Electronic Supplementary Information for:

Triplet Excited State Properties in Variable Gap π-Conjugated Donor-Acceptor-Donor Chromophores

Seda Cekli,[a] Russell W. Winkel,[a] Erkki Alarousu,[b] Omar F. Mohammed,[b] Kirk S. Schanze*[a]

[a] Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611-7200, United States

[b] Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

*Author to whom correspondence should be addressed; electronic mail: k.schanze@chem.ufl.edu;

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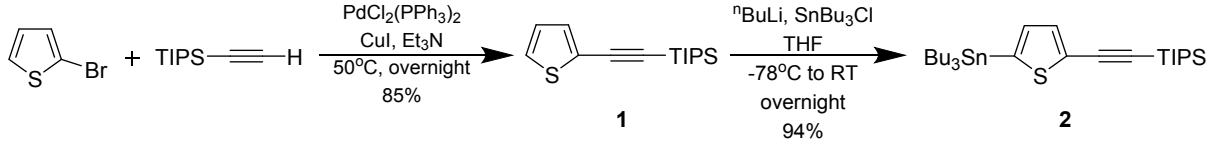
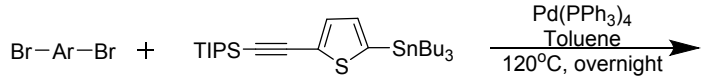
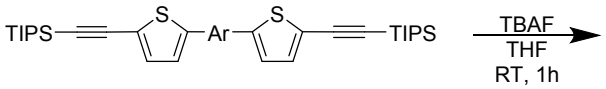
Scheme S1. Synthesis of precursor **2**.

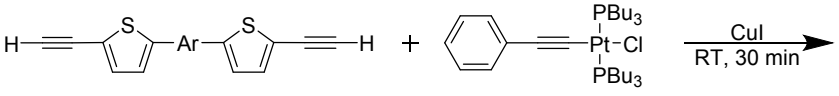


Scheme S2. Synthesis of thiophene containing molecules.



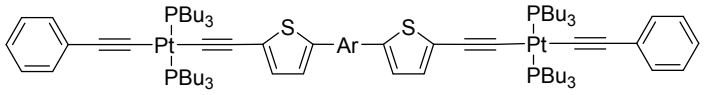


3a Ar = BTz 89% **3d** Ar = BT 74%
3b Ar = TPd 77% **3e** Ar = TP 78%
3c Ar = Qx 78%

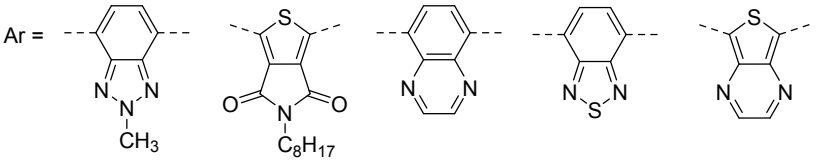


4a Ar = BTz 85% **4d** Ar = BT 93%
4b Ar = TPd 89% **4e** Ar = TP 70%
4c Ar = Qx 60%

3

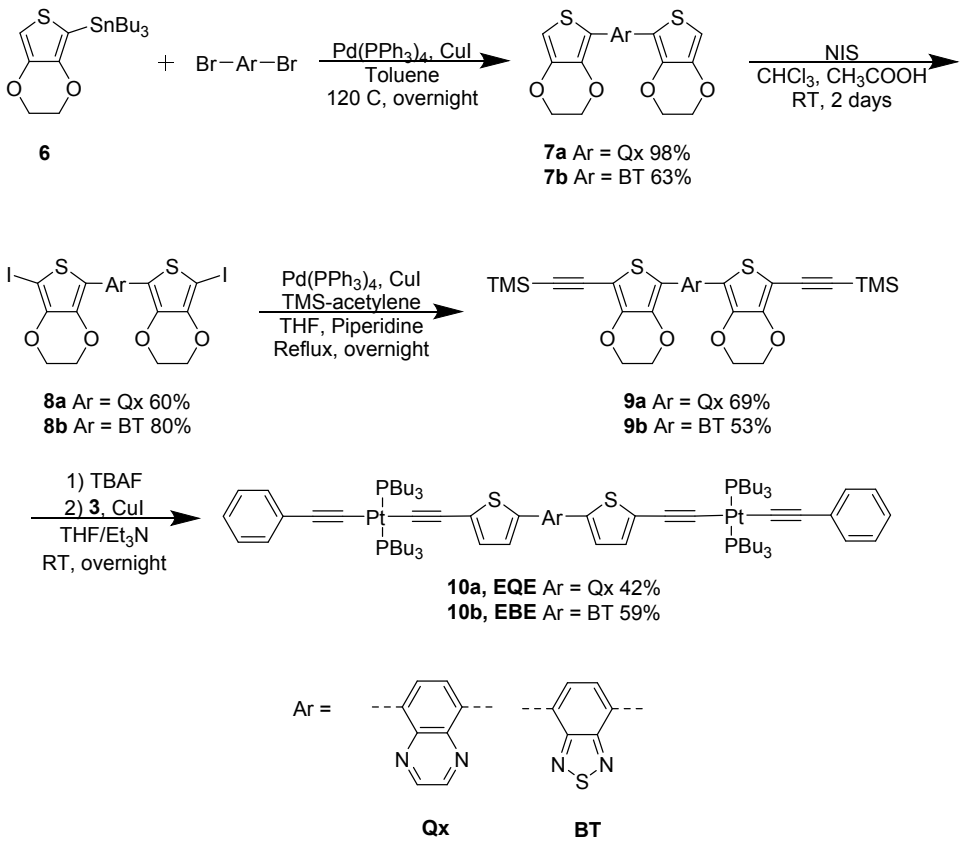


5a, TBTz Ar = BTz 85% **5d, TBT** Ar = BT 49%
5b, TPD Ar = TPd 30% **5e, TPT** Ar = TP 41%
5c, TQT Ar = Qx 78%



BTz **TPd** **Qx** **BT** **TP**

Scheme S3. Synthesis of EDOT containing molecules.

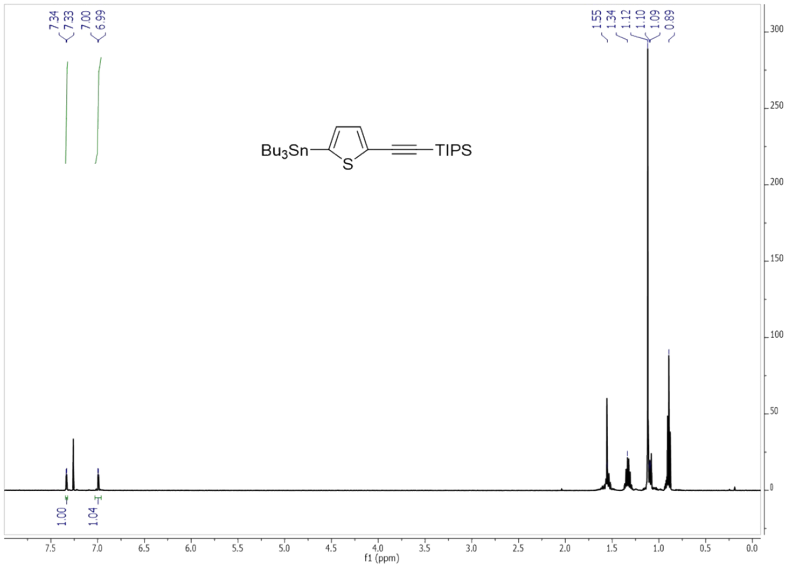


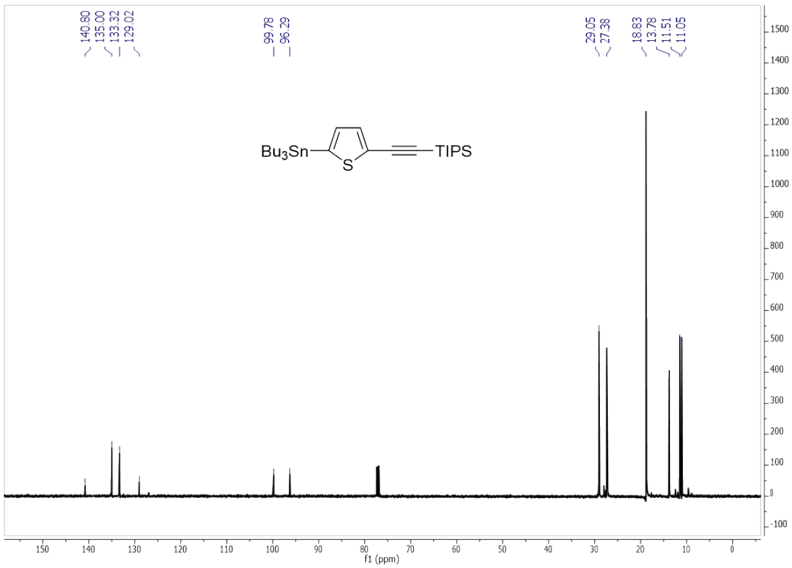
Materials and Instrumentation

Starting materials used in the synthesis of acceptors and precursor **2**, $Pd(PPh_3)_4$, CuI and TBAF were obtained from commercial sources. Compounds **1**[1], **5**[2], **6**,[3] 2-methyl-2*H*-benzo[*d*][1,2,3]triazole (**BTz**),[4] 5-methyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**TPd**),[5] quinoxaline (**Qx**)[6], thieno[3,4-*b*]pyrazine (**TP**),[7] **TBT**[8] and **EBE**[8] were synthesized according to the literature procedures. All reactions were performed under argon atmosphere in anhydrous solvents, which were dried prior use by the standard procedures. Merck silica gel 60 (particle size 0.04−0.063 mm) was used for flash chromatography.

Triisopropyl-(4-tributylstannanyl-thienylethynyl)-silane (2) To a solution of 0.500 g of **1** (1.92 mmol, 1 equiv) in 20 mL of THF, 0.85 mL of n-Butyllithium (2.11 mmol, 1.1 equiv) was added dropwise at -78°C via syringe. The reaction mixture was stirred for 45 min before 0.60 mL of tri-n-butyltin chloride was added dropwise (2.11 mmol, 1.1 equiv). The reaction mixture was allowed

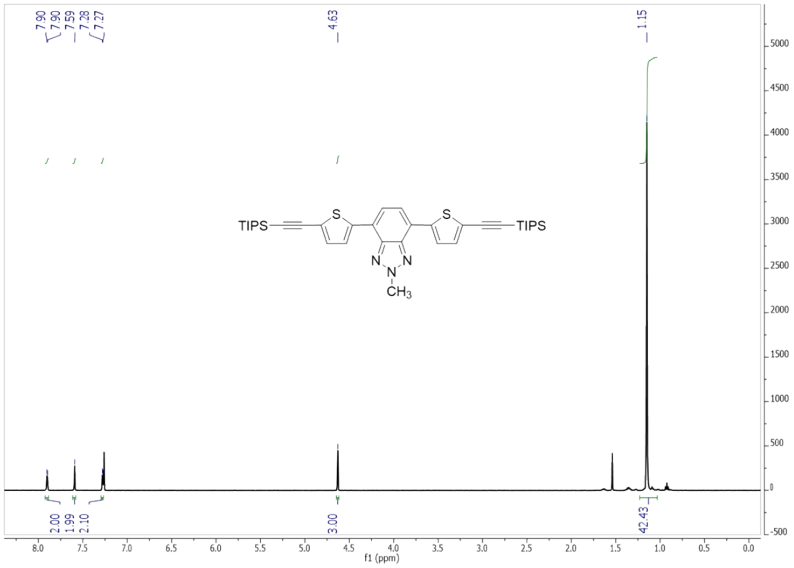
to warm up to room temperature, then quenched with water (50 mL), extracted with Et_2O (25 mL), and dried over $MgSO_4$. The resulting product was a yellowish liquid and used for the next step without further purification (1.00 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.33 (d, J = 3.5 Hz, 1H), 6.99 (d, J = 3.5 Hz, 1H) 1.55 (m), 1.34 (m), 1.12 (s), 1.09 (m), 0.89 (t, 3H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 140.80, 135.00, 133.32, 129.02, 99.78, 96.29, 29.05, 27.38, 18.83, 13.78, 11.51, 11.05.

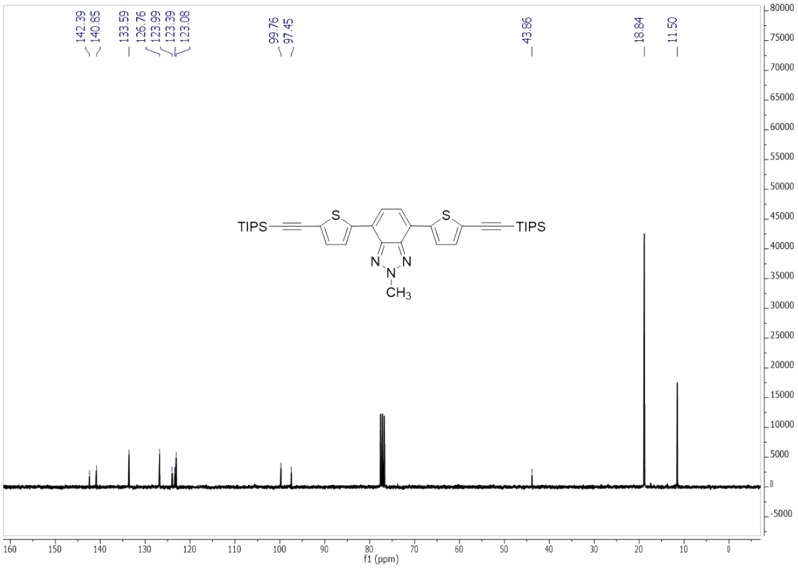




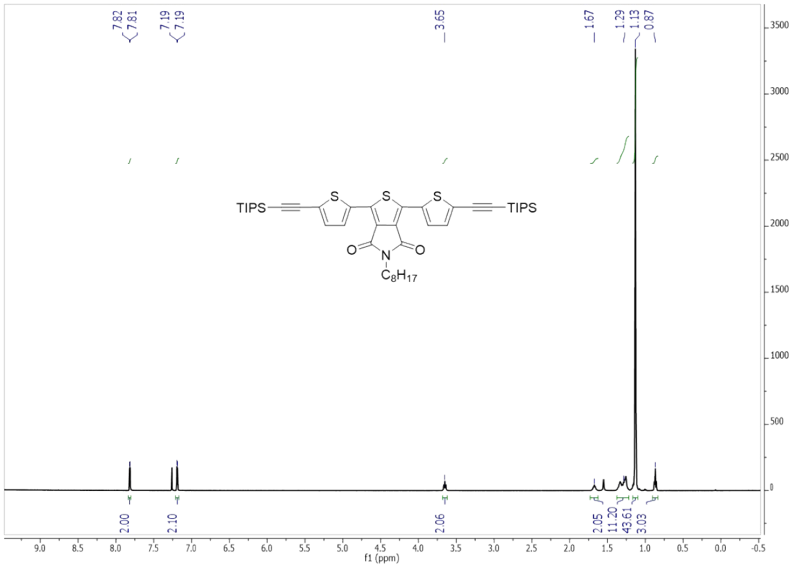
4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)2-methyl-benzo[*d*][1,2,3]triazole (3a) A Solution of 0.200 g of dibromo-**BTz** (0.7 mmol, 1 equiv) and 0.92 g of compound **2** (1.75 mmol,

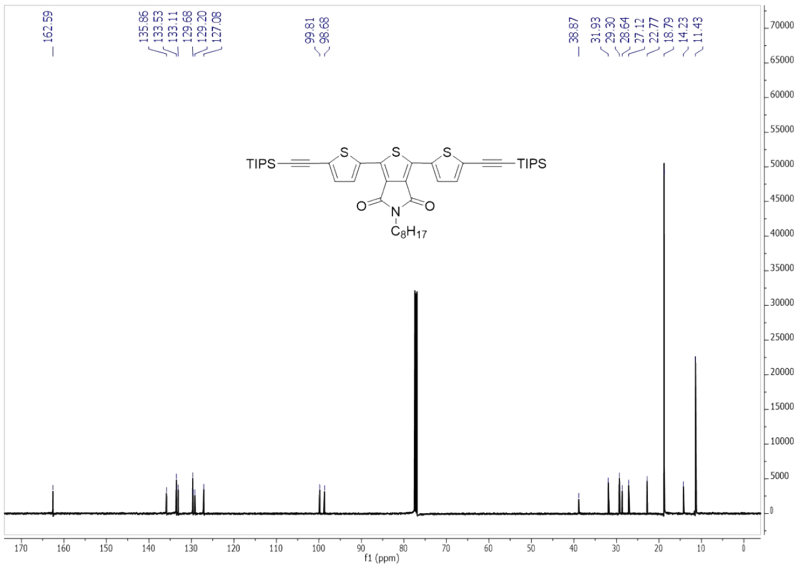
2.5 equiv) in 45 mL toluene was degassed for 45 min by bubbling with argon. 80 mg of $Pd(PPh_3)_4$ (0.07 mmol, 0.1 equiv) was added under argon and the resulting mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The residue was purified by silica column chromatography with CH_2Cl_2 / hexane (3:7). The desired product was obtained a yellow solid (0.410 g, 89%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.90 (d, J = 4 Hz, 2H), 7.59 (s, 2H), 7.28 (d, J = 4 Hz, 2H), 4.63 (s, 3H), 1.15 (s, 42H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): 142.39, 140.85, 133.59, 126.76, 123.99, 123.39, 123.08, 99.76, 97.45, 43.86, 18.84, 11.50; HRMS (ESI) Calculated for $C_{37}H_{51}N_3S_2Si_2$ $(M+H)^+$: *m/z* 658.3165. Found: *m/z* 658.3136.



