI^+) calcd for $C_{78}H_{45}N_3$ 1023.3613, found 1023.3619.

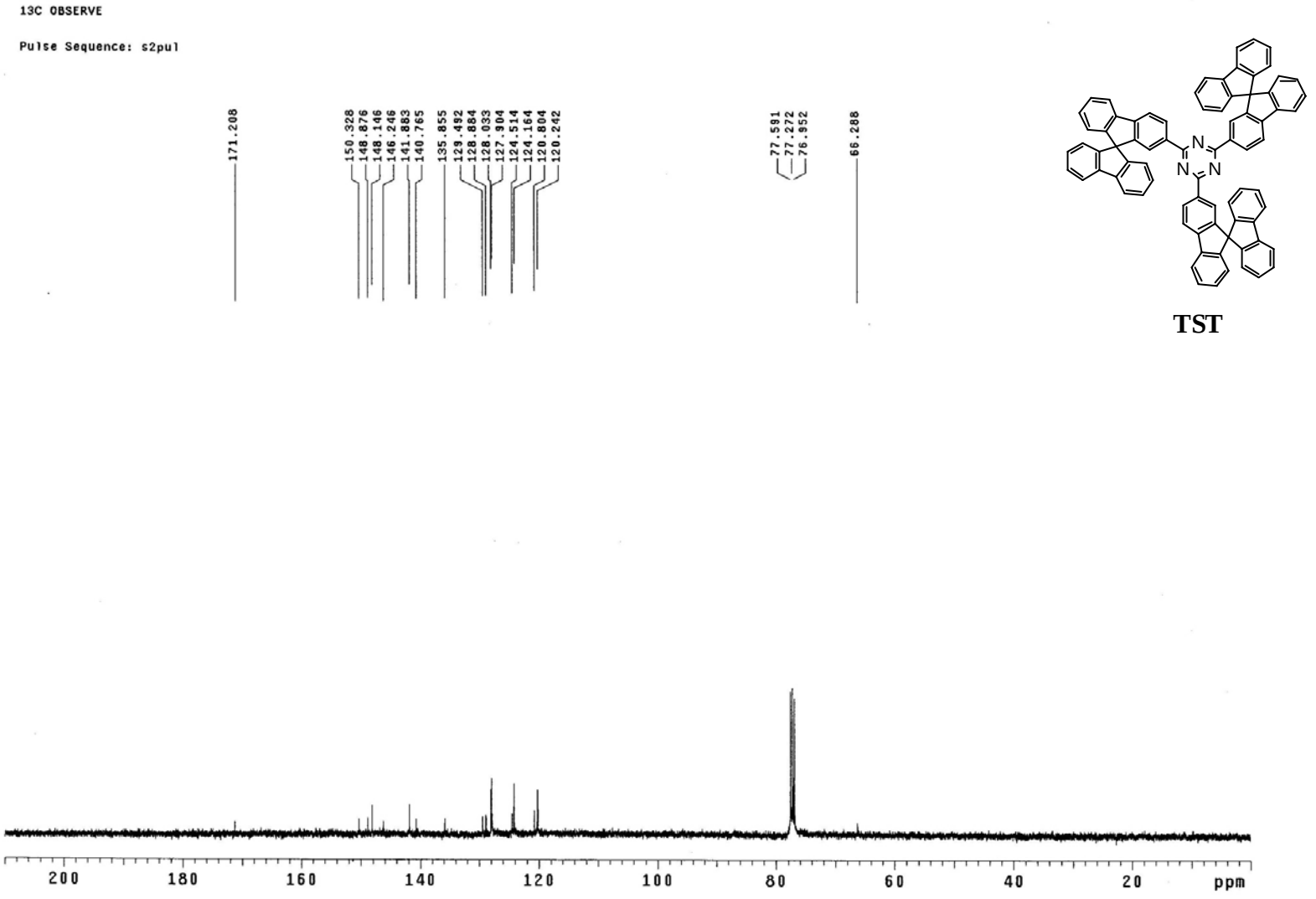









STANDARD 1H OBSERVE
Pulse Sequence: s2pul
8.595
8.591
8.575
8.571
7.933
7.917
7.899
7.882
7.864
7.776
7.773
7.425
7.406
7.388
7.369
7.351
7.253
7.149
7.130
7.111
7.088
7.069
7.053
7.050
6.709
6.687
6.667
1.557
N
N
N
TST
9
8
7
6
5
4
3
2
1
0 ppm
1.03
4.18
0.95
3.20
3.12
3.00



TST

ITO/PEDOT/NPB (20 nm)/TCTA (5 nm)/**T2T**:Ir(PPy)$_3$ 10% (25 nm)/ETL (50 nm)/LiF/Al

