# Electronic Supplementary Information

# D-A-D-Type Narrow-Bandgap Small-Molecule Photovoltaic Donors: Pre-Synthesis Virtual Screening by Density Functional Theory

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**S1. Dihedral energy curves between two component units in the compounds 1-4**

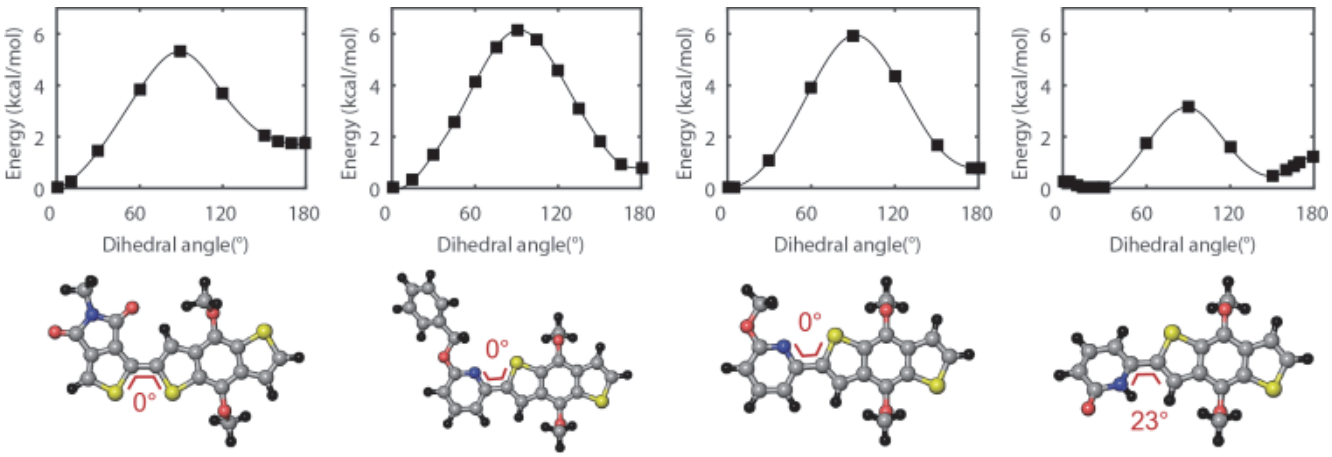



**Figure S1.** Dihedral energy curve for each pair of component units in **1-4** (TPD-BDT and four different SA-BDT combinations), which predicts a planar minimum-energy structure for **1-3** and a slight twist at pyridone termini for **4**.