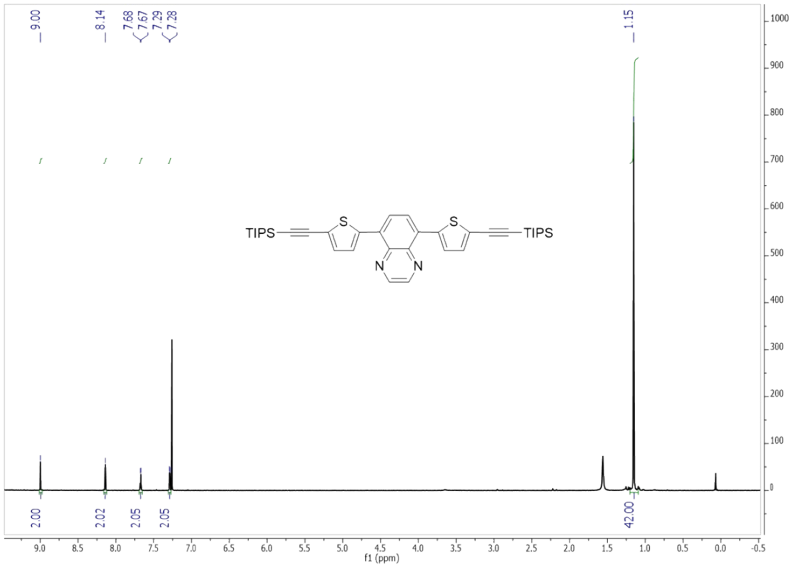


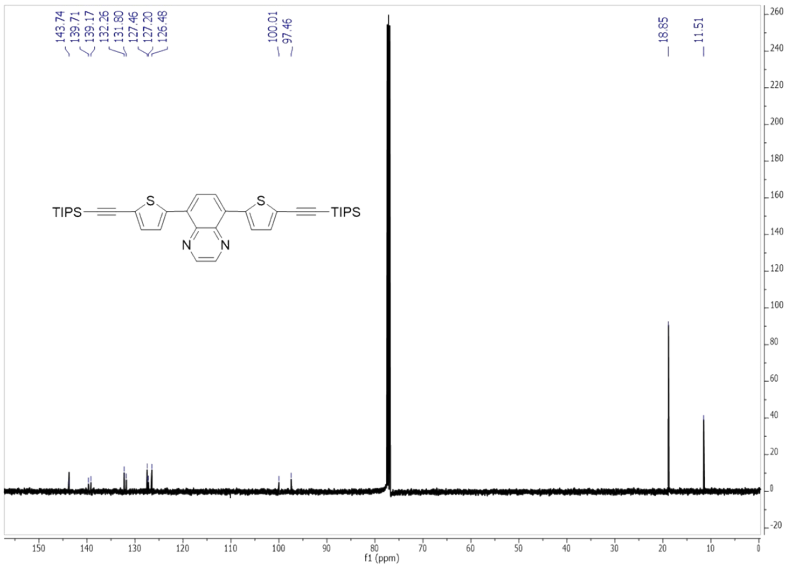
4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)5-octyl-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (3b) Compound **3b** was synthesized by the same procedure as **3a**. The residue was purified by silica column chromatography with CH_2Cl_2 / hexane (1:2). The desired product was obtained as an orange-yellow solid (0.433 g, 77%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.82 (d, J = 4 Hz, 2H), 7.19 (d, J = 4 Hz, 2H), 3.65 (t, 2H), 1.67 (m, 2H), 1.28 (m, 12H) 1.13 (s, 42H), 0.87 (t, 3H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 162.59, 135.86, 133.53, 133.11, 129.68, 129.20, 127.08, 99.81, 98.68, 38.87, 31.93 (2C), 29.30, 28.64, 27.12, 22.77, 18.79, 14.23, 11.43; HRMS (ESI) Calculated for $C_{44}H_{63}NO_2S_3Si_2$ $(M+H)^+$: *m/z* 790.3632. Found: *m/z* 790.3612.



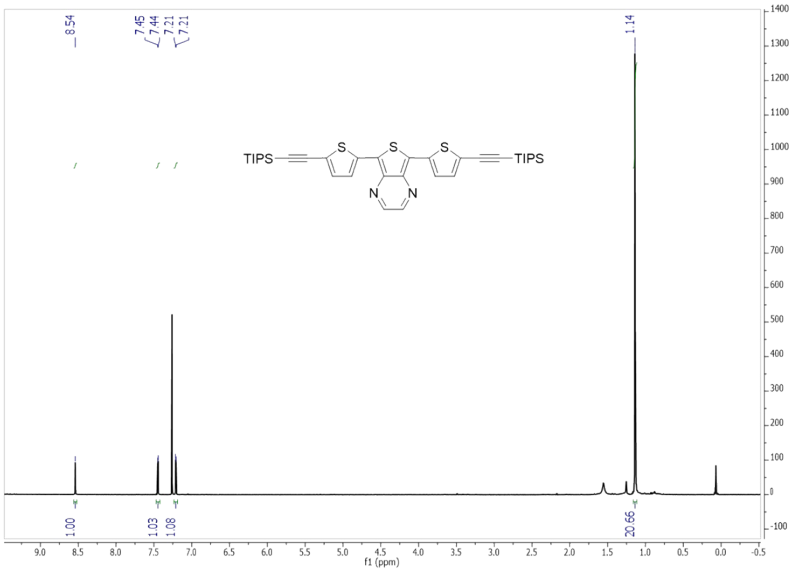


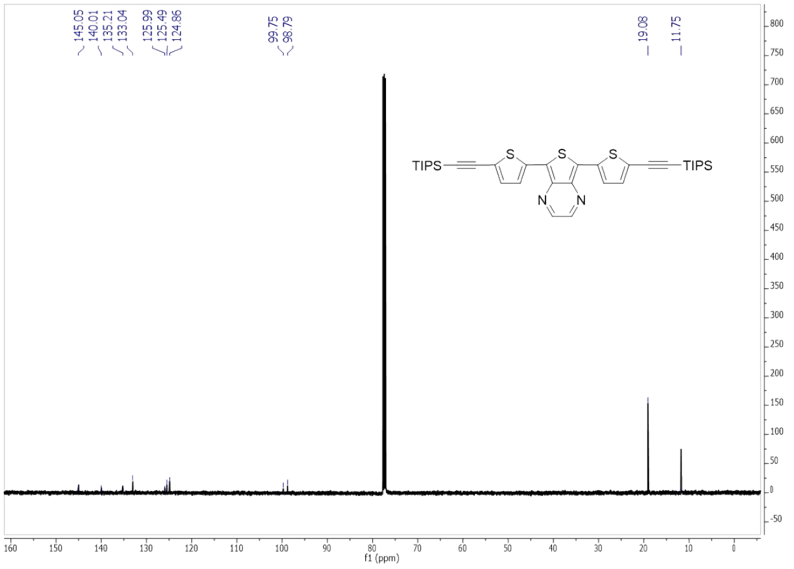
4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)quinoxaline (3c) Compound **3c** was synthesized by the same procedure as **3a**. The residue was purified by silica column chromatography with CH_2Cl_2 / hexane (1:3). The desired product was obtained as an orange solid (0.220 g, 78%). ^{1}H-NMR (500 MHz, $CDCl_3$): 9.00 (s, 2H), 8.14 (s, 2H), 7.68 (d, J = 4 Hz, 2H), 7.29 (d, J = 4 Hz, 2H), 1.15 (s, 42H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 143.74, 139.71, 139.17, 132.26, 131.80, 127.46, 127.20, 126.48, 100.01, 97.46, 18.85, 11.51; HRMS (MALDI) Calculated for $C_{38}H_{52}N_2S_2Si_2$ $(M+H)^+$: *m/z* 656.3104. Found: *m/z* 656.3115.





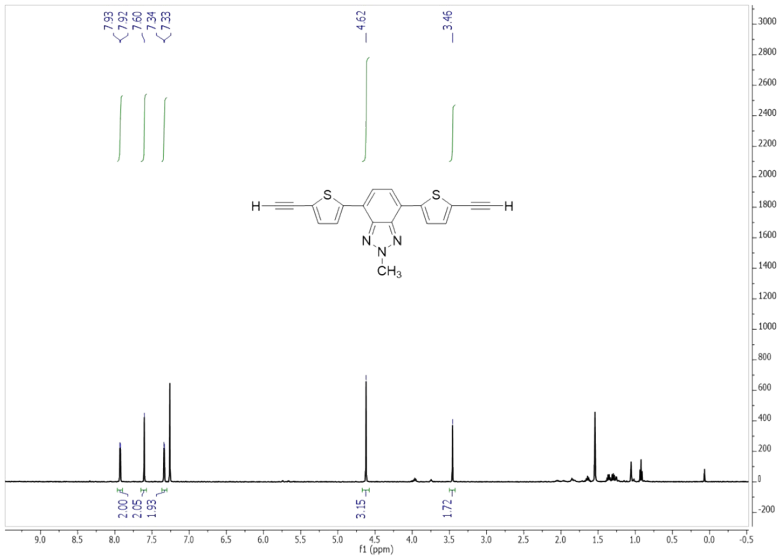
4,7-bis(5-((Triisopropylsilyl)ethynyl)thiophen-2-yl)thieno[3,4-*b*]pyrazine (3e) Compound **3e** was synthesized by the same procedure as **3a**. The residue was purified by silica column chromatography with CH_2Cl_2 / hexane (3:7). The desired product was obtained as a blue solid (0.3494 g, 78%). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.54 (s, 2H), 7.45 (d, J = 4 Hz, 2H), 7.21 (d, J = 4 Hz, 2H), 1.14 (s, 42H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 145.05, 140.01, 135.21, 133.04, 125.99, 125.49, 124.86, 99.75, 98.79, 19.08, 11.75; HRMS (ESI) Calculated for $C_{36}H_{48}N_2S_3Si_2$ $(M+H)^+$: *m/z* 661.2591. Found: *m/z* 661.2606.

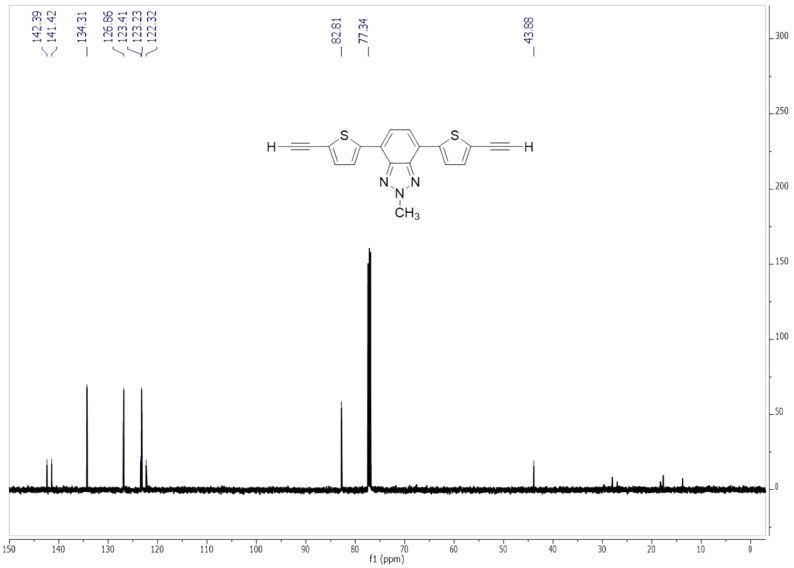




4,7-bis(5-Ethynylthiophen-2-yl) 2-methyl-benzo[*d*][1,2,3]triazole (4a) 0.180 g of compound **3a** (0.27 mmol, 1 equiv) was dissolved in 20 mL of THF and degassed for 45 min by bubbling with argon. 0.8 mL of 1 M TBAF in THF (0.822 mmol, 3 equiv) was then added via syringe. The resulting solution was stirred at room temperature for 90 minutes. The reaction mixture was quenched with water, extracted with DCM, and dried over $MgSO_4$. Removal of the solvent gave the desired product as a yellow solid (0.080 g, 80%). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.93 (d, J = 3.5 Hz, 2H), 7.60 (s, 2H), 7.34 (d, J = 3.5 Hz, 2H), 4.62 (s, 3H), 3.46 (s, 2H); ^{13}C-NMR (125.7

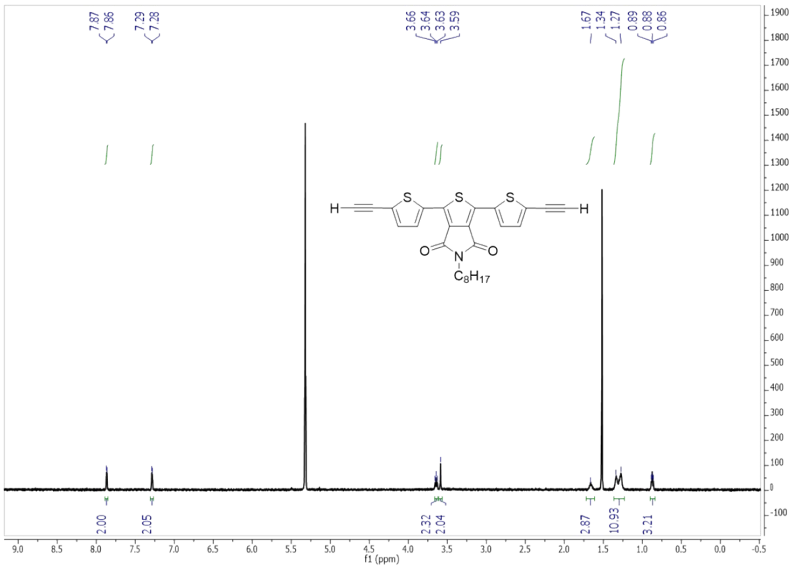
MHz, $CDCl_3$): 142.39, 141.42, 134.31, 126.86, 123.41, 123.23, 122.32, 82.81, 77.34, 43.88; HRMS (ESI) Calculated for $C_{19}H_{11}N_3S_2$ ($M+H^+$): *m/z* 346.0467. Found: *m/z* 346.0466.

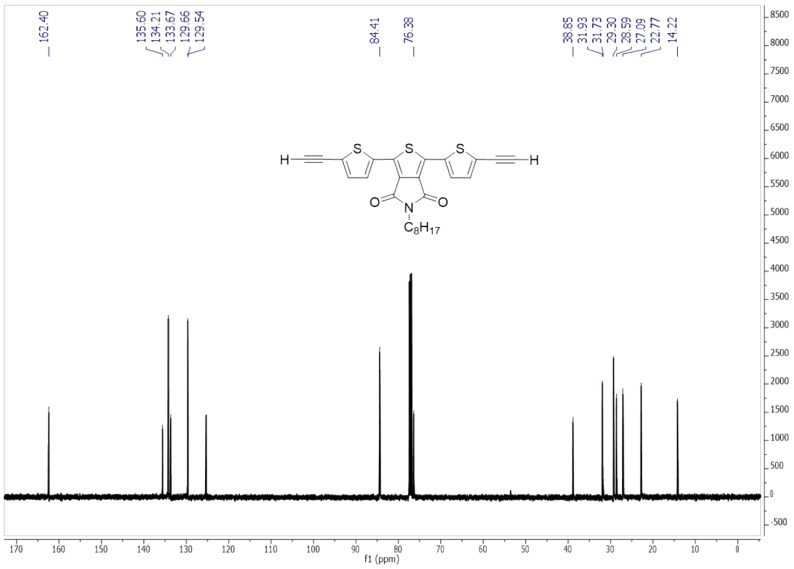




4,7-bis(5-Ethynylthiophen-2-yl) 5-octyl-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (4b) Compound **4b** was synthesized by the same procedure as **4a**. The desired product was obtained as a yellow solid (0.213 g, 89%). ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.87 (d, J = 3.5 Hz, 2H), 7.29 (d, J = 3.5 Hz, 2H), 3.66 (t, 2H), 3.59 (s, 2H), 1.67 (m, 2H), 1.30 (m, 10H), 0.88 (t, 3H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 162.40, 135.60, 134.21, 133.67, 129.66, 129.54, 84.41, 76.38, 38.85, 31.93, 31.73, 29.30,

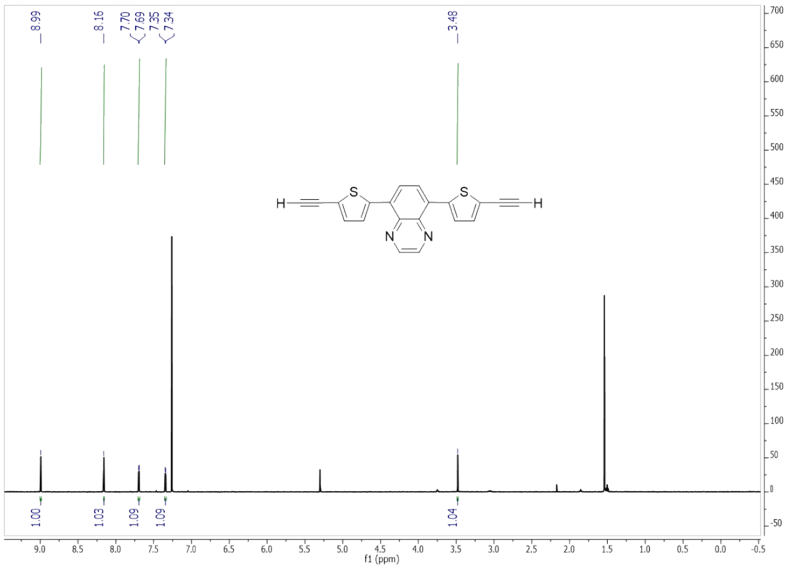
28.59, 27.09, 22.77, 14.22; HRMS (ESI) Calculated for $C_{26}H_{23}NO_3S_3$ $(M+H)^+$: *m/z* 478.0964. Found: *m/z* 478.0983.