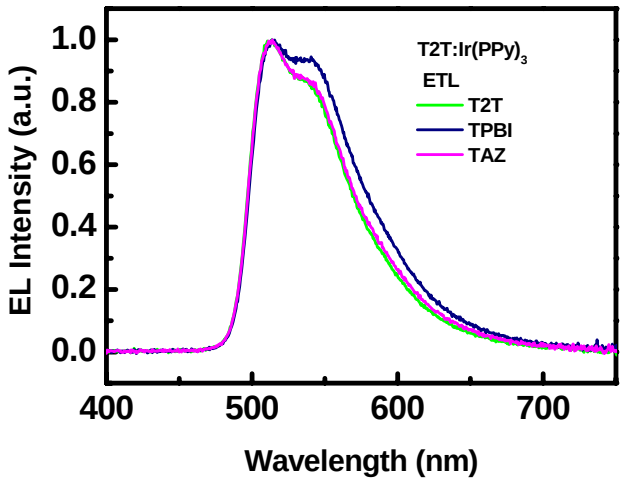


Fig. S-1. EL spectra of **T2T** doped with Ir(PPy)$_3$ and featuring various ETLs.

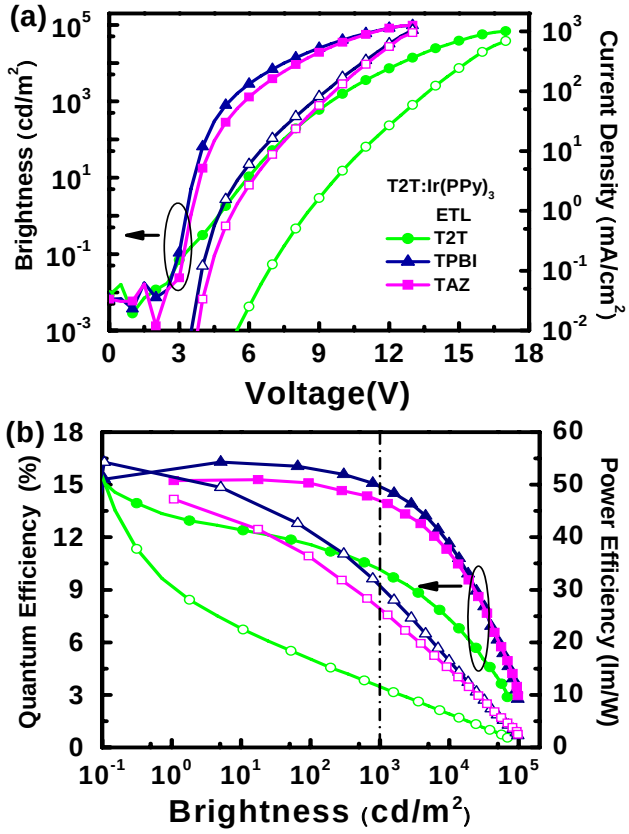


Fig. S-2. (a) *I–V–L* characteristics and (b) plots of EL efficiency versus brightness for **T2T** doped with Ir(PPy)$_3$ and featuring various ETLs.

ITO/PEDOT/NPB (20 nm)/TCTA (5 nm)/**T3T**:**dopant** 10% (25 nm)/ETL (50 nm)/LiF/Al

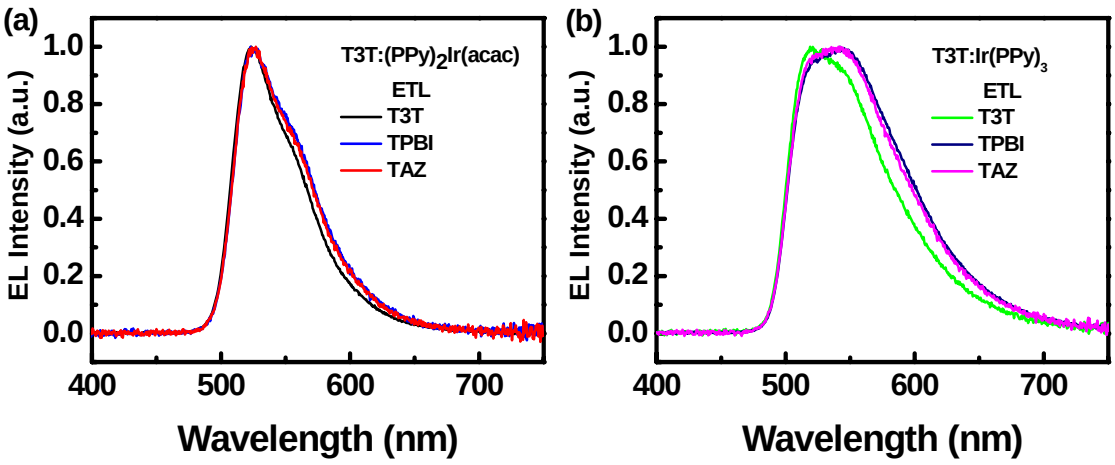


Fig. S-3. EL spectra of **T3T** doped with (a) $(PPy)_2Iracac$ and (b) $Ir(PPy)_3$ and featuring various ETLs.