## S2. Cartesian coordinates of the DFT optimized structures of the compounds 0-7 and $PC_{61}BM$

**Table S1.** Cartesian coordinates (Å) of the DFT optimized structure of the compound **0**, $DTS(PTTh_2)_2$

| **0** | | x (Å) | y (Å) | z (Å) | | x (Å) | y (Å) | z (Å) | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N | 1 | 9.69211 | -0.49721 | 0.06434 | H 25 | 13.86358 | -9.67365 | -0.23882 | C 49 | -8.12482 | -1.23733 | 0.08161 |
| C | 2 | 8.57383 | -1.22499 | 0.04253 | N 26 | -6.31285 | 1.20244 | 0.06113 | C 50 | -9.17726 | -2.17981 | 0.11705 |
| C | 3 | 7.37186 | -0.41149 | 0.02438 | C 27 | -5.37126 | 0.25728 | 0.05615 | C 51 | -8.75305 | -3.48811 | 0.18523 |
| N | 4 | 7.61505 | 0.89728 | 0.03308 | C 28 | -4.02626 | 0.80168 | 0.02230 | S 52 | -7.00399 | -3.55605 | 0.23070 |
| S | 5 | 9.24303 | 1.07978 | 0.06489 | N 29 | -3.99095 | 2.13243 | 0.00270 | C 53 | -9.53230 | -4.70718 | 0.22042 |
| C | 6 | 6.07973 | -1.05478 | 0.00181 | S 30 | -5.54528 | 2.65112 | 0.02442 | C 54 | -9.15215 | -5.98477 | -0.12507 |
| C | 7 | 8.46696 | -2.65783 | 0.03571 | C 31 | -2.89691 | -0.09673 | 0.01400 | C 55 | -10.18488 | -6.94704 | 0.02992 |
| C | 8 | 7.15807 | -3.12381 | 0.01527 | C 32 | -5.56494 | -1.16618 | 0.07965 | C 56 | -11.34919 | -6.40512 | 0.49280 |
| N | 9 | 6.03636 | -2.37989 | -0.00156 | C 33 | -4.38197 | -1.89498 | 0.05909 | S 57 | -11.20090 | -4.70107 | 0.76275 |
| C | 10 | 9.60795 | -3.55269 | 0.05330 | N 34 | -3.13014 | -1.40157 | 0.03049 | H 58 | -4.42906 | -2.97920 | 0.06506 |
| C | 11 | 10.95321 | -3.26136 | 0.14591 | C 35 | 4.82023 | -0.35156 | -0.01249 | H 59 | 5.31415 | 1.74821 | -0.01738 |
| C | 12 | 11.78528 | -4.40323 | 0.16296 | C 36 | 4.52875 | 1.00617 | -0.01947 | H 60 | -1.55822 | 2.48351 | -0.02038 |
| C | 13 | 11.09983 | -5.59472 | 0.08148 | S 37 | 3.34968 | -1.32194 | -0.01747 | H 61 | 1.25157 | 4.53445 | -1.63560 |
| S | 14 | 9.37926 | -5.29636 | -0.04525 | C 38 | 3.14774 | 1.28851 | -0.02761 | H 62 | 3.00930 | 4.34639 | -1.63113 |
| C | 15 | 11.60770 | -6.94990 | 0.08984 | C 39 | 2.38875 | 0.11573 | -0.02553 | H 63 | 1.99749 | 3.17696 | -2.49168 |
| C | 16 | 10.95411 | -8.11461 | 0.42493 | Si 40 | 1.94633 | 2.75293 | -0.03755 | H 64 | 1.24870 | 4.55662 | 1.53355 |
| C | 17 | 11.76898 | -9.27336 | 0.32495 | C 41 | 0.95590 | 0.26916 | -0.02502 | H 65 | 1.98996 | 3.21018 | 2.41084 |
| C | 18 | 13.04027 | -8.99337 | -0.08630 | C 42 | 0.46218 | 1.57605 | -0.03001 | H 66 | 3.00616 | 4.36658 | 1.53782 |
| S | 19 | 13.26309 | -7.30039 | -0.37464 | C 43 | -0.94722 | 1.59225 | -0.02024 | H 67 | -8.27102 | -0.16978 | 0.01787 |
| H | 20 | 6.97828 | -4.19411 | 0.01574 | C 44 | -1.51878 | 0.32701 | -0.00745 | H 68 | -10.22321 | -1.90677 | 0.06768 |
| H | 21 | 11.31671 | -2.24718 | 0.21223 | S 45 | -0.28702 | -0.93252 | -0.00876 | H 69 | -8.16547 | -6.21864 | -0.50258 |
| H | 22 | 12.86194 | -4.35419 | 0.25968 | C 46 | 2.06184 | 3.80026 | -1.59677 | H 70 | -10.06896 | -7.99734 | -0.20166 |
| H | 23 | 9.92456 | -8.13175 | 0.75728 | C 47 | 2.05824 | 3.82103 | 1.50764 | H 71 | -12.28764 | -6.89756 | 0.69428 |
| H | 24 | 11.42599 | -10.27268 | 0.55736 | C 48 | -6.86721 | -1.80317 | 0.11954 | | | | |