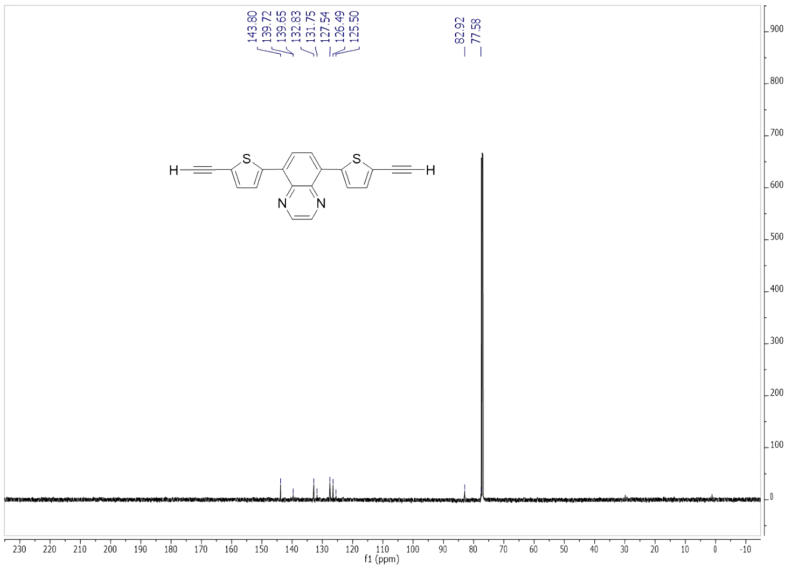




4,7-bis(5-Ethynylthiophen-2-yl)quinoxaline (4c) Compound **4c** was synthesized by the same procedure as **4a**. The desired product was obtained as a red solid (0.108 g, 60%). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.99 (s, 2H), 8.16 (s, 2H), 7.70 (d, J = 4 Hz, 2H), 7.35 (d, J = 4 Hz, 2H), 3.48 (s, 2H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 143.80, 139.72, 139.65, 132.83, 131.75, 127.54, 126.49,

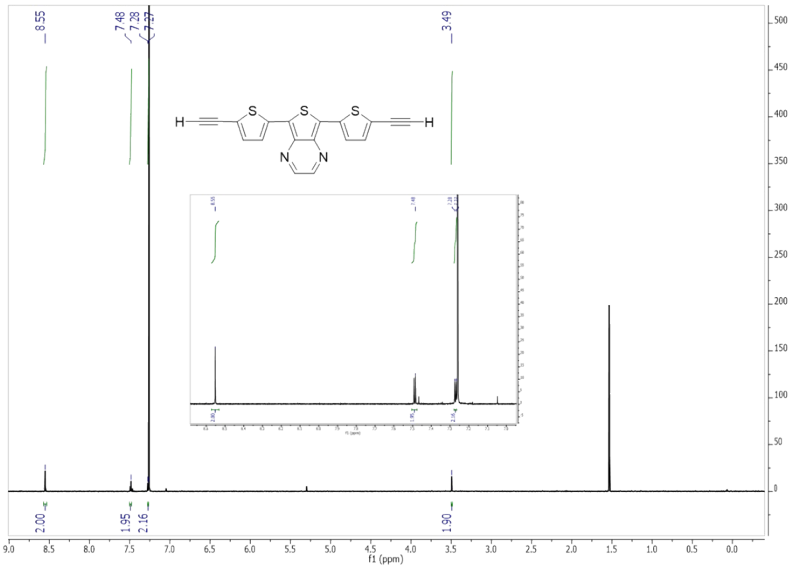
125.50, 82.92, 77.58; HRMS (ESI) Calculated for $C_{20}H_{12}N_2S_2$ $(M+H)^+$: *m/z* 344.0320. Found: *m/z* 344.0353.

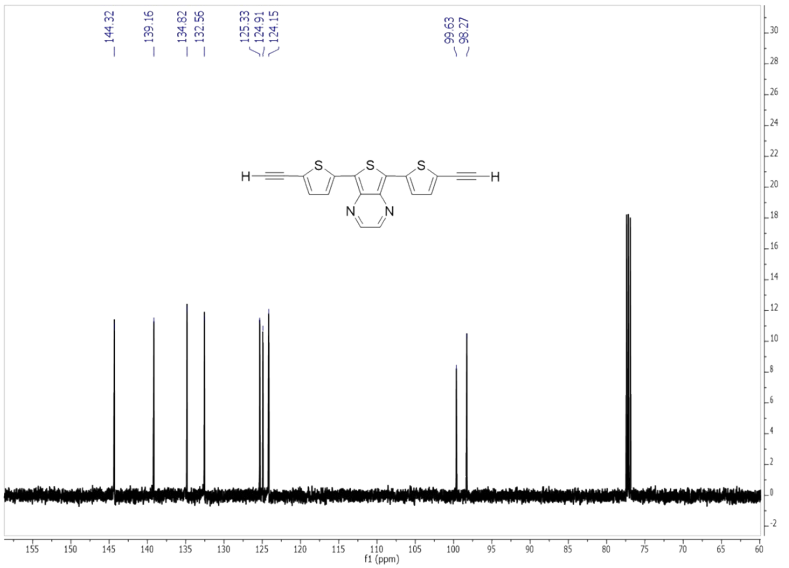




4,7-bis(5-Ethynylthiophen-2-yl) thieno[3,4-*b*]pyrazine (4e) 0.290 g of compound **3e** (0.38 mmol, 1 equiv) was dissolved in 15 mL of THF and degassed for 45 min by bubbling with argon. 0.492 g of TBAT (0.91 mmol, 2.4 equiv) was added under argon. The resulting solution was stirred at 50°C overnight. The reaction mixture was quenched with water, extracted with DCM, and dried

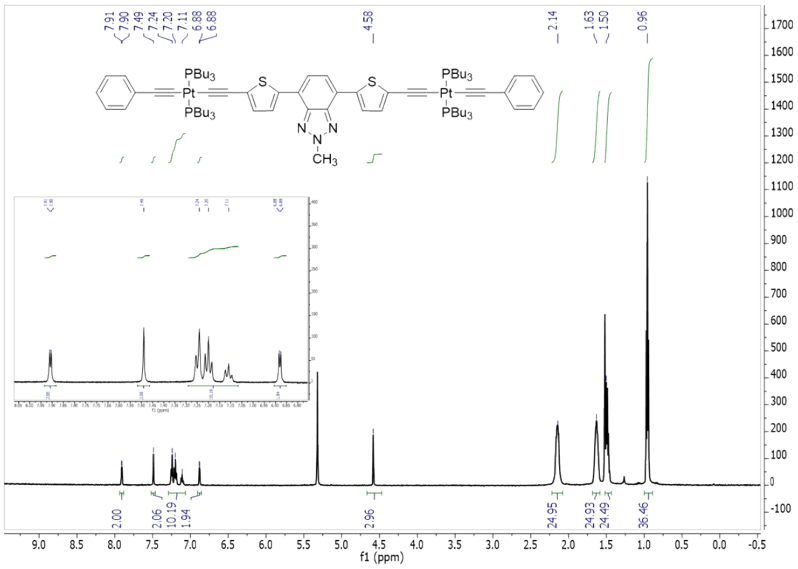
over $MgSO_4$. The desired product was obtained as a dark red solid (0.107 g, 70%). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.55 (s, 2H), 7.48 (d, J = 4 Hz, 2H), 7.28 (d, J = 4 Hz, 2H), 3.49 (s, 2H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 144.32, 139.16, 134.82, 132.56, 125.33, 124.91, 124.15, 99.63, 98.27; HRMS (ESI) Calculated for $C_{18}H_8N_2S_3$ ($M+H^+$): *m/z* 348.9922. Found: *m/z* 348.9934.

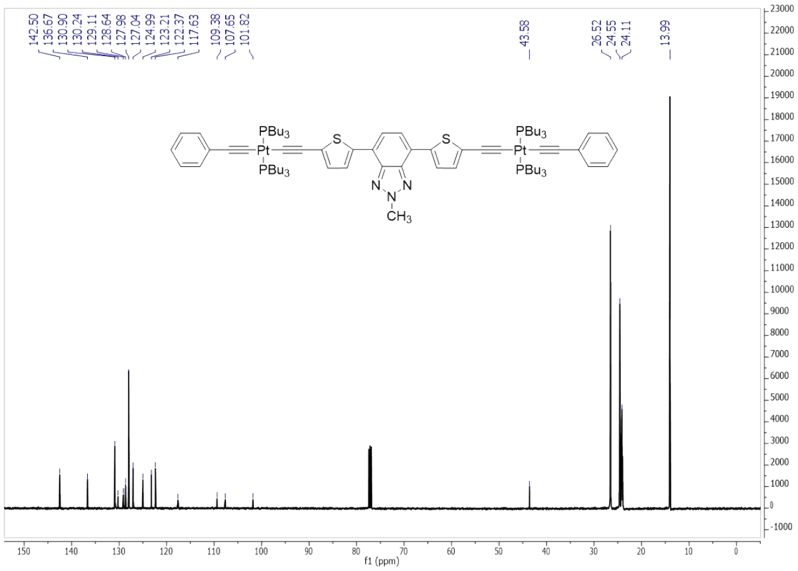


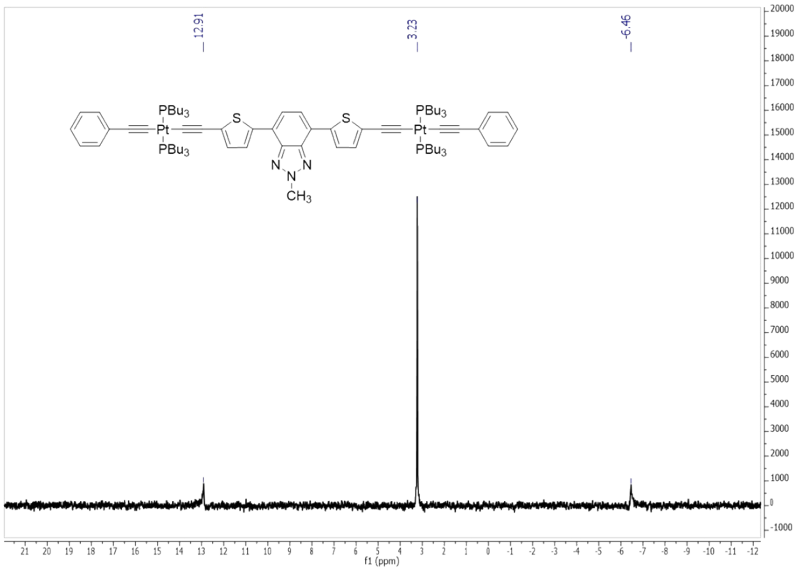


TBTz (5a) 0.052 g of compound **4a** (0.15 mmol, 1 equiv) and 0.235 g of trans-ethynylphenylchlorobis(tri-n-butylphosphine)platinum(II) (**5**) (0.32 mmol, 2.1 equiv) were dissolved in a piperidine/toluene mixture [1:1 (v/v), 20 mL] and degassed for 45 min by bubbling

with argon. Then 1 mg CuI (0.008 mmol, 0.05 equiv) was added. The resulting mixture was stirred at room temperature for 1 hour. Silica gel was then added to the reaction mixture, and the solvent was evaporated. The product was purified by silica column chromatography using CH_2Cl_2 / hexane (1:1) as the eluent. The product was obtained as a viscous orange oil (176 mg, 85%). ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.90 (d, J = 3.5 Hz, 2H), 7.49 (s, 2H), 7.24 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.88 (d, J = 3.5 Hz, 2H), 4.58 (s, 3H), 2.14 (m, 24H), 1.63 (m, 24H), 1.50 (sext, 24H), 0.96 (t, 36H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 142.50, 136.67, 130.90, 130.24, 129.11, 128.64, 127.98, 127.04, 124.99, 123.21, 122.37, 117.63, 109.38, 107.65, 101.82, 43.58, 26.52, 24.55, 24.11, 13.99; ^{31}P-NMR (121.44 MHz, $CDCl_3$): 3.23 ($J_{Pt\text{-}P}$ = 2352 Hz); HRMS (MALDI) Calculated for $C_{83}H_{127}N_3P_4Pt_2S_2$ (M^+): *m/z* 1744.7727. Found: *m/z* 1744.7744.

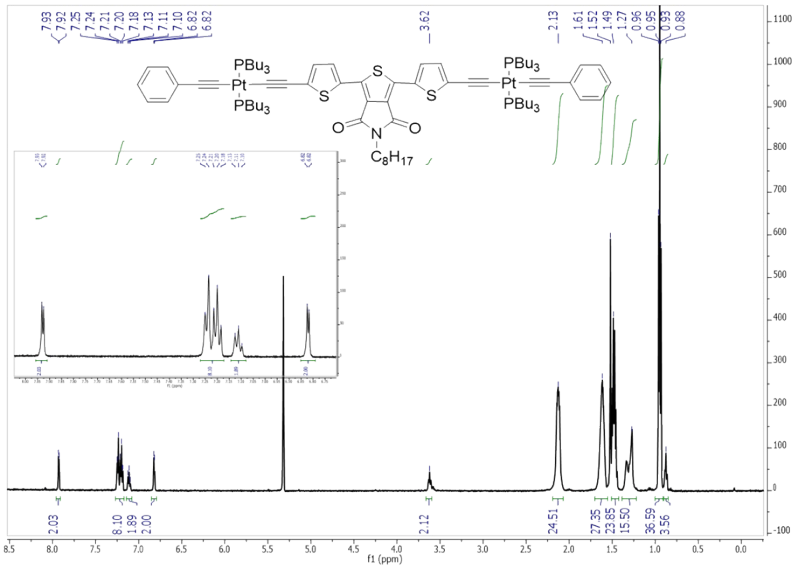


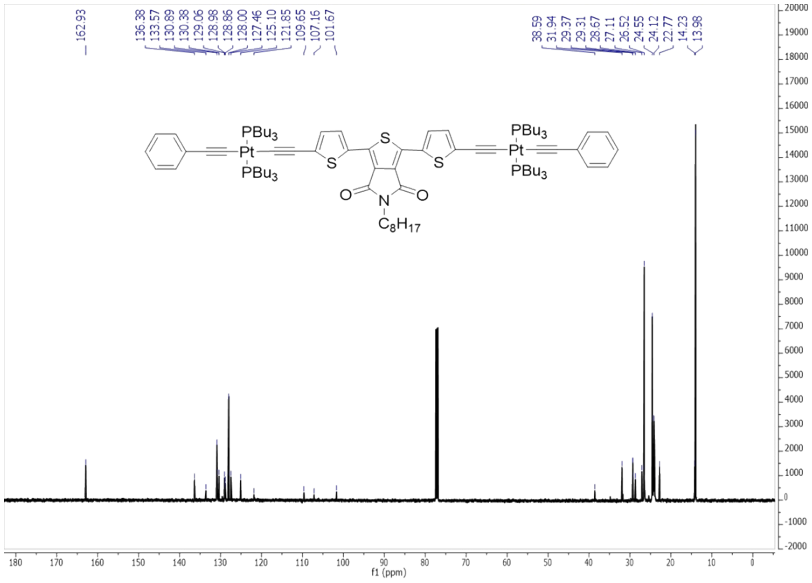


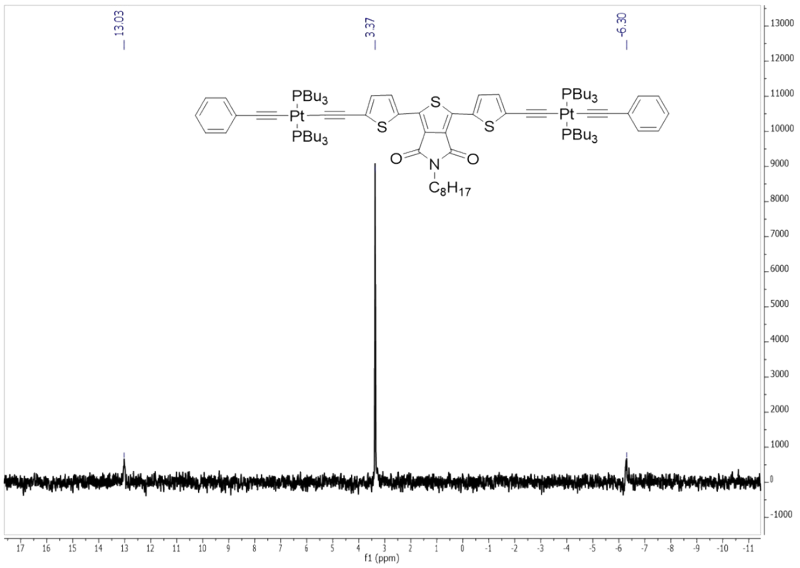


TPD (5b) Compound **5b** was synthesized by the same procedure as **5a**. The product was purified by silica column chromatography using CH_2Cl_2 / hexane (2:3) as the eluent. The desired product was obtained as an orange oil (74 mg, 30%). ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.93 (d, J = 3.5 Hz, 2H), 7.24 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.82 (d, J = 3.5 Hz, 2H), 3.62 (t, 2H), 2.13 (m, 24H), 1.61 (m, 24H), 1.49 (m, 24H), 1.27 (m, 12H), 0.95 (t, 36H), 0.88 (t, 3H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 162.93, 136.38, 133.57, 130.89, 130.38, 129.06, 128.98, 128.86, 128.00, 127.46, 125.10, 121.85, 109.65, 107.16, 101.67, 38.59, 31.94, 29.37, 29.31, 28.67, 27.11, 26.52, 24.54,

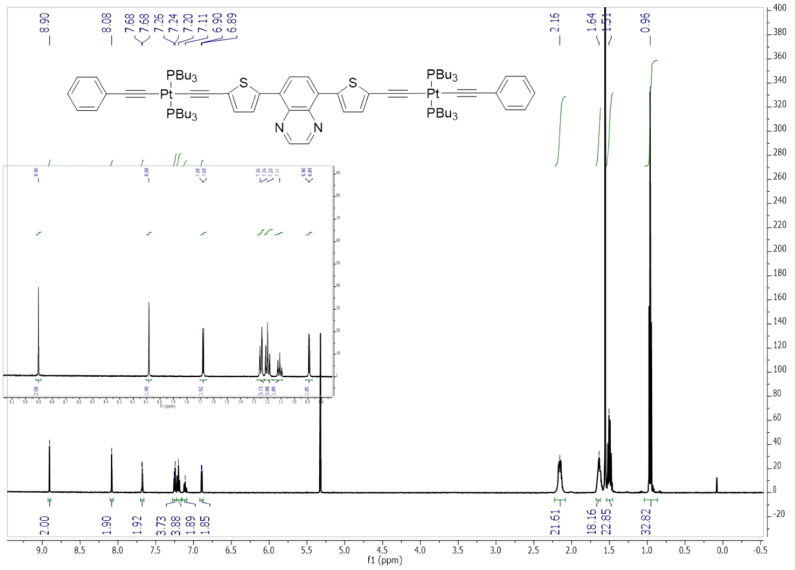
24.12, 22.77, 14.22, 13.98; ^{31}P-NMR (121.44 MHz, $CDCl_3$): 3.37 ($J_{Pt\text{-}P}$ = 2352 Hz); HRMS (MALDI) Calculated for $C_{90}H_{139}NO_2P_4Pt_2S_3$ (M^+): *m/z* 1876.8223. Found: *m/z* 1876.8253.