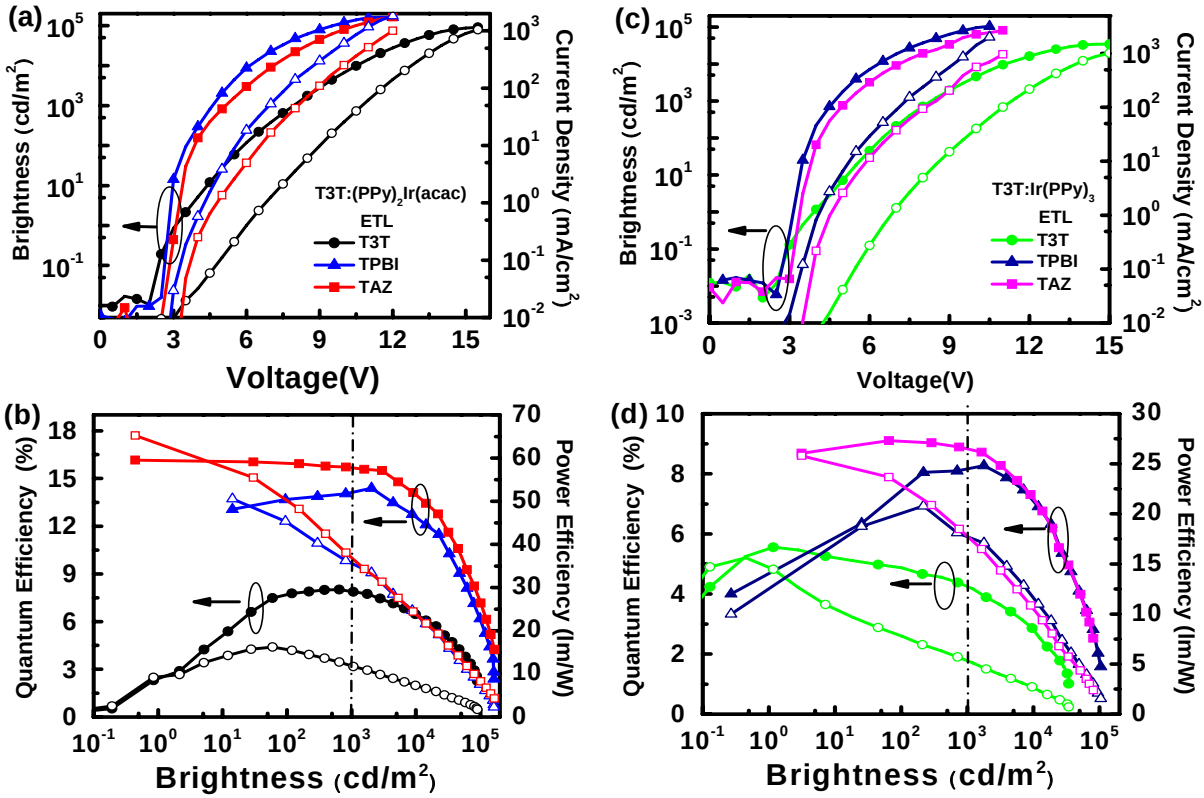


Fig. S-4. (a, c) *I–V–L* characteristics and (b, d) plots of EL efficiency versus brightness for **T3T** doped with $(PPy)_2Ir(acac)$ and $Ir(PPy)_3$ and featuring various ETLs.

ITO/PEDOT/NPB (20 nm)/TCTA (5 nm)/**TST**:**dopant** 10% (25 nm)/ETL (50 nm)/LiF/Al