**Table S2.** Cartesian coordinates (Å) of the DFT optimized structure of the compound $PC_{61}BM$

| PCBM | | x (Å) | y (Å) | z (Å) | | x (Å) | y (Å) | z (Å) | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| O | 1 | -0.77432 | 3.55150 | -3.98296 | C 31 | -0.98541 | -1.64281 | -2.86662 | C 61 | -3.85046 | -3.47511 | 0.08436 |
| O | 2 | -0.65760 | 5.67213 | -4.72607 | C 32 | 0.43832 | -1.76896 | -2.68369 | C 62 | -3.61535 | -3.81626 | 1.41419 |
| C | 3 | 0.33144 | 1.73307 | 0.61393 | C 33 | 0.73293 | -3.14532 | -2.32907 | C 63 | 1.31709 | 2.56423 | -0.18753 |
| C | 4 | 1.24558 | 1.09662 | -0.55758 | C 34 | 1.72893 | -3.42630 | -1.40056 | C 64 | 2.54562 | 3.06492 | 0.53638 |
| C | 5 | 2.18016 | 0.01796 | -0.11934 | C 35 | 1.51615 | -4.44545 | -0.39137 | C 65 | 2.39937 | 3.89143 | 1.65544 |
| C | 6 | 2.39038 | -0.31679 | 1.20507 | C 36 | 2.13098 | -3.98705 | 0.84159 | C 66 | 3.51303 | 4.42684 | 2.29504 |
| C | 7 | 1.55978 | 0.26670 | 2.27301 | C 37 | 1.51552 | -4.24726 | 2.06246 | C 67 | 4.79317 | 4.14294 | 1.82391 |
| C | 8 | 0.54952 | 1.16210 | 1.97535 | C 38 | 1.46753 | -3.21655 | 3.08411 | C 68 | 4.95013 | 3.32330 | 0.71003 |
| C | 9 | -0.73044 | 1.02150 | 2.62235 | C 39 | 0.18927 | -3.31866 | 3.76502 | C 69 | 3.83361 | 2.78812 | 0.07084 |
| C | 10 | -1.76823 | 1.31370 | 1.65542 | C 40 | -0.47002 | -2.16546 | 4.18095 | C 70 | 0.72962 | 3.58502 | -1.17036 |
| C | 11 | -1.14256 | 1.63955 | 0.39873 | C 41 | -1.90641 | -2.04875 | 4.00227 | C 71 | 1.61677 | 3.85369 | -2.39254 |
| C | 12 | -1.71157 | 1.18450 | -0.77664 | C 42 | -2.62222 | -3.08829 | 3.41341 | C 72 | 1.07686 | 4.96692 | -3.29382 |
| C | 13 | -0.87920 | 0.60247 | -1.84432 | C 43 | -3.66263 | -2.79567 | 2.44344 | C 73 | -0.21017 | 4.61756 | -4.01410 |
| C | 14 | 0.49123 | 0.49729 | -1.69919 | C 44 | -3.94456 | -1.47530 | 2.10161 | C 74 | -1.87441 | 5.45938 | -5.46561 |
| C | 15 | 1.14600 | -0.72695 | -2.08650 | C 45 | -4.18726 | -1.11980 | 0.71480 | H 75 | 1.40633 | 4.10896 | 2.03340 |
| C | 16 | 2.18208 | -1.01985 | -1.11827 | C 46 | -4.13924 | -2.10072 | -0.27163 | H 76 | 3.38125 | 5.06023 | 3.16485 |
| C | 17 | 2.47251 | -2.34233 | -0.78565 | C 47 | -3.49165 | -1.82136 | -1.54081 | H 77 | 5.66192 | 4.55472 | 2.32451 |
| C | 18 | 2.72180 | -2.68649 | 0.59102 | C 48 | -2.81291 | -3.02940 | -1.97414 | H 78 | 5.94240 | 3.09431 | 0.33851 |
| C | 19 | 2.66625 | -1.69044 | 1.56650 | C 49 | -1.58527 | -2.94085 | -2.62402 | H 79 | 3.96702 | 2.14372 | -0.79006 |
| C | 20 | 2.02646 | -1.96608 | 2.83777 | C 50 | -0.52163 | -3.87155 | -2.29161 | H 80 | -0.25053 | 3.25812 | -1.51481 |
| C | 21 | 1.34236 | -0.76216 | 3.26752 | C 51 | -0.72890 | -4.84969 | -1.32218 | H 81 | 0.57854 | 4.51679 | -0.61307 |
| C | 22 | 0.11981 | -0.86372 | 3.93242 | C 52 | 0.31125 | -5.14246 | -0.35211 | H 82 | 1.71426 | 2.93404 | -2.97682 |
| C | 23 | -0.94350 | 0.05061 | 3.60029 | C 53 | -0.32736 | -5.41382 | 0.92122 | H 83 | 2.62023 | 4.13973 | -2.06665 |
| C | 24 | -2.20015 | -0.67468 | 3.64326 | C 54 | 0.26419 | -4.97624 | 2.10380 | H 84 | 0.90607 | 5.88997 | -2.72957 |
| C | 25 | -3.19612 | -0.39449 | 2.71411 | C 55 | -0.55597 | -4.40203 | 3.15664 | H 85 | 1.81134 | 5.22663 | -4.06344 |
| C | 26 | -2.97851 | 0.62323 | 1.70246 | C 56 | -1.93330 | -4.28954 | 2.98262 | H 86 | -1.74169 | 4.66306 | -6.19952 |
| C | 27 | -3.58860 | 0.17929 | 0.47422 | C 57 | -2.54769 | -4.74111 | 1.74772 | H 87 | -2.68844 | 5.18915 | -4.79143 |
| C | 28 | -2.95511 | 0.44558 | -0.73970 | C 58 | -1.76193 | -5.29116 | 0.73913 | H 88 | -2.08295 | 6.40541 | -5.96000 |
| C | 29 | -2.90872 | -0.57784 | -1.76511 | C 59 | -2.00922 | -4.94082 | -0.64737 | | | | |
| C | 30 | -1.62938 | -0.48144 | -2.43975 | C 60 | -3.03004 | -4.04932 | -0.96843 | | | | |