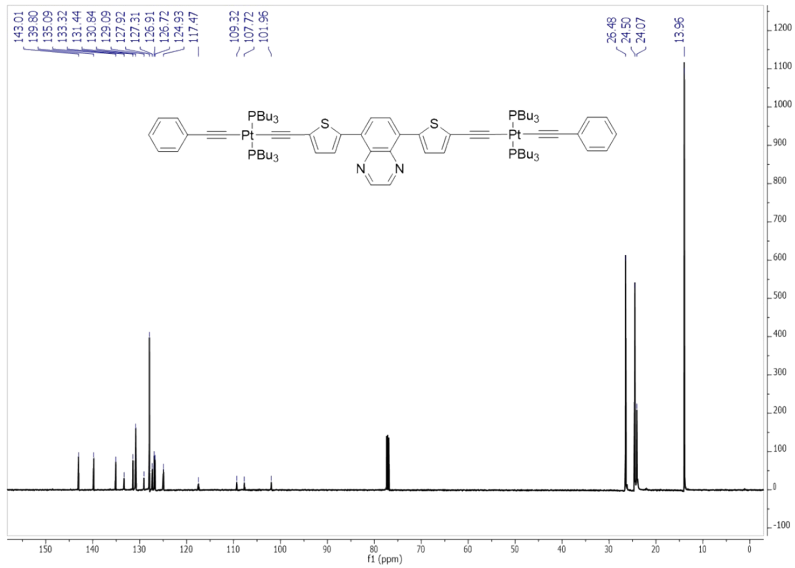


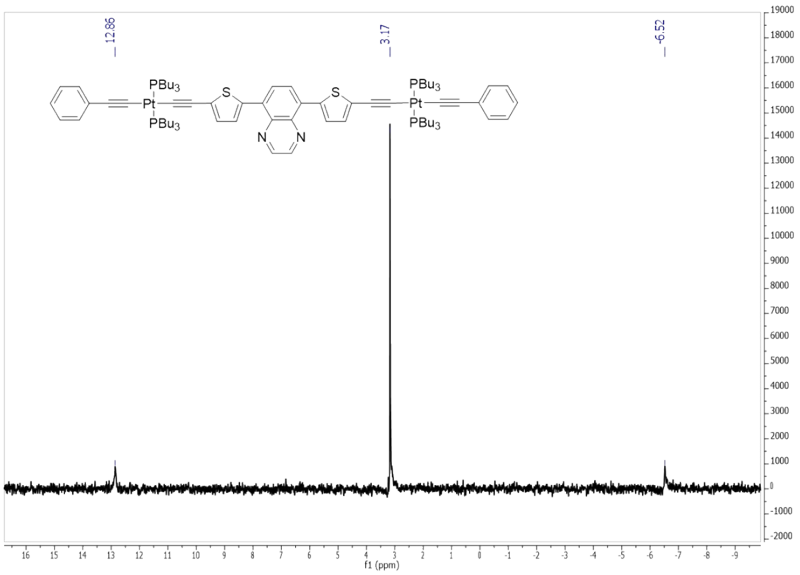




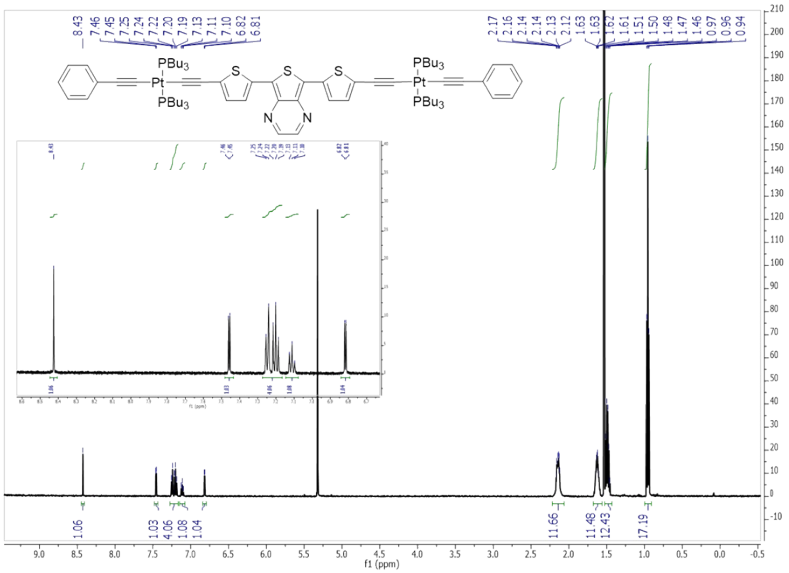
TQT (5c) Compound **5c** was synthesized by the same procedure as **5a**. The product was purified by silica column chromatography using CH_2Cl_2 / hexane (1:1) as the eluent. The desired product was obtained as a dark red solid (240 mg, 78%). ^{1}H-NMR (500 MHz, CD_2Cl_2): 8.90 (s, 2H), 8.08 (s, 2H), 7.68 (d, J = 4 Hz, 2H), 7.24 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.90 (d, J = 4 Hz, 2H), 2.16 (m, 24H), 1.64 (m, 24H), 1.50 (m, 24H), 0.96 (t, 36H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 143.01, 139.80, 135.09, 133.32, 131.44, 130.84, 129.09, 127.92, 127.31, 126.91, 126.72, 124.93, 117.47, 109.32, 107.72, 101.96, 26.48, 24.50, 24.07, 13.96; ^{31}P-NMR (121.44 MHz, $CDCl_3$): 3.17 ($J_{Pt\text{-}P}$ = 2354 Hz); HRMS (MALDI) Calculated for $C_{84}H_{126}N_2P_4Pt_2S_2$ (M^+): *m/z* 1741.7618. Found: *m/z* 1741.7615.

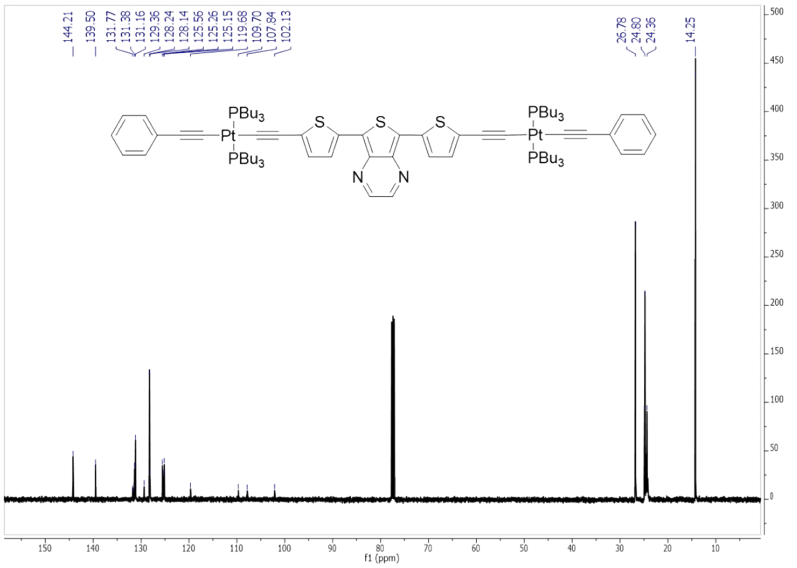

8.90
8.08
7.68
7.68
7.26
7.24
7.20
7.11
6.90
6.89
2.16
1.64
1.51
0.96
PBu3
Pt
PBu3
S
N
N
2.00
1.90
1.92
3.73
3.88
1.89
1.85
21.61
18.16
22.85
32.82
f1 (ppm)

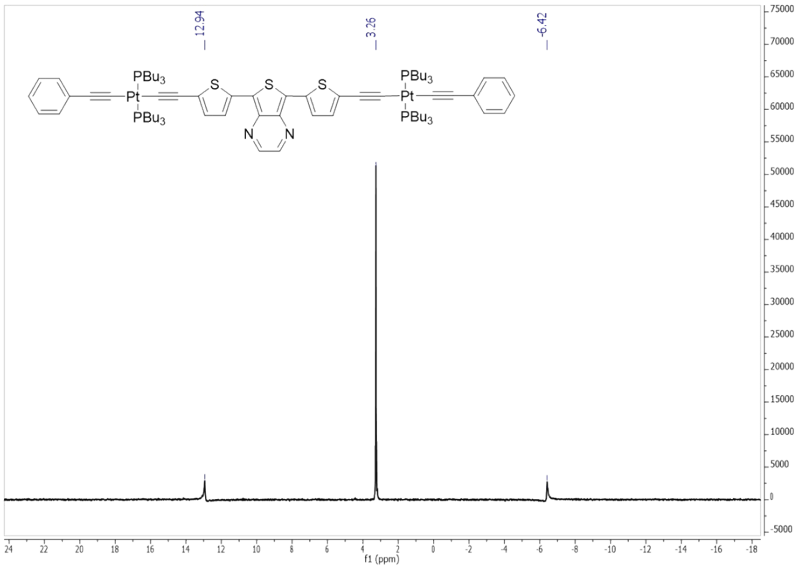

143.01
139.80
135.09
133.32
131.44
130.84
129.09
127.92
127.31
126.91
126.72
124.93
117.47
109.32
107.72
101.96
26.48
24.50
24.07
13.96
PBu3
Pt
PBu3
S
N
N
f1 (ppm)



TPT (5e) Compound **5e** was synthesized by the same procedure as **5a**. The product was purified by silica column chromatography using CH_2Cl_2 / hexane (1:1) as the eluent. The desired product was obtained as a green oil (54 mg, 41%). ^{1}H-NMR (500 MHz, CD_2Cl_2): 8.43 (s, 2H), 7.46 (d, J = 4 Hz, 2H), 7.25 (m, 4H), 7.20 (m, 4H), 7.11 (m, 2H), 6.82 (d, J = 4 Hz, 2H), 2.14 (m, 24H), 1.62 (m, 24H), 1.48 (m, 24H), 0.96 (t, 36H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 144.21, 139.50, 131.77, 131.38, 131.16, 129.36, 128.24, 128.14, 125.56, 125.26, 125.15, 119.68, 109.70, 107.84, 102.13, 26.78, 24.80, 24.36, 14.25; ^{31}P-NMR (121.44 MHz, $CDCl_3$): 3.26 ($J_{Pt\text{-}P}$ = 2351 Hz); HRMS (MALDI) Calculated for $C_{82}H_{124}N_2P_4Pt_2S_3$ (M^+): *m/z* 1747.7180. Found: *m/z* 1747.7178.

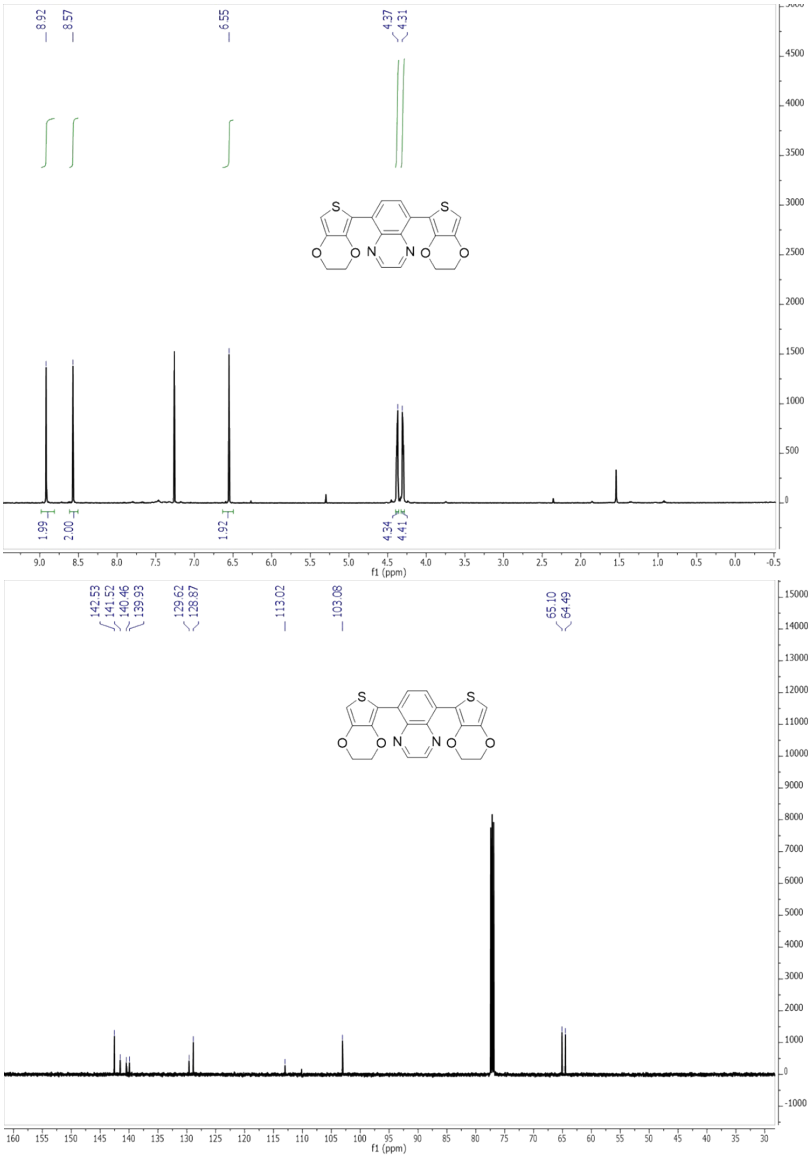






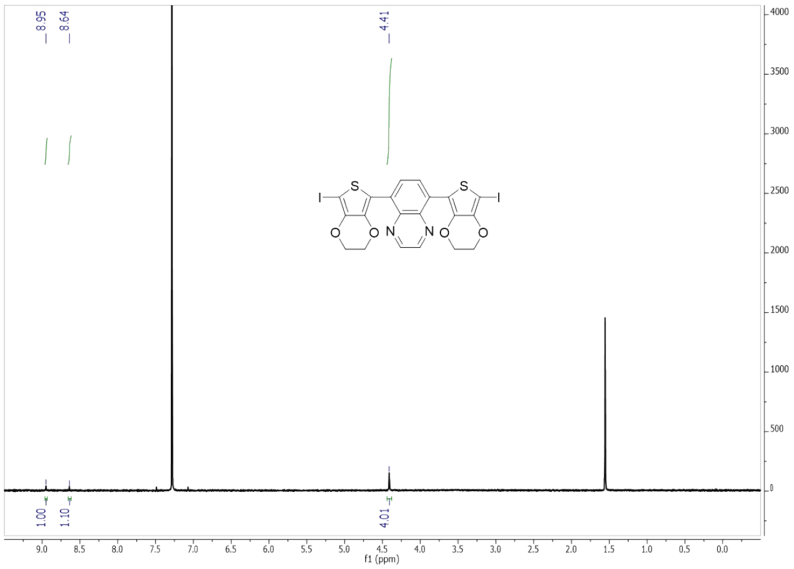
5,8-bis(3,4-dihydro-2*H*-thieno[3,4-*b*]pyran-5-yl)quinoxaline (7a) A solution of 0.250 g of dibromo-**Qx** (0.87 mmol, 1 equiv) and 0.90 g of compound **6** (2.08 mmol, 2.6 equiv) in 20 mL of toluene was degassed for 1 hour by bubbling with argon. Then 100 mg of $Pd(PPh_3)_4$ (0.09 mmol, 0.1 equiv) and 8 mg CuI (0.004 mmol, 0.05 equiv) were added under argon. The resulting mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water water (50 mL), extracted with Et_2O (25 mL), and dried over $MgSO_4$. The product was purified by silica column chromatography using CH_2Cl_2 / hexane (4:1) as the eluent. The product was obtained as dark orange solid (0.35 g, 98%). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.92 (s, 2H), 8.57

(s, 2H), 6.55 (s, 2H), 4.37-4.31 (m, 8H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 142.53, 141.52, 140.46, 139.93, 129.62, 128.87, 113.02, 103.08, 65.10, 64.49; HRMS (ESI) Calculated for $C_{20}H_{14}N_2O_4S_2$ $(M+H)^+$: *m/z* 411.0468. Found: *m/z* 411.0472.