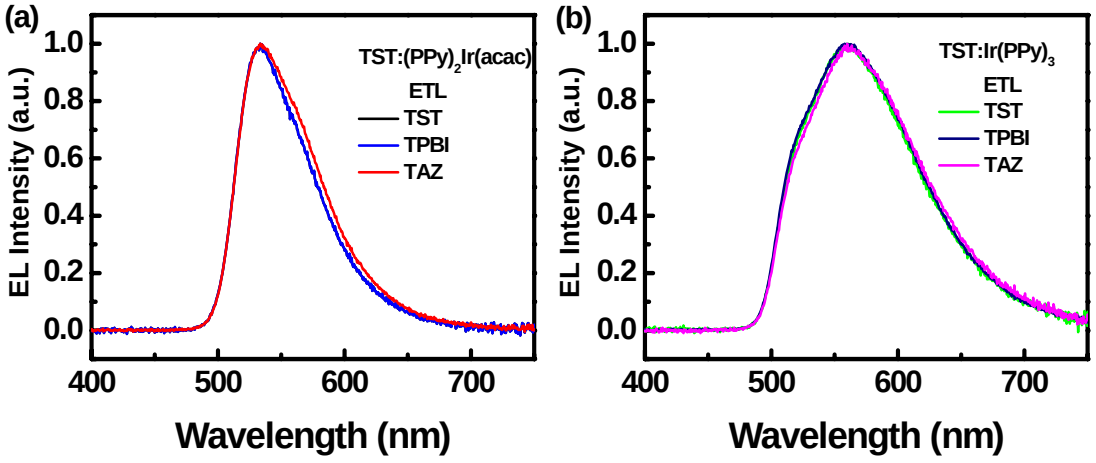


Fig. S-5. EL spectra of **TST** doped with (a) $(PPy)_2Ir(acac)$ and (b) $Ir(PPy)_3$ and featuring various ETLs.

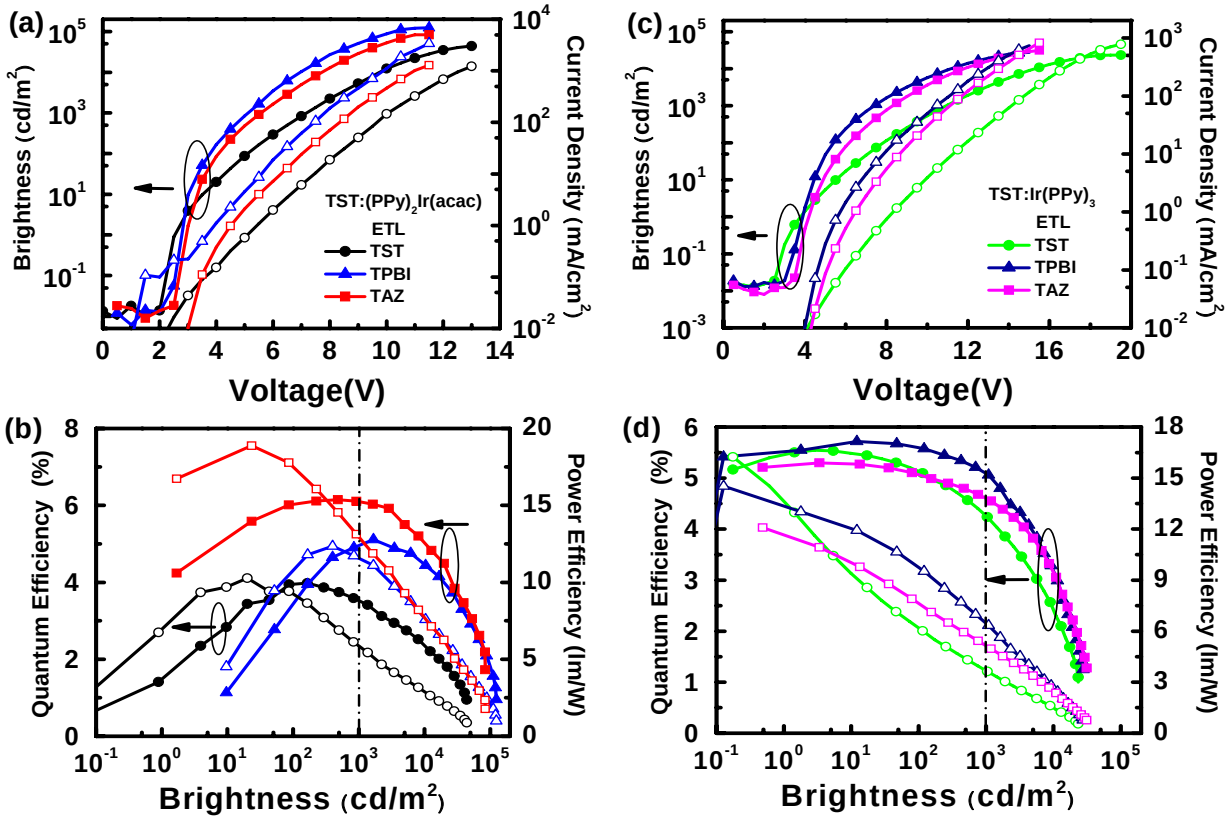


Fig. S-6. (a,c) *I*–*V*–*L* characteristics and (b, d) plots of EL efficiency versus brightness for **TST** doped with $(PPy)_2Ir(acac)$ and $Ir(PPy)_3$ and featuring various ETLs.