**Table S3.** Cartesian coordinates (Å) of the DFT-optimized structure of the compound **1**.

| **1** | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | -6.33012 | 0.63288 | 0.06662 | C | 41 | 3.76006 | 0.85145 | -0.14680 | H | 81 | -10.66312 | -4.06822 | -0.30080 |
| C | 2 | -7.38367 | -0.27064 | 0.01890 | C | 42 | 2.65945 | 0.04276 | -0.03085 | H | 82 | -16.17611 | 0.72004 | 0.38481 |
| C | 3 | -7.18113 | -1.67402 | -0.11020 | S | 43 | 3.10276 | -1.66776 | 0.16496 | H | 83 | -17.98106 | 2.40461 | 0.55870 |
| C | 4 | -5.87453 | -2.18602 | -0.18925 | O | 44 | 6.55005 | 1.99645 | -0.34054 | H | 84 | -17.42833 | 4.82261 | 0.61603 |
| O | 5 | -5.64483 | -3.53302 | -0.34384 | C | 45 | 1.15616 | 3.10276 | -0.08310 | H | 85 | -15.05290 | 5.54066 | 0.49594 |
| C | 6 | -9.51601 | -1.57282 | -0.06721 | C | 46 | -1.19117 | 3.09821 | -0.10820 | H | 86 | -13.25856 | 3.85823 | 0.31883 |
| C | 7 | -8.42043 | -2.38284 | -0.16631 | N | 47 | -0.01747 | 3.87133 | -0.10782 | H | 87 | -14.70813 | -2.59009 | -0.12848 |
| S | 8 | -9.08916 | 0.13310 | 0.10162 | O | 48 | 2.27287 | 3.57861 | -0.07955 | H | 88 | 8.46545 | -3.41339 | 0.24454 |
| C | 9 | -4.82373 | -1.28248 | -0.14637 | O | 49 | -2.31269 | 3.56211 | -0.12459 | H | 89 | 3.67700 | 1.92083 | -0.28030 |
| C | 10 | -5.02082 | 0.12260 | -0.01476 | C | 50 | 1.27665 | 0.44542 | -0.04680 | H | 90 | -1.04781 | 5.65594 | -0.12520 |
| C | 11 | -3.78694 | 0.83671 | 0.03744 | C | 51 | 0.69515 | 1.69591 | -0.06863 | H | 91 | 0.51104 | 5.71567 | 0.74299 |
| C | 12 | -2.68279 | 0.03259 | -0.07543 | C | 52 | -0.72351 | 1.69376 | -0.08015 | H | 92 | 0.49016 | 5.68856 | -1.03050 |
| S | 13 | -3.11844 | -1.68194 | -0.25310 | C | 53 | -1.30153 | 0.44127 | -0.06933 | H | 93 | 6.68517 | 3.82468 | 0.52678 |
| O | 14 | -6.58205 | 1.96953 | 0.23367 | S | 54 | -0.01069 | -0.76081 | -0.04135 | H | 94 | 5.36129 | 2.82822 | 1.17649 |
| C | 15 | -6.43607 | 2.78156 | -0.94353 | C | 55 | -0.01119 | 5.32399 | -0.13177 | H | 95 | 7.05494 | 2.47300 | 1.63237 |
| C | 16 | -5.55987 | -4.27183 | 0.88476 | C | 56 | 6.39765 | 2.81876 | 0.82866 | H | 96 | 5.37479 | -5.28801 | -0.65351 |
| O | 17 | -13.97865 | -0.14196 | 0.10943 | C | 57 | 5.55838 | -4.25349 | -0.94117 | H | 97 | 4.73518 | -3.89683 | -1.56774 |
| N | 18 | -11.80095 | -0.90486 | 0.01998 | O | 58 | 13.95951 | -0.07285 | -0.08522 | H | 98 | 6.49560 | -4.18891 | -1.50300 |