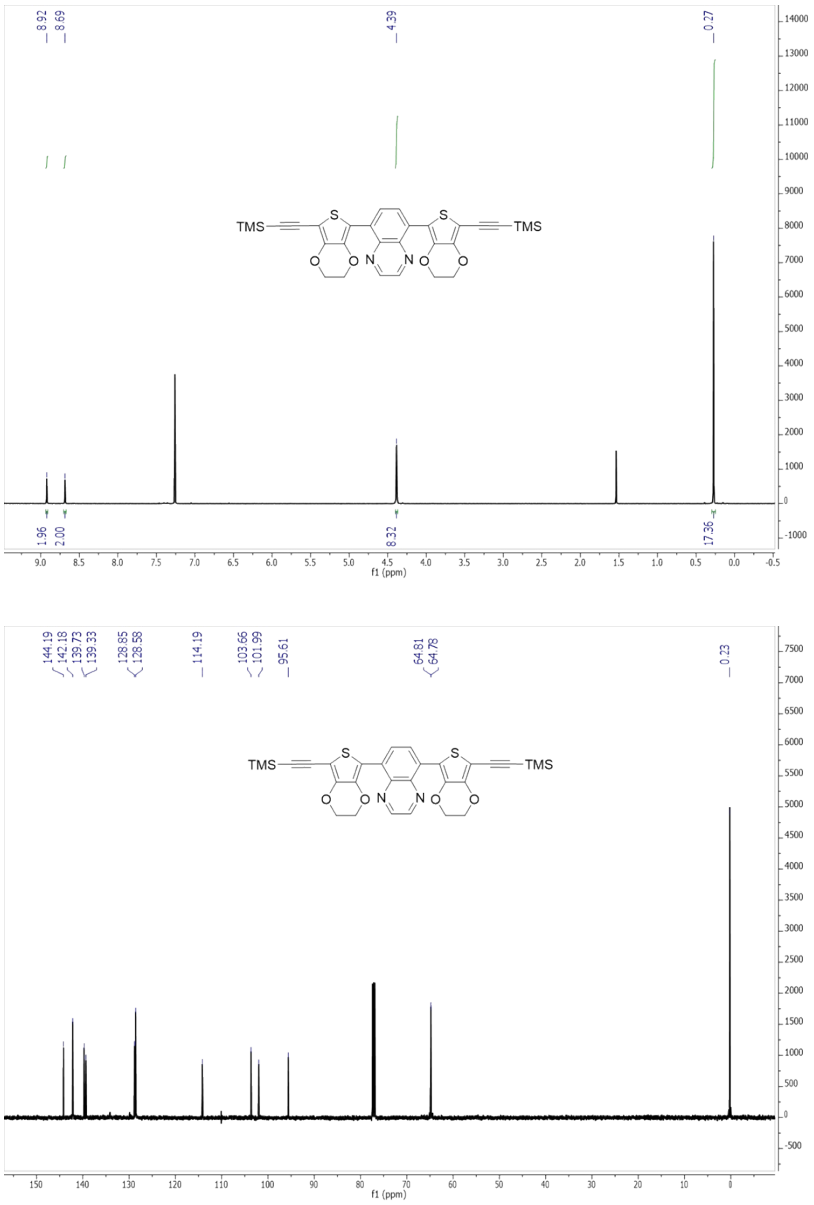


5,8-bis(7-iodo-3,4-dihydro-2*H*-thieno[3,4-*b*]pyran-5-yl)quinoxaline (8a) To a solution of 0.358 g of **7a** (0.87 mmol, 1 equiv) in $CHCl_3$/acetic acid [2:1 (v/v), 120 mL], 0.50 g of NIS (2.17 mmol, 2.5 equiv) was added. The reaction mixture was stirred at room temperature for 2 days. The precipitate formed was collected by suction filtration, washed with water, ethanol, and chloroform. The desired product was obtained as dark red solid (0.34 g, 60%). **8a** could not be characterized

by ^{13}C-NMR due to solubility problems. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.95 (s, 2H), 8.64 (s, 2H), 4.41 (s, 8H); HRMS (ESI) Calculated for $C_{20}H_{12}I_2N_2O_4S_2$ $(M+H)^+$: *m/z* 662.8401. Found: *m/z* 662.84010.

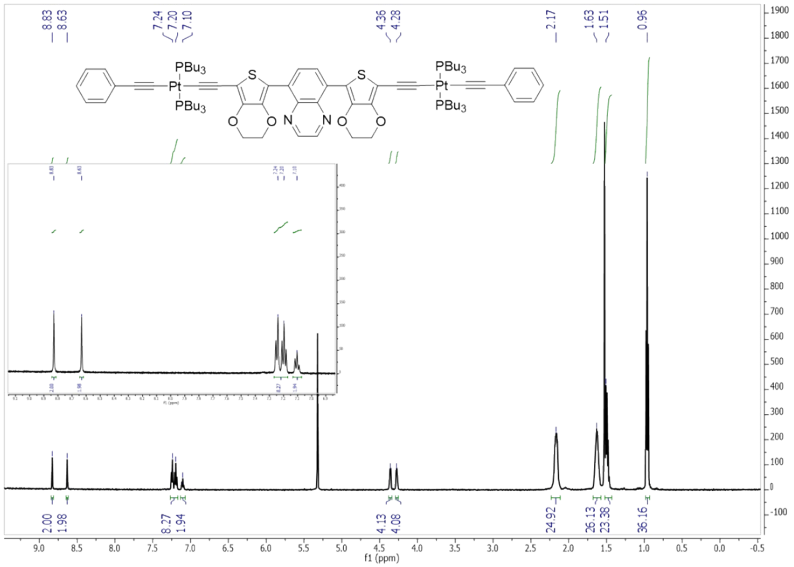


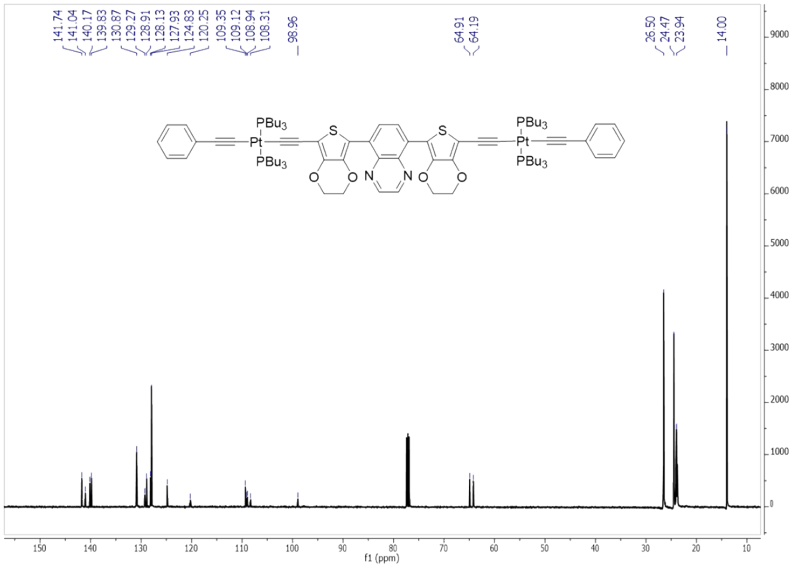
5,8-bis(7-(trimethylsilyl)-3,4-dihydro-2*H*-thieno[3,4-*b*]pyran-5-yl)quinoxaline (9a) A solution of 0.335 g of **8a** (0.5 mmol, 1 equiv) in THF/piperidine [5:1 (v/v), 25 mL] was degassed for 45 min by bubbling with argon. Then 58 mg of $Pd(PPh_3)_4$ (0.05 mmol, 0.1 equiv) and 5 mg of CuI (0.002 mmol, 0.05 equiv) were added under argon. Then 0.2 mg of trimethylsilylacetylene (2 mmol, 4 equiv) was added via syringe. The resulting mixture was refluxed overnight. Upon cooling to room temperature silica gel was added to the reaction mixture, and the solvent was evaporated under reduced pressure. The product was purified by silica column chromatography using CH_2Cl_2 / hexane (1:1) as the eluent. The product was obtained as red solid (0.21 g, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.92 (s, 2H), 8.69 (s, 2H), 4.39 (s, 8H), 0.27 (s, 18H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 144.19, 142.18, 139.73, 139.33, 128.85, 128.58, 114.19, 103.66, 101.99, 95.61, 64.81, 64.78, 0.23; HRMS (ESI) Calculated for $C_{30}H_{30}N_2O_4S_2Si_2$ $(M+H)^+$: *m/z* 603.1258. Found: *m/z* 603.1263.

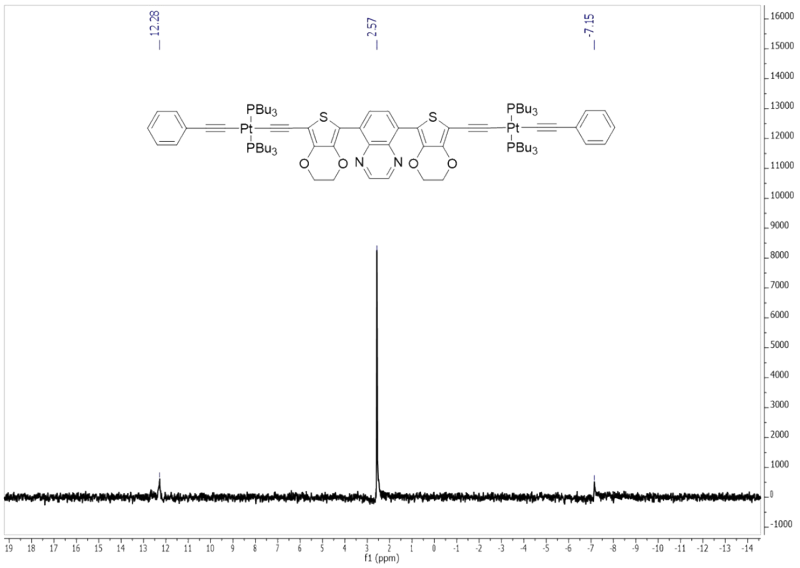


EQE (10a) 0.075 g of compound **9a** (0.124 mmol, 1 equiv), 0.22 g of trans-ethynylphenylchlorobis(tri-n-butylphosphine)platinum(II) (**3**) (0.30 mmol, 2.4 equiv) and 1 mg of CuI (0.006 mmol, 0.05 equiv) were dissolved in a THF/triethylamine mixture [1:1 (v/v), 40 mL] and degassed for 1 hour by bubbling with argon. Then 81 mg of TBAF (0.311 mmol, 2.5 equiv) was added via syringe. The resulting mixture was stirred at room temperature overnight. Silica gel was then added to the reaction mixture, and the solvent was evaporated. The product was purified by silica column chromatography using ethylacetate / hexane (1:4) as the eluent. The product was obtained as a purple solid (0.098 g, 42%). ^{1}H-NMR (500 MHz, CD_2Cl_2): 8.83 (s, 2H), 8.63 (s, 2H),

7.24 (d, 4H), 7.20 (m, 4H), 7.10 (t, 2H), 4.36 (m, 4H), 4.28 (m, 4H), 2.17 (m, 24H), 1.63 (m, 24H), 1.51 (m, 24H), 0.96 (t, 36H); ^{13}C-NMR (125.7 MHz, $CDCl_3$): 141.74, 141.04, 140.17, 139.83, 130.87, 129.27, 128.91, 128.13, 127.93, 124.83, 120.25, 109.35, 109.12, 108.94, 108.31, 98.96, 64.91, 64.19, 26.50, 24.47, 23.94, 14.00; ^{31}P-NMR (121.44 MHz, $CDCl_3$): 2.57 ($J_{Pt\text{-}P}$ = 2347 Hz); HRMS (MALDI) Calculated for $C_{84}H_{126}N_2P_4Pt_2S_2$ (M^+): *m/z* 1857.7745. Found: *m/z* 1857.7728.



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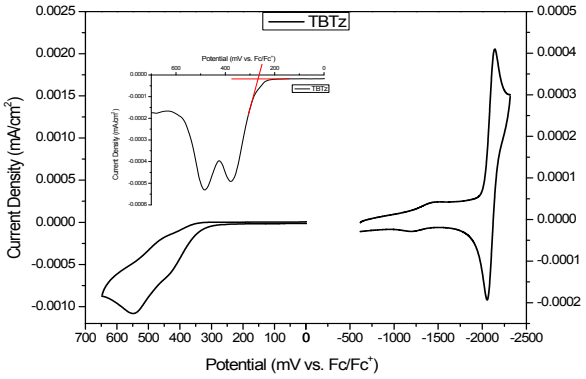
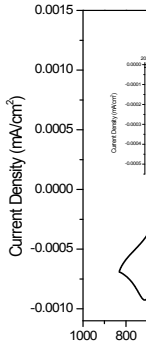
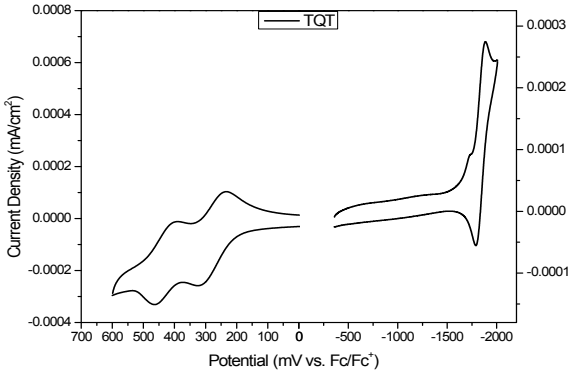
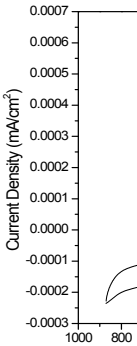
2.57
-7.15
PBu3
Pt
PBu3
S
O
O
N
N
O
O
S
PBu3
Pt
PBu3
f1 (ppm)

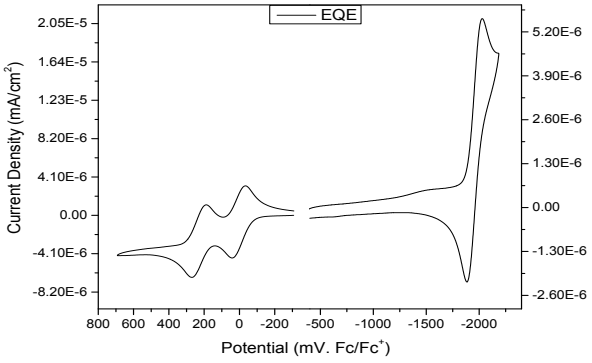
II. Electrochemical Data

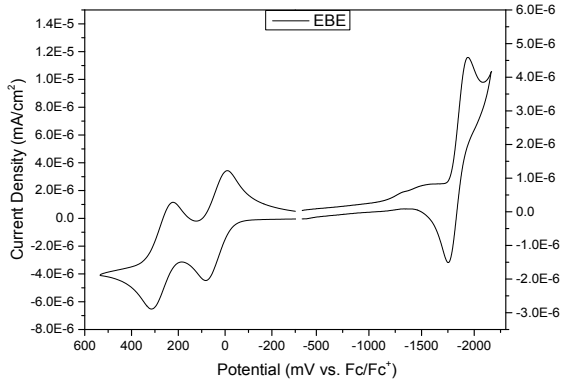


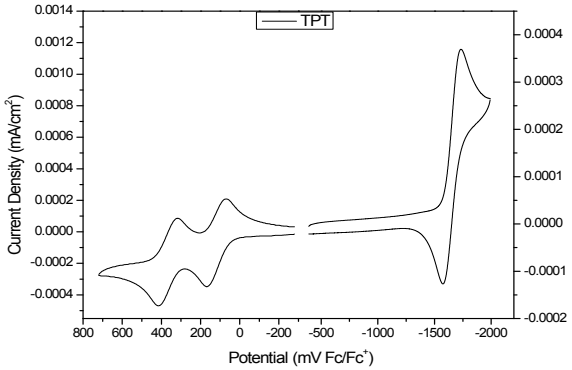












III. Photophysical Data

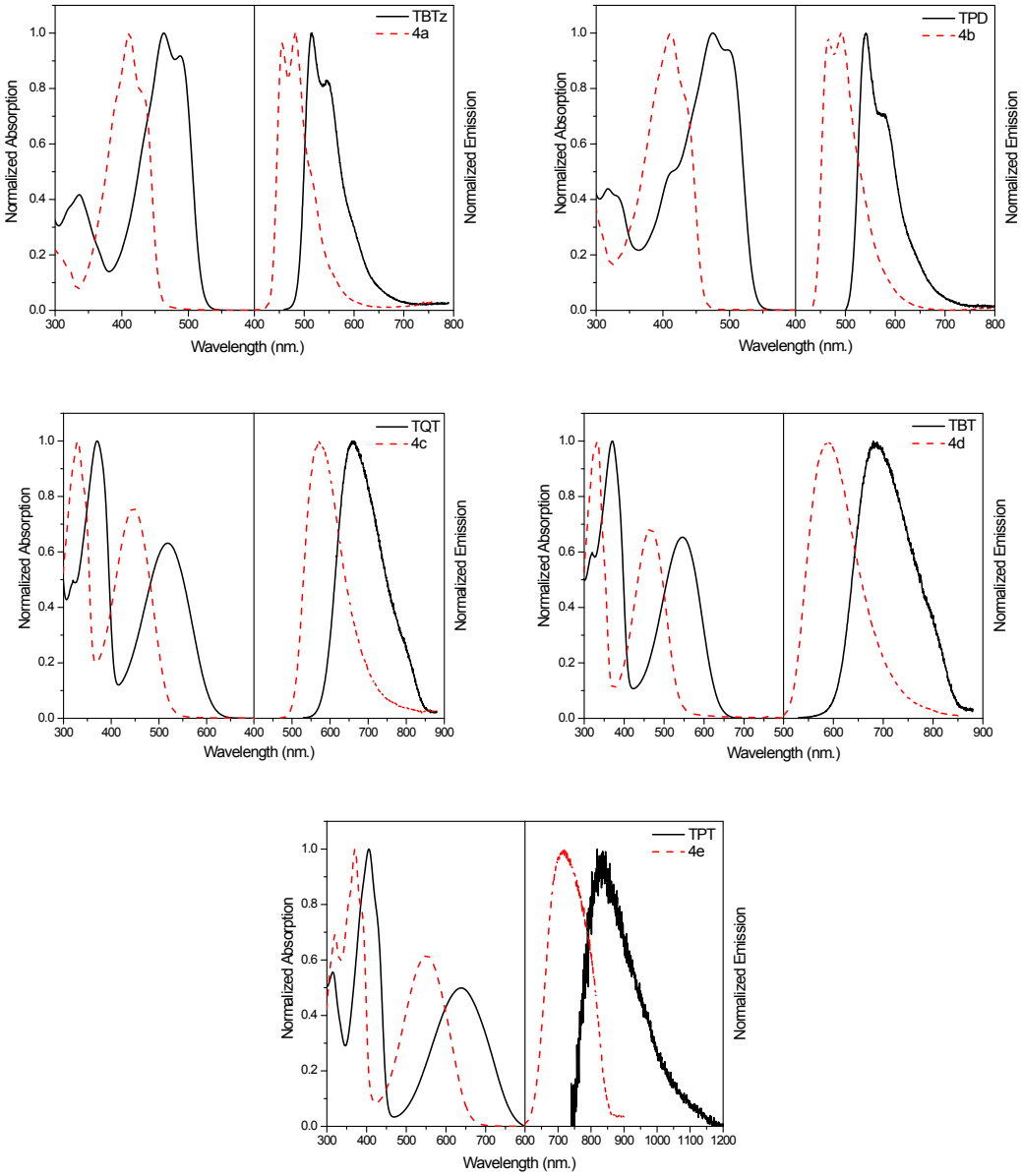


Figure S1. Normalized absorption and emission spectra of the unmetallated DAD chromophores (**4a-e**) and their Pt complexes.

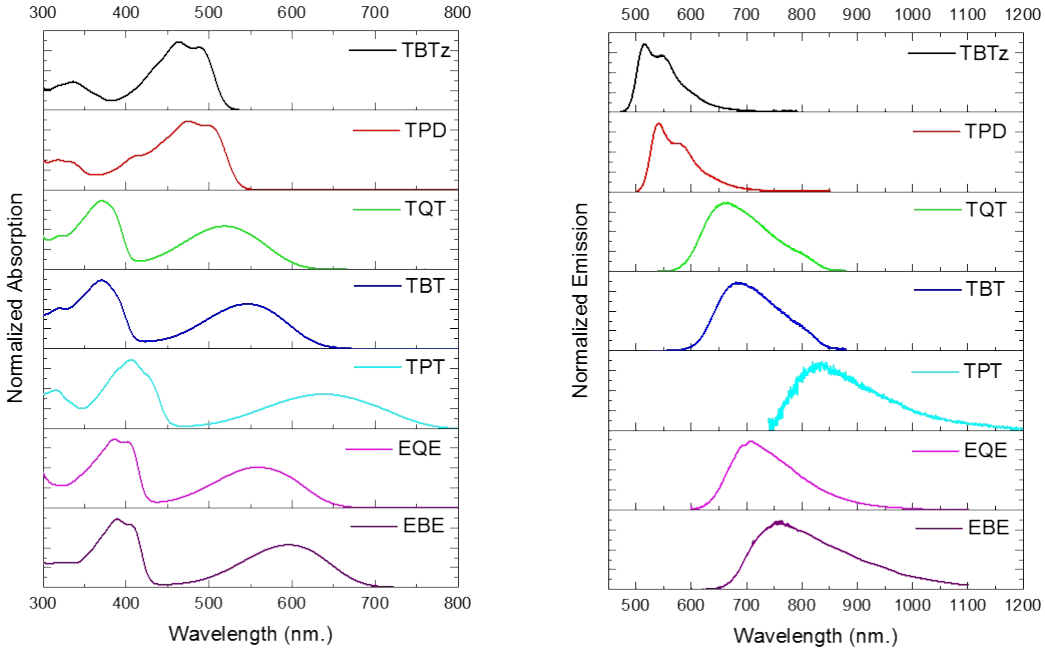


Figure S2. UV-VIS spectra (in THF, left), and photoluminescence spectra (in THF, right).

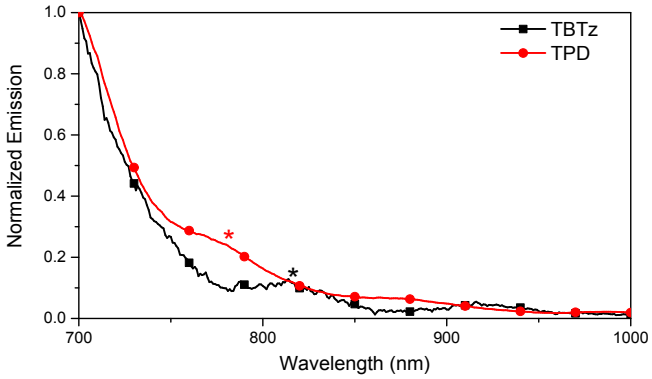


Figure S3. Low-temperature luminescence spectra (77 K) of **TBTz** and **TPD** in 2-MeTHF, degassed by five repeated cycles of freeze-pump-thaw on a high-vacuum line. The stared feature is the phosphorescence band.

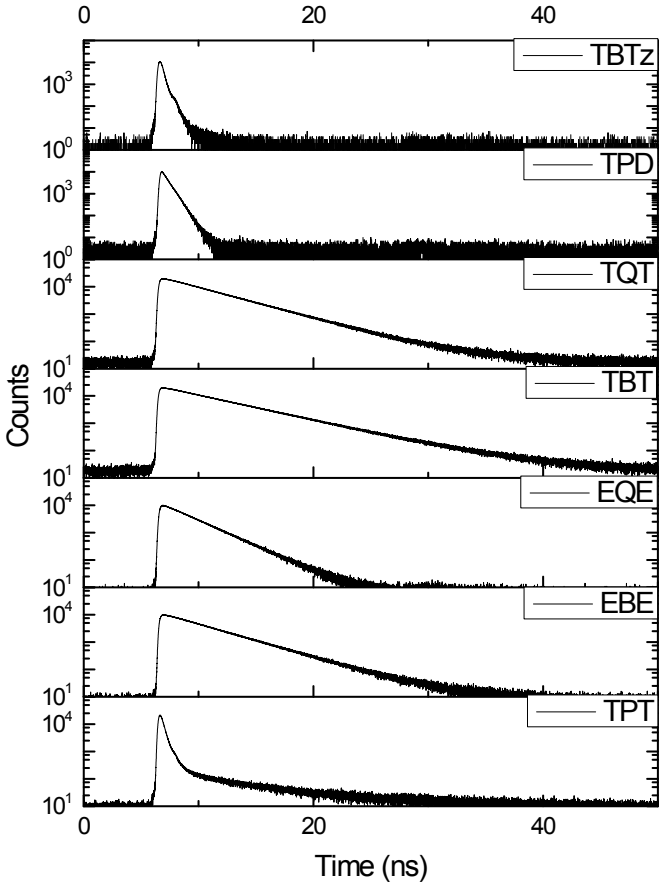


Figure S4. Fluorescence decay plots of molecules collected by TCSPC in anhydrous THF.

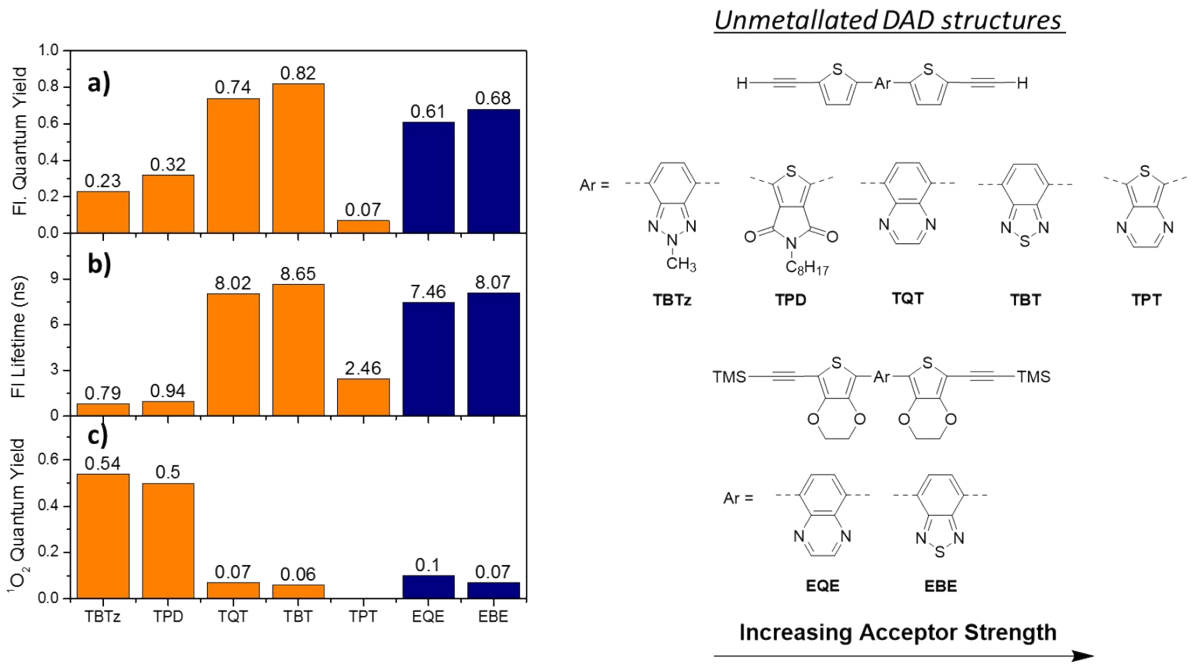


Figure S5. Photophysical properties of the unmetallated ligands (thiophene series are in orange, EDOT series are in blue) on the left panel and the structures of the ligands on the right panel. a) Fluorescence quantum yield measured in THF using quaninine sulfate in 0.1 M H_2SO_4 solution (Φ_f=0.577)[9] as an actinometer. b) Fluorescence lifetime measured in THF by TCSPC. C) Singlet oxygen quantum yield measured in deuterated chloroform using terthiophene (Φ_f=0.84) as an actinometer

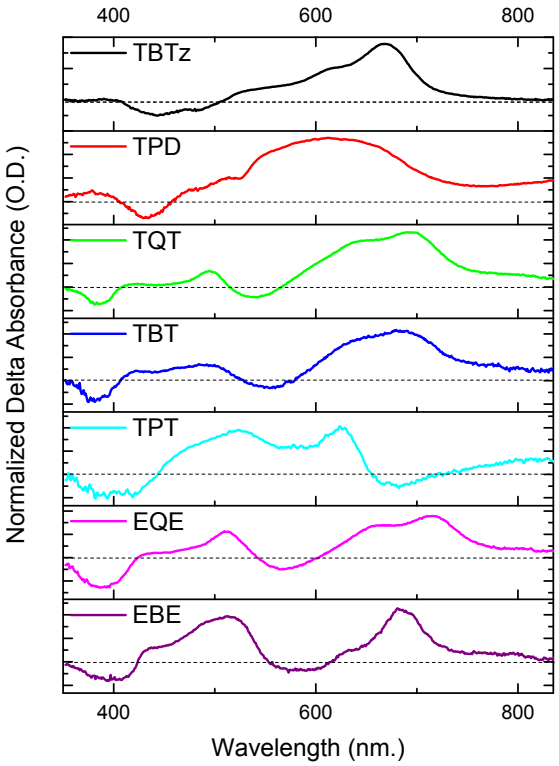


Figure S6. Normalized nanosecond transient absorption difference spectra of Pt-substituted chromophores, following nanosecond-pulsed 355 nm excitation (4mJ/pulse) in argon-purged THF.

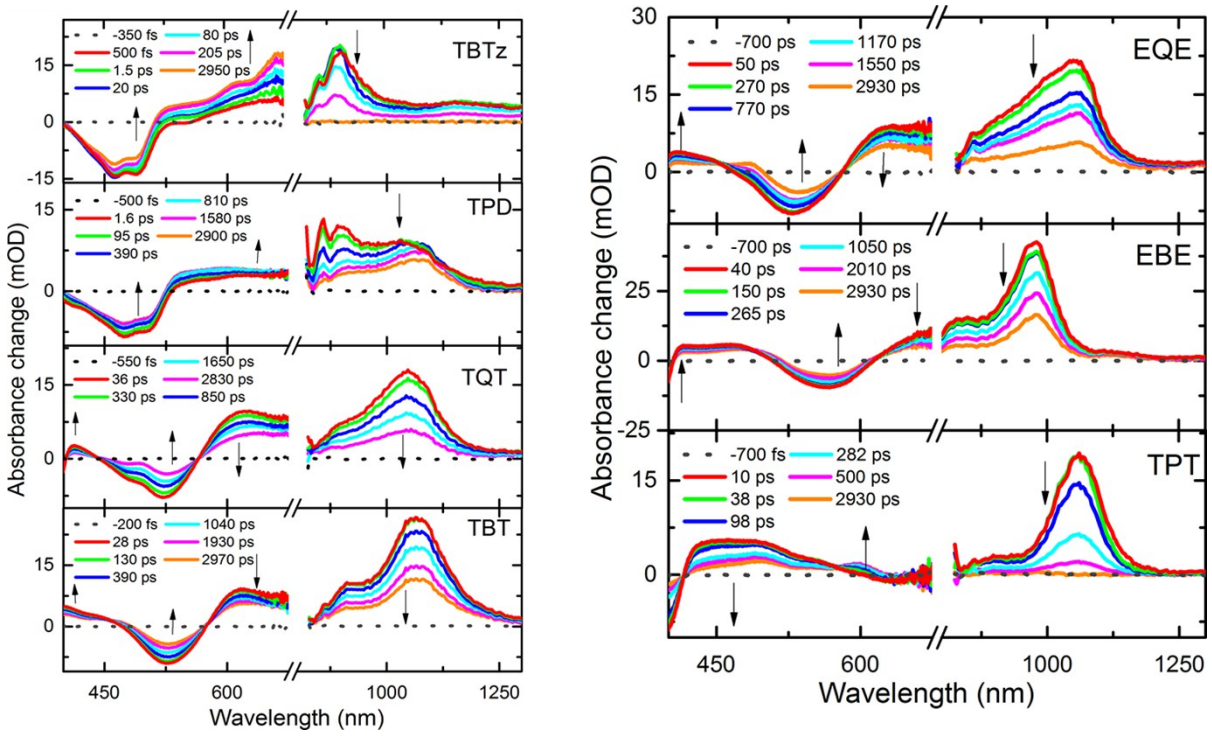


Figure S7. Femtosecond transient absorption difference spectra of the Pt-substituted chromophores at indicated delay times following 355 nm laser excitation pulse (35 fs pulse width, 1.5 μJ/pulse) in air saturated THF.

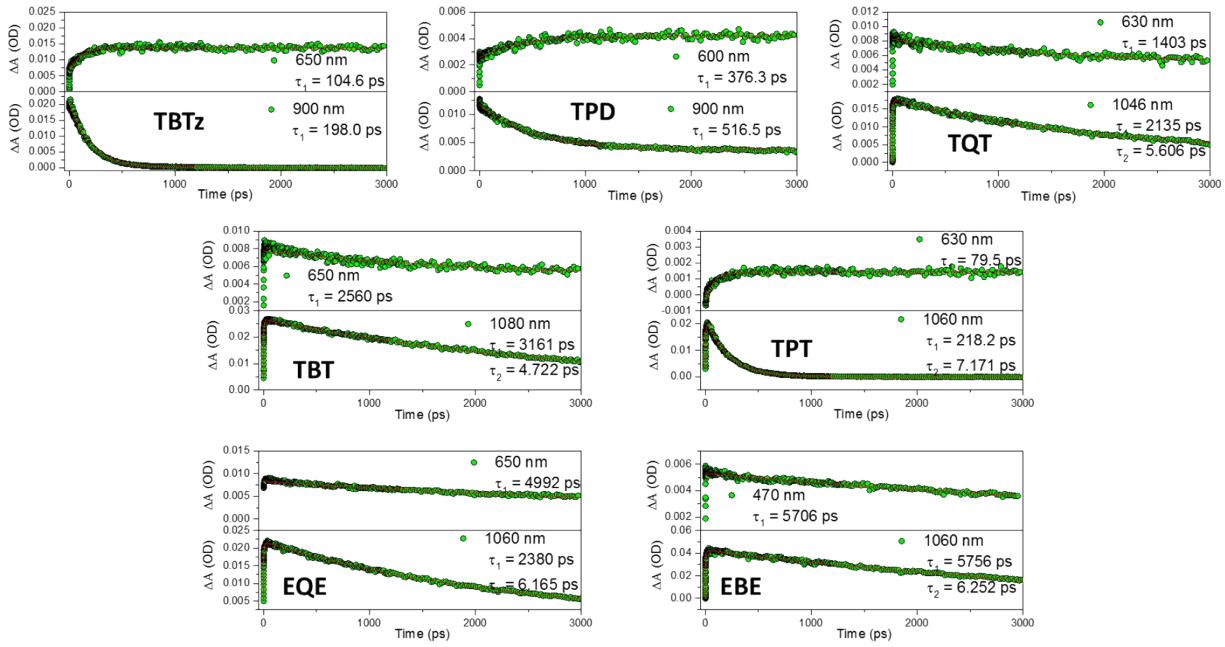


Figure S8. Fitting of the fs transient absorption decay kinetics at the indicated wavelengths. The lifetimes are fitted by mono or bi exponential parameters on Surface Xplorer v4. The The τ_S is reported from the decay of near-IR band. A short-lived rise component is observed for some of the entries.

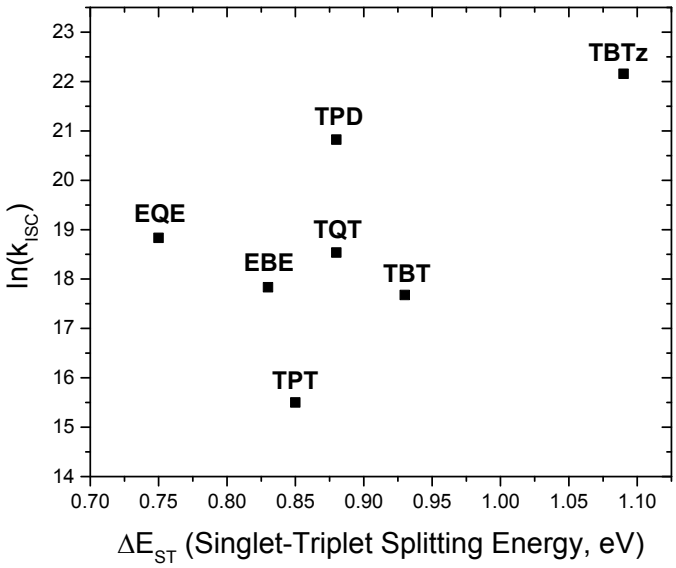


Figure S9. The natural log of intersystem crossing rate vs. singlet-triplet splitting energy.