| C | 19 | -13.63567 | -2.45033 | -0.12107 | N | 59 | 11.78276 | -0.84628 | -0.04017 | H | 99 | 13.10738 | -4.45932 | 0.23378 |
| C | 20 | -12.74329 | -3.50089 | -0.23096 | C | 60 | 13.62369 | -2.38632 | 0.08497 | H | 100 | 10.65760 | -4.02246 | 0.18835 |
| C | 21 | -11.36996 | -3.25429 | -0.21564 | C | 61 | 12.73600 | -3.44356 | 0.15807 | H | 101 | 13.94113 | 3.31095 | -1.87845 |
| C | 22 | -10.93427 | -1.93427 | -0.08892 | C | 62 | 11.36133 | -3.20315 | 0.13444 | H | 102 | 15.78799 | 4.95243 | -1.78947 |
| C | 23 | -13.09767 | -1.15836 | 0.00381 | C | 63 | 10.92065 | -1.88260 | 0.03582 | H | 103 | 17.50087 | 4.79978 | -0.00062 |
| C | 24 | -13.45684 | 1.18628 | 0.24889 | C | 64 | 13.08102 | -1.09326 | -0.01409 | H | 104 | 17.34928 | 2.99648 | 1.69752 |
| C | 25 | -14.59799 | 2.17074 | 0.34257 | C | 65 | 13.42995 | 1.26811 | -0.16316 | H | 105 | 15.49360 | 1.36353 | 1.60975 |
| C | 26 | -15.93330 | 1.77383 | 0.41087 | C | 66 | 14.58499 | 2.23371 | -0.13340 | H | 106 | 14.69702 | -2.51869 | 0.09861 |
| C | 27 | -16.94687 | 2.72720 | 0.50814 | C | 67 | 14.68322 | 3.24586 | -1.08927 | H | 107 | -12.81504 | 1.41587 | -0.60687 |
| C | 28 | -16.63857 | 4.08373 | 0.54048 | C | 68 | 15.72524 | 4.17108 | -1.04036 | H | 108 | -12.82718 | 1.23353 | 1.14324 |
| C | 29 | -15.30514 | 4.48630 | 0.47324 | C | 69 | 16.68694 | 4.08449 | -0.03807 | H | 109 | 12.75263 | 1.42730 | 0.68113 |
| C | 30 | -14.29436 | 3.53626 | 0.37352 | C | 70 | 16.60104 | 3.07045 | 0.91612 | H | 110 | 12.84437 | 1.37809 | -1.07862 |
| C | 31 | 6.30438 | 0.66024 | -0.16167 | C | 71 | 15.55579 | 2.15411 | 0.87065 | | | | | |
| C | 32 | 7.36226 | -0.23739 | -0.10010 | H | 72 | -8.47245 | -3.45482 | -0.29399 | | | | | |
| C | 33 | 7.16608 | -1.64072 | 0.03933 | H | 73 | -3.70886 | 1.90767 | 0.15899 | | | | | |
| C | 34 | 5.86170 | -2.15849 | 0.11738 | H | 74 | -6.72764 | 3.78893 | -0.65036 | | | | | |
| O | 35 | 5.63824 | -3.50545 | 0.28206 | H | 75 | -5.40062 | 2.79276 | -1.29390 | | | | | |
| C | 36 | 9.50058 | -1.52829 | 0.00587 | H | 76 | -7.09357 | 2.42521 | -1.74245 | | | | | |
| C | 37 | 8.40856 | -2.34296 | 0.10632 | H | 77 | -5.37081 | -5.30733 | 0.60428 | | | | | |
| S | 38 | 9.06623 | 0.17438 | -0.17561 | H | 78 | -4.73814 | -3.90620 | 1.50804 | | | | | |
| C | 39 | 4.80661 | -1.26066 | 0.06229 | H | 79 | -6.49696 | -4.20848 | 1.44692 | | | | | |
| C | 40 | 4.99720 | 0.14411 | -0.08190 | H | 80 | -13.11062 | -4.51615 | -0.32913 | | | | | |