IV. Computational Data

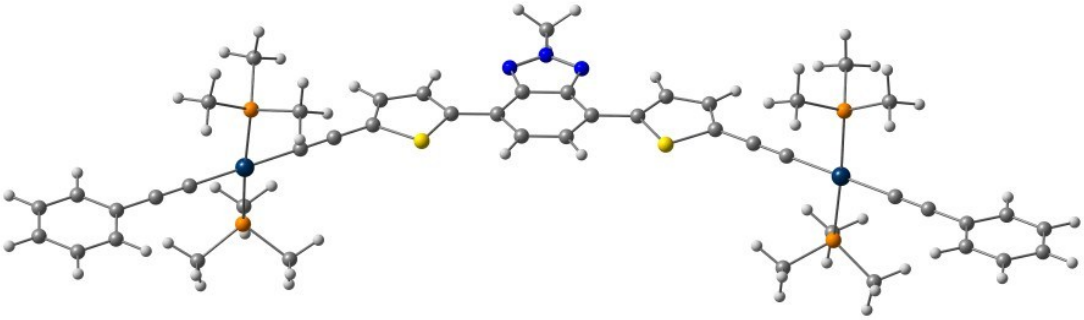


Figure S10. DFT optimized singlet state structure of **TBTz'**.

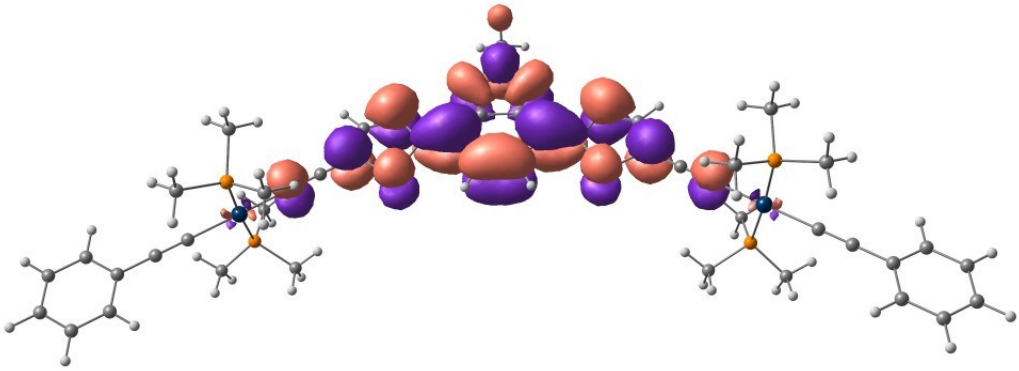


Figure S11. LUMO of **TBTz'**.

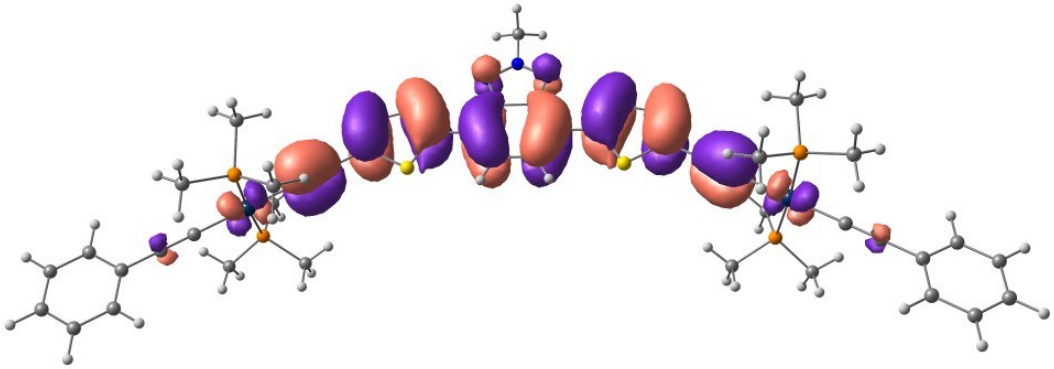


Figure S12. HOMO of **TBTz'**.

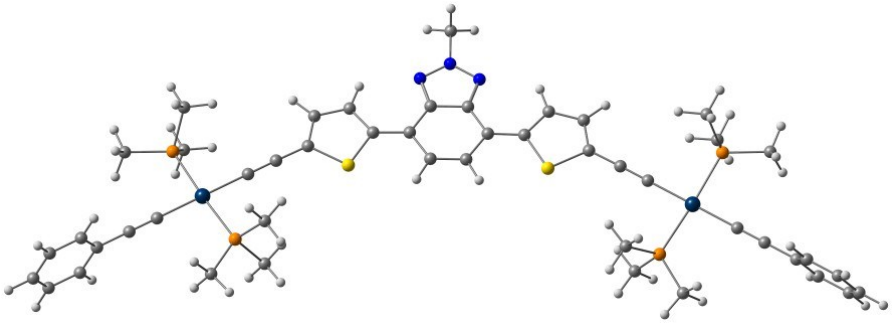


Figure S13. DFT optimized triplet state structure of **TBTz'**.

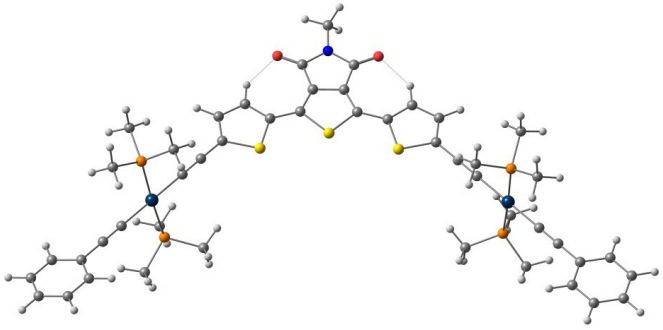


Figure S14. DFT optimized singlet state structure of **TPD'**.

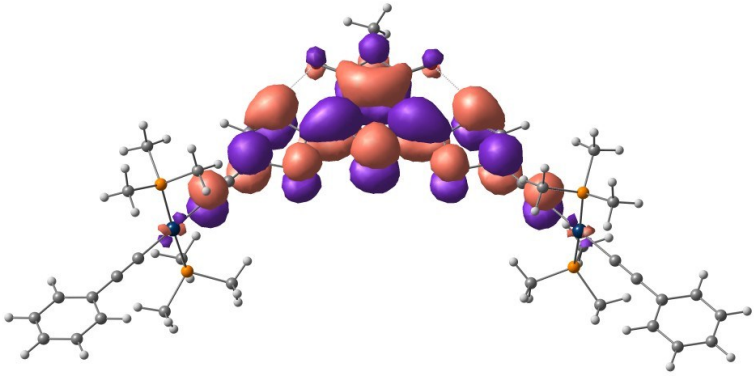


Figure S15. LUMO of **TPD'**.

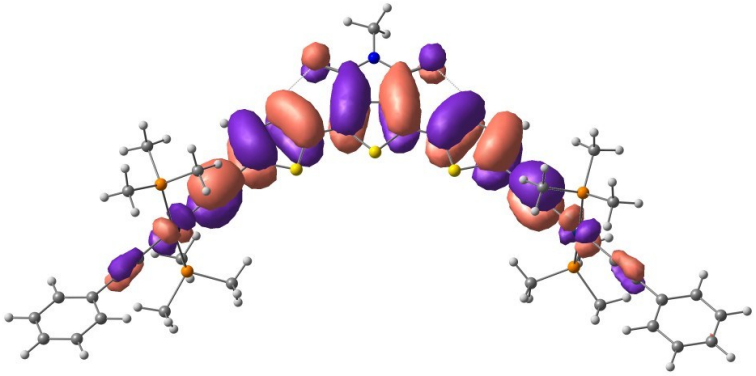


Figure S16. HOMO of **TPD'**.

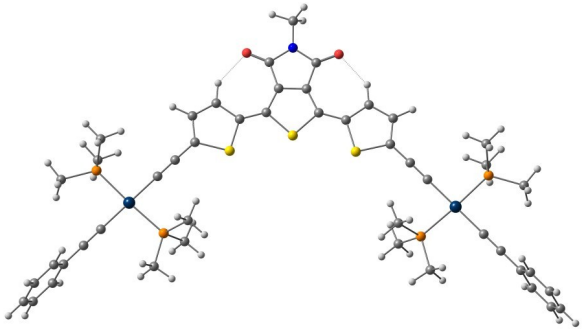


Figure S17. DFT optimized triplet state structure of **TPD'**.

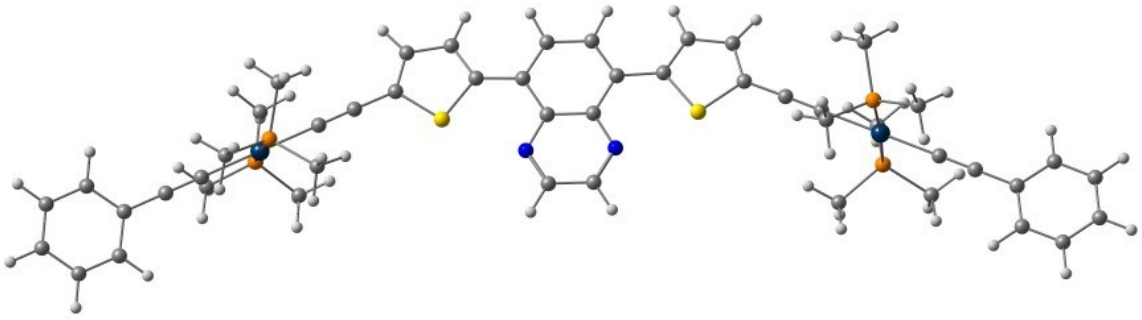


Figure S18. DFT optimized singlet state structure of **TQT'**.

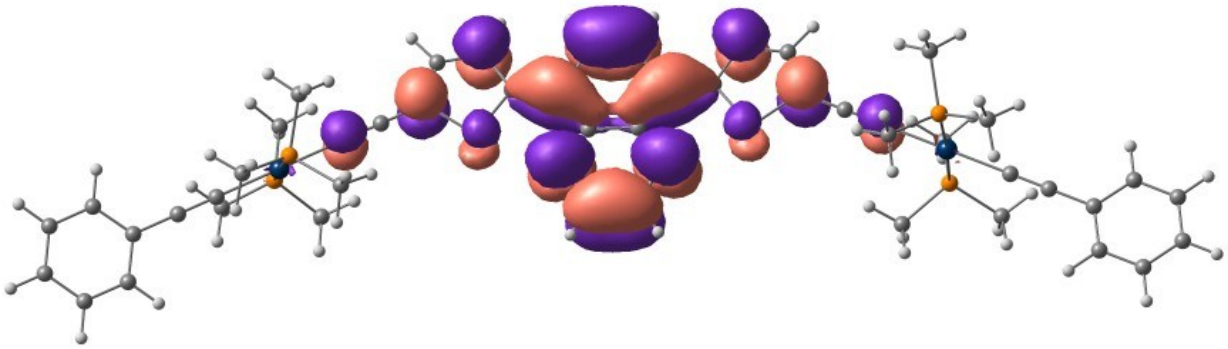


Figure S19. LUMO of **TQT'**.

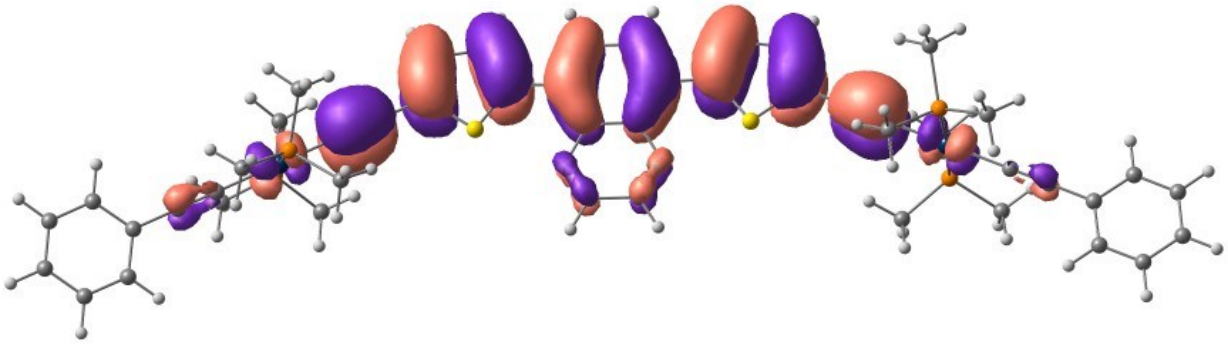


Figure S20. HOMO of **TQT'**.

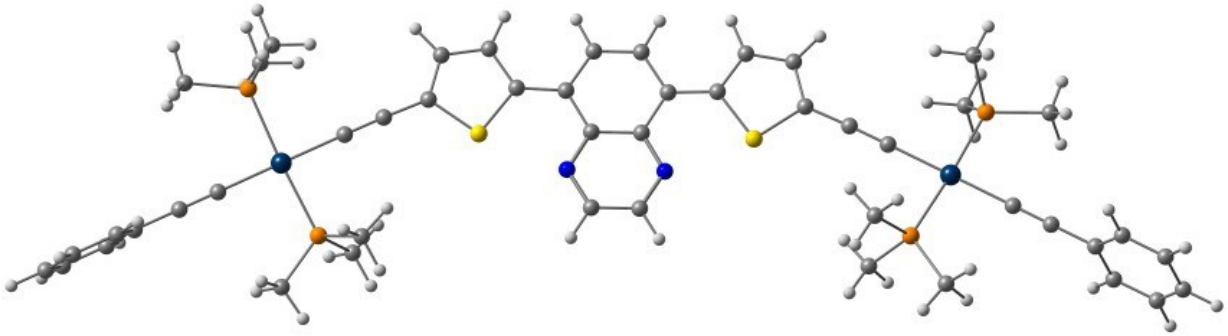


Figure S21. DFT optimized triplet state structure of **TQT'**.

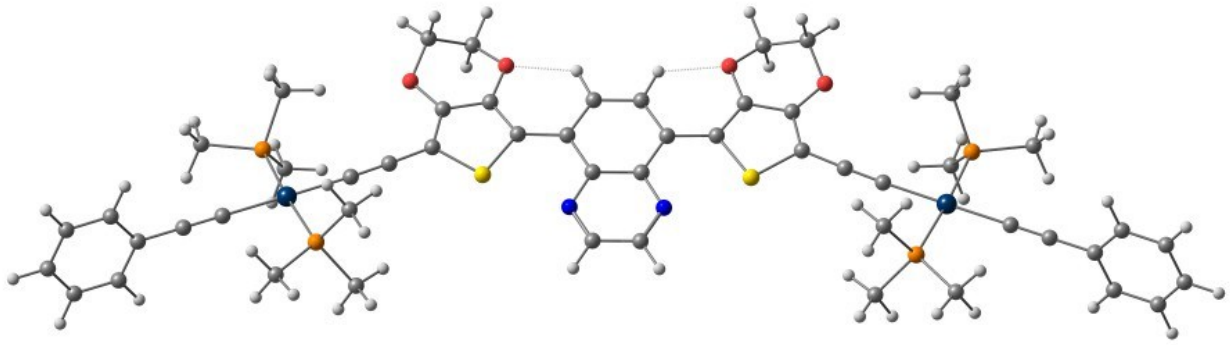


Figure S22. DFT optimized singlet state structure of **EQE'**.

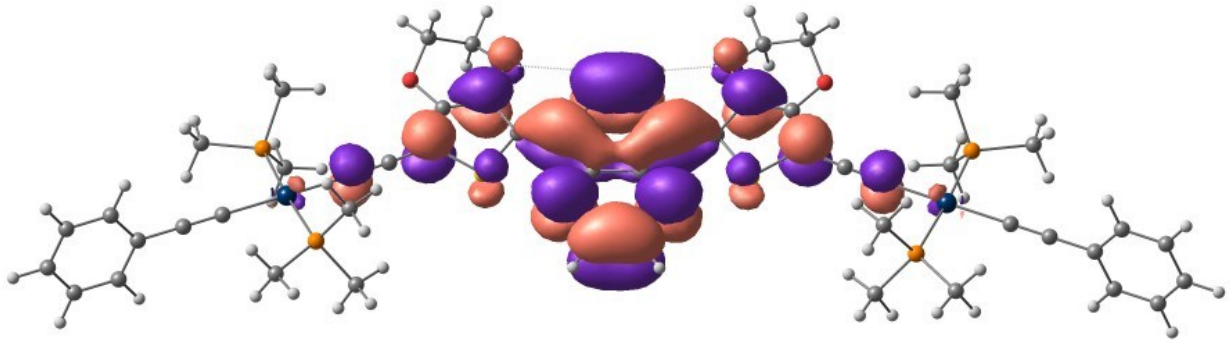


Figure S23. LUMO of **EQE'**.