**Table S4.** Cartesian coordinates (Å) of the DFT optimized structure of the compound **2**.

| **2** | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 0.01728 | 0.02811 | -0.00963 | C | 31 | -15.00936 | -0.54664 | 0.05138 | H | 61 | -2.36710 | 1.68460 | -0.27931 |
| C | 2 | 0.91386 | -1.01996 | 0.15223 | S | 32 | -15.25253 | 2.05881 | 0.09180 | H | 62 | 0.91715 | 3.13977 | 0.36383 |
| C | 3 | 0.49080 | -2.35046 | 0.43179 | C | 33 | -11.27991 | -0.05677 | 0.03019 | H | 63 | -0.54595 | 2.44229 | 1.09922 |
| C | 4 | -0.88043 | -2.63676 | 0.54761 | C | 34 | -11.24182 | 1.36762 | 0.03728 | H | 64 | 1.07087 | 1.86190 | 1.60061 |
| O | 5 | -1.32128 | -3.90504 | 0.84508 | C | 35 | -9.90692 | 1.87051 | 0.04688 | H | 65 | -1.87703 | -5.70672 | 0.09189 |
| C | 6 | 2.81183 | -2.62680 | 0.40929 | C | 36 | -8.95095 | 0.88869 | 0.02107 | H | 66 | -2.28298 | -4.33058 | -0.96724 |
| C | 7 | 1.60161 | -3.23650 | 0.58206 | S | 37 | -9.66388 | -0.73954 | -0.01477 | H | 67 | -0.59414 | -4.89860 | -0.84989 |
| S | 8 | 2.66161 | -0.90386 | 0.04892 | O | 38 | -12.47567 | 3.46112 | 0.10309 | H | 68 | 7.77697 | -4.44041 | 0.63300 |
| C | 9 | -1.77422 | -1.58845 | 0.39054 | C | 39 | -6.97863 | 3.65627 | -0.24617 | H | 69 | 3.54924 | -5.23088 | 0.93021 |
| C | 10 | -1.35630 | -0.25578 | 0.10843 | C | 40 | -4.66193 | 3.28134 | -0.18923 | H | 70 | 5.89506 | -6.05636 | 1.03106 |
| C | 11 | -2.46063 | 0.63494 | -0.03986 | N | 41 | -5.69742 | 4.22608 | -0.29379 | H | 71 | 8.09456 | -0.09291 | -0.29495 |
| C | 12 | -3.67860 | 0.03381 | 0.14401 | O | 42 | -8.00521 | 4.30034 | -0.31657 | H | 72 | 6.52837 | -0.49323 | -1.06528 |
| S | 13 | -3.52120 | -1.69795 | 0.51497 | O | 43 | -3.48079 | 3.56022 | -0.20982 | H | 73 | 6.58753 | -0.12641 | 0.67154 |
| O | 14 | 0.47735 | 1.28147 | -0.31905 | C | 44 | -7.52147 | 1.06500 | 0.01291 | H | 74 | -15.23832 | -1.60233 | 0.01620 |
| C | 15 | 0.47180 | 2.22919 | 0.76168 | C | 45 | -6.74788 | 2.20160 | -0.09568 | H | 75 | -9.65280 | 2.92058 | 0.07666 |
| C | 16 | -1.52720 | -4.75110 | -0.29686 | C | 46 | -5.34764 | 1.97528 | -0.06415 | H | 76 | -4.39549 | 5.81670 | -0.43994 |
| C | 17 | 6.73964 | -4.13589 | 0.60147 | C | 47 | -4.97688 | 0.65354 | 0.07271 | H | 77 | -5.90576 | 6.01714 | -1.36963 |
| C | 18 | 6.41350 | -2.79565 | 0.32997 | S | 48 | -6.44323 | -0.32345 | 0.16088 | H | 78 | -5.92747 | 6.19588 | 0.39502 |
| N | 19 | 5.17302 | -2.34320 | 0.27419 | C | 49 | -5.47179 | 5.65422 | -0.43601 | H | 79 | -12.31957 | 5.19570 | -0.93600 |
| C | 20 | 4.15504 | -3.20389 | 0.48695 | C | 50 | -12.19788 | 4.13247 | -1.13723 | H | 80 | -11.17466 | 3.94310 | -1.47225 |
| C | 21 | 4.37587 | -4.55410 | 0.76276 | C | 51 | -12.50123 | -2.78083 | 1.30493 | H | 81 | -12.90503 | 3.82056 | -1.91198 |
| C | 22 | 5.69309 | -5.01266 | 0.81814 | C | 52 | -20.16379 | 0.25369 | 0.04071 | H | 82 | -12.48688 | -3.85407 | 1.11875 |
| O | 23 | 7.44275 | -1.95186 | 0.12016 | C | 53 | -19.41875 | 1.44570 | 0.05919 | H | 83 | -11.63024 | -2.50257 | 1.90610 |
| C | 24 | 7.13106 | -0.58071 | -0.15922 | N | 54 | -18.09765 | 1.48068 | 0.06667 | H | 84 | -13.41483 | -2.51370 | 1.84547 |
| C | 25 | -12.44871 | 2.09179 | 0.05471 | C | 55 | -17.41465 | 0.31631 | 0.05668 | H | 85 | -21.24452 | 0.29588 | 0.03504 |
| C | 26 | -13.63732 | 1.37377 | 0.06878 | C | 56 | -18.06326 | -0.91937 | 0.03935 | H | 86 | -17.50143 | -1.84333 | 0.03227 |
| C | 27 | -13.66977 | -0.04970 | 0.06395 | C | 57 | -19.45900 | -0.93547 | 0.03095 | H | 87 | -19.98997 | -1.88061 | 0.01679 |
| C | 28 | -12.46582 | -0.77490 | 0.04923 | O | 58 | -20.11788 | 2.59744 | 0.06917 | H | 88 | -20.12913 | 4.61039 | 0.09685 |
| O | 29 | -12.46199 | -2.14979 | 0.01557 | C | 59 | -19.37640 | 3.82424 | 0.08886 | H | 89 | -18.74901 | 3.88799 | 0.98002 |
| C | 30 | -15.95577 | 0.43842 | 0.06489 | H | 60 | 1.48293 | -4.28253 | 0.82679 | H | 90 | -18.74284 | 3.91219 | -0.79591 |

**Table S5.** Cartesian coordinates (Å) of the DFT optimized structure of the compound **3**.

| **3** | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | -0.00337 | -0.01523 | 0.01095 | C | 31 | -10.64976 | 8.68835 | -6.08170 | H | 61 | -2.13606 | -1.69218 | 0.15937 |
| C | 2 | 1.35020 | -0.05844 | -0.29645 | S | 32 | -12.58781 | 7.37111 | -4.91589 | H | 62 | -0.59748 | -2.60428 | 0.09954 |
| C | 3 | 1.91989 | 0.71495 | -1.34738 | C | 33 | -8.23613 | 6.34383 | -4.40023 | H | 63 | 2.48203 | 4.05768 | -3.69384 |
| C | 4 | 1.10131 | 1.56494 | -2.11118 | C | 34 | -9.16949 | 5.53870 | -3.68528 | H | 64 | 1.33052 | 4.21554 | -2.34129 |
| O | 5 | 1.61513 | 2.30386 | -3.15080 | C | 35 | -8.52836 | 4.51020 | -2.93311 | H | 65 | 2.94361 | 3.50273 | -2.06138 |
| C | 6 | 3.80683 | -0.42613 | -0.57226 | C | 36 | -7.16172 | 4.52803 | -3.03393 | H | 66 | 8.65894 | -2.38192 | 0.25028 |
| C | 7 | 3.32131 | 0.47063 | -1.48133 | S | 37 | -6.58461 | 5.84007 | -4.08556 | H | 67 | 8.33255 | -0.73094 | -1.61501 |
| S | 8 | 2.55789 | -1.03564 | 0.51830 | O | 38 | -11.49298 | 5.04261 | -3.17062 | H | 68 | 6.06648 | 0.20543 | -2.02511 |
| C | 9 | -0.25085 | 1.60362 | -1.80640 | C | 39 | -7.56494 | 2.08904 | -0.68768 | H | 69 | -10.10410 | 9.41647 | -6.66504 |
| C | 10 | -0.82536 | 0.83275 | -0.75468 | C | 40 | -5.61611 | 0.95832 | -0.02913 | H | 70 | -9.05222 | 3.77548 | -2.33832 |
| C | 11 | -2.22563 | 1.06742 | -0.61778 | N | 41 | -7.00654 | 1.09213 | 0.12623 | H | 71 | -7.11506 | -0.40472 | 1.53852 |
| C | 12 | -2.72484 | 1.95622 | -1.53379 | O | 42 | -8.74824 | 2.35915 | -0.70588 | H | 72 | -8.29633 | 0.91257 | 1.77308 |
| S | 13 | -1.46593 | 2.56294 | -2.63295 | O | 43 | -4.93641 | 0.15860 | 0.58043 | H | 73 | -8.55263 | -0.28182 | 0.48692 |
| O | 14 | -0.49090 | -0.74935 | 1.06012 | C | 44 | -6.23054 | 3.63602 | -2.39192 | H | 74 | -12.47862 | 4.65163 | -1.44186 |
| C | 15 | -4.09049 | 2.39458 | -1.66756 | C | 45 | -6.42337 | 2.65418 | -1.44278 | H | 75 | -10.75481 | 5.02582 | -1.20540 |
| C | 16 | -1.21954 | -1.93618 | 0.70301 | C | 46 | -5.24559 | 1.97207 | -1.04276 | H | 76 | -11.91153 | 6.33823 | -1.58291 |