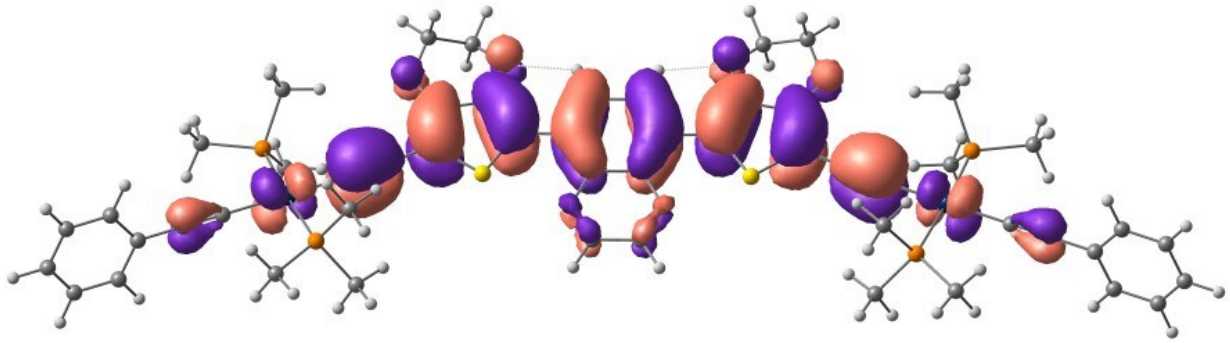


Figure S24. HOMO of **EQE'**.

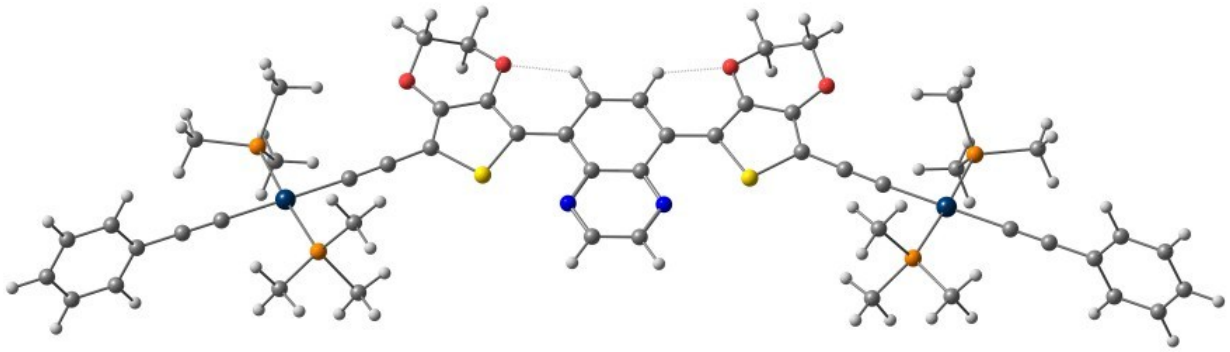


Figure S25. DFT optimized triplet state structure of **EQE'**.

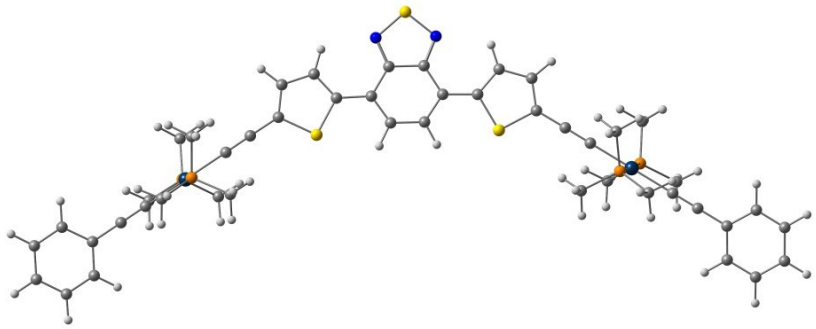


Figure S26. DFT optimized singlet state structure of **TBT'**.

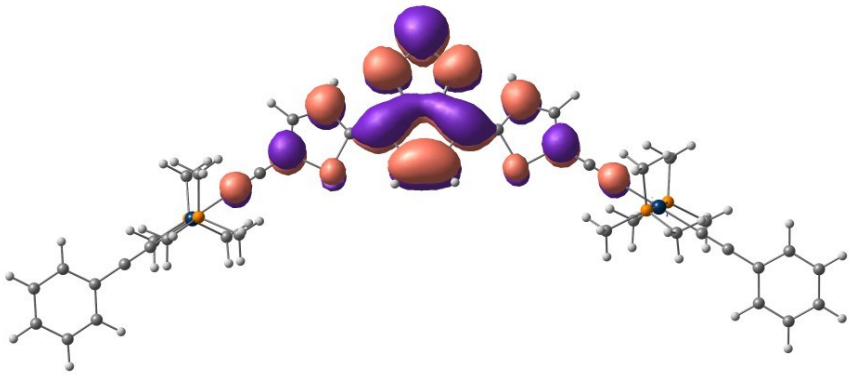


Figure S27. LUMO of **TBT'**.

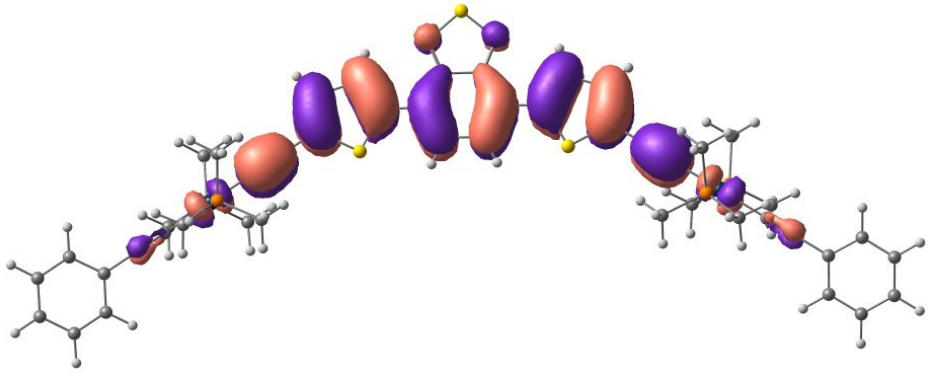


Figure S28. HOMO of **TBT'**.

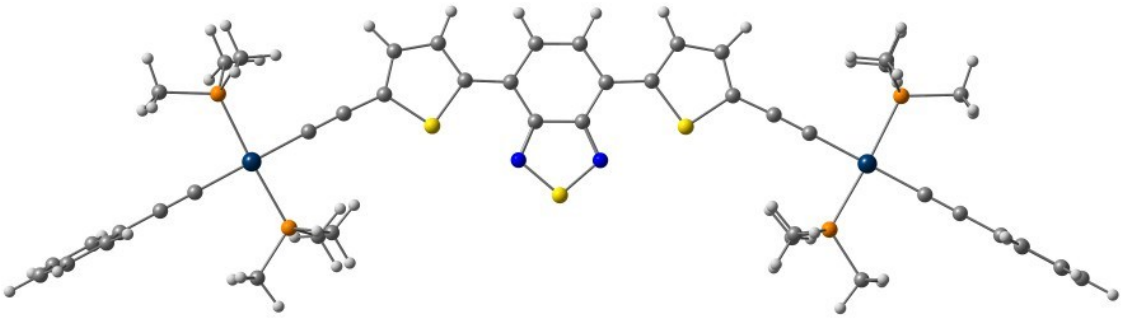


Figure S29. DFT optimized triplet state structure of **TBT'**.

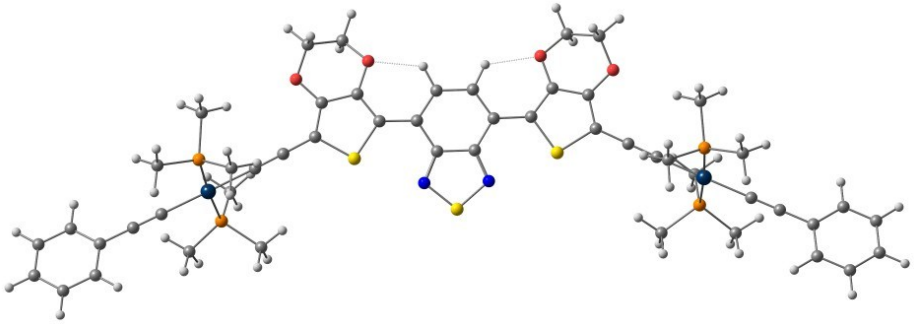


Figure S30. DFT optimized singlet state structure of **EBE'**.

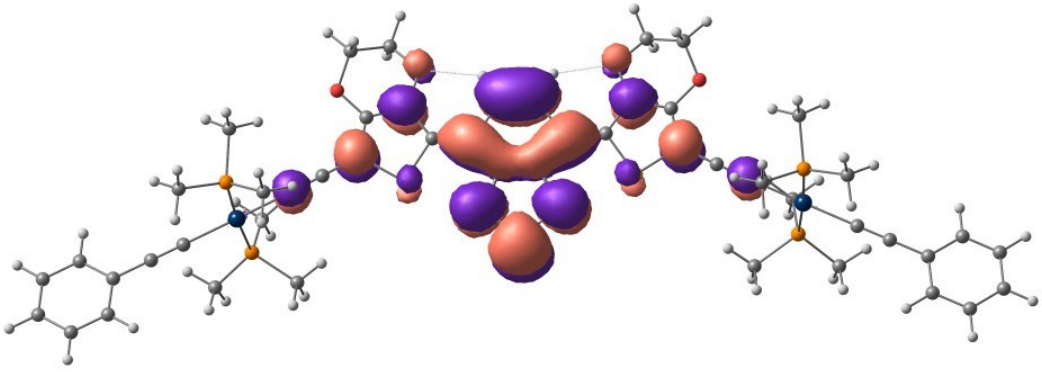


Figure S31. LUMO of **EBE'**.

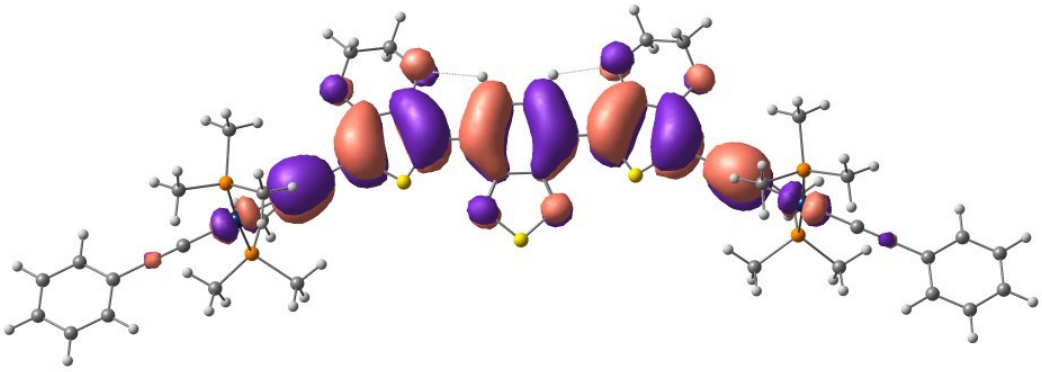


Figure S32. HOMO of **EBE'**.

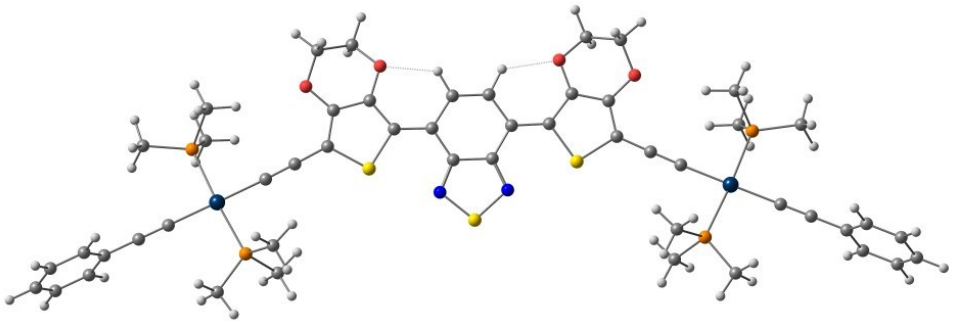


Figure S33. DFT optimized triplet state structure of **EBE'**.

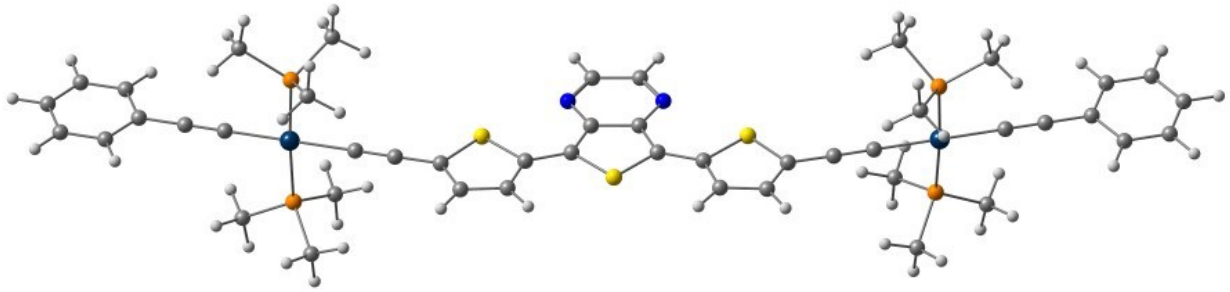


Figure S34. DFT optimized singlet state structure of **TPT'**.

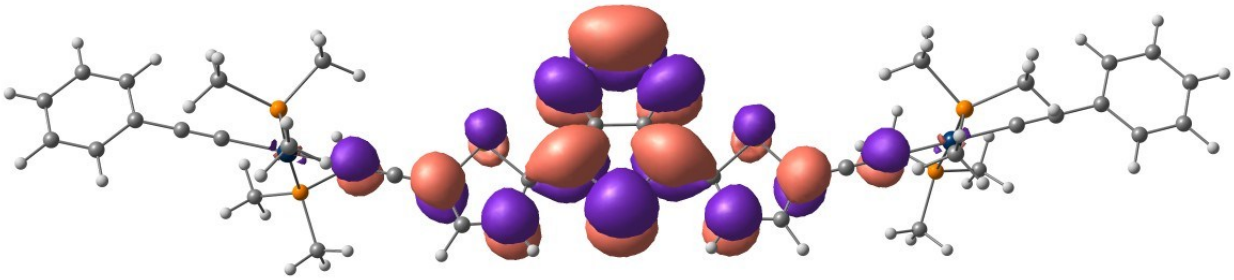


Figure S35. LUMO of **TPT'**.

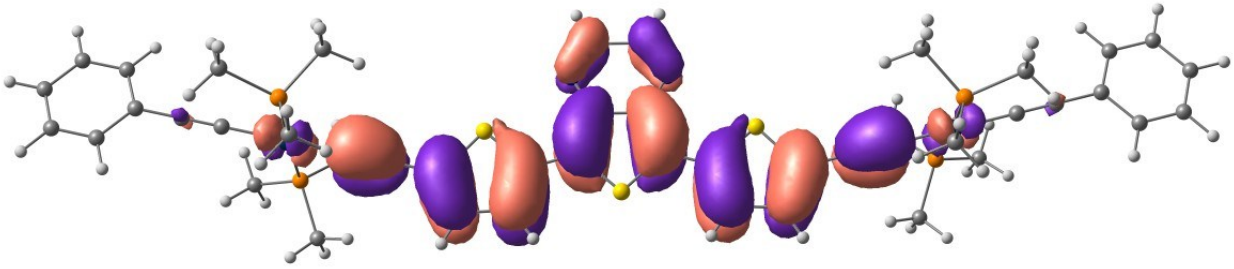


Figure S36. HOMO of **TPT'**.

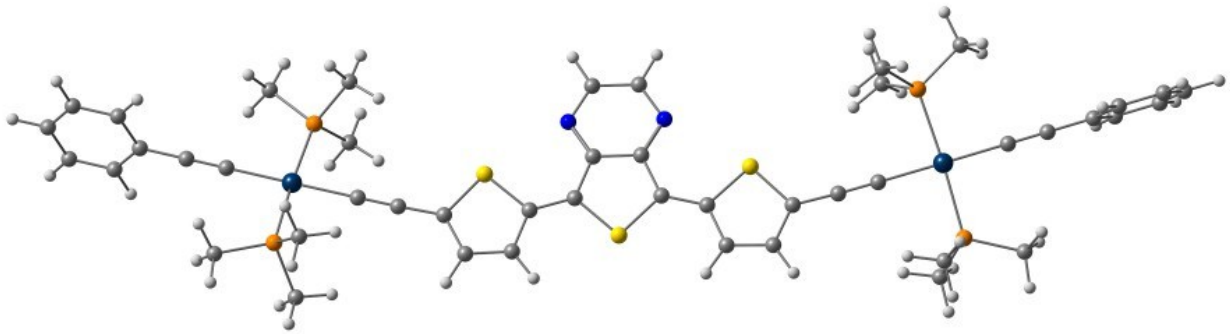


Figure S37. DFT optimized triplet state structure of **TPT'**.

Table S1. Computed energies of the lowest energy singlet and triplet state geometries.

	E_{S0} (hartrees)	E_{T1} (hartrees)	ΔE_{S0-T1} (hartrees)	ΔE_{S0-T1} (eV)
TBTz'	-4388.93193130	-4388.88125333	0.05067797	1.38
TPD'	-4826.90725642	-4826.85257302	0.05468340	1.49
TQT'	-4371.70555980	-4371.66073650	0.04482330	1.22
TBT'	-4692.46417727	-4692.42440783	0.03976944	1.08
TPT'	-4692.45961639	-4692.43370426	0.02591213	0.705
EQE'	-4827.38100037	-4827.33673145	0.04426892	1.20
EBE'	-5148.13771349	-5148.10073296	0.03698053	1.01

Table S2. Computed frontier orbital energies of the molecules.

	E_{LUMO} (eV)	**E_{HOMO} (eV)**	**$\Delta E_{HOMO-LUMO}$ (eV)**
TBTz'	-1.78	-4.47	2.69
TPD'	-2.04	-4.73	2.69
TQT'	-2.06	-4.62	2.56
EQE'	-2.40	-4.61	2.21
TBT'	-2.42	-4.37	1.95
EBE'	-1.98	-4.25	2.27
TPT'	-2.15	-4.28	2.13

V. References for Electronic Supplementary Information

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