| C | 17 | 2.11998 | 3.59521 | -2.77641 | S | 47 | -4.51219 | 3.69110 | -2.78707 | H | 77 | -6.63496 | 8.41967 | -7.59085 |
| C | 18 | 7.69403 | -1.94562 | 0.03098 | C | 48 | -7.79588 | 0.28067 | 1.03700 | H | 78 | -6.96777 | 6.71078 | -7.20460 |
| C | 19 | 7.49750 | -1.03397 | -0.99357 | C | 49 | -11.65689 | 5.28944 | -1.76374 | H | 79 | -8.26901 | 7.74966 | -7.84960 |
| C | 20 | 6.22894 | -0.50600 | -1.22722 | C | 50 | -7.38137 | 7.72386 | -7.20959 | H | 80 | -15.79849 | 11.73952 | -8.03289 |
| C | 21 | 5.17479 | -0.91957 | -0.40731 | C | 51 | -14.97899 | 11.15101 | -7.64354 | H | 81 | -13.40323 | 12.25033 | -8.59271 |
| N | 22 | 5.36163 | -1.80621 | 0.59038 | C | 52 | -13.65313 | 11.41940 | -7.94277 | H | 82 | -11.60286 | 10.82670 | -7.63771 |
| C | 23 | 6.57380 | -2.29489 | 0.79596 | C | 53 | -12.64024 | 10.62393 | -7.40997 | H | 83 | -16.48322 | 8.99957 | -5.90269 |
| O | 24 | 6.72736 | -3.17991 | 1.80343 | C | 54 | -12.99840 | 9.56142 | -6.57490 | H | 84 | 5.85524 | -3.28810 | 2.20781 |
| C | 25 | -10.54634 | 5.80697 | -3.80055 | N | 55 | -14.28690 | 9.29691 | -6.28127 | | | | | |
| C | 26 | -10.93672 | 6.85705 | -4.62120 | C | 56 | -15.23327 | 10.06365 | -6.79791 | | | | | |
| C | 27 | -10.00040 | 7.65774 | -5.33483 | O | 57 | -16.51333 | 9.77152 | -6.48493 | | | | | |
| C | 28 | -8.62503 | 7.38943 | -5.22374 | H | 58 | 3.92431 | 0.94312 | -2.24379 | | | | | |
| O | 29 | -7.69353 | 8.16113 | -5.87770 | H | 59 | -2.84918 | 0.60251 | 0.13243 | | | | | |
| C | 30 | -12.01076 | 8.67022 | -5.96471 | H | 60 | -1.47686 | -2.42332 | 1.64224 | | | | | |

**Table S6.** Cartesian coordinates (Å) of the DFT optimized structure of the compound **4**.

| **4** | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 0.00620 | 0.00642 | 0.00137 | C | 31 | -10.66509 | 8.72163 | -6.03248 | H | 61 | -2.25041 | -1.39131 | 0.64445 |
| C | 2 | 1.31188 | -0.16994 | -0.43545 | S | 32 | -12.54547 | 7.67705 | -4.54608 | H | 62 | -0.83780 | -2.47275 | 0.45354 |
| C | 3 | 1.81598 | 0.42958 | -1.62254 | C | 33 | -8.23710 | 6.41618 | -4.31678 | H | 63 | 2.31902 | 3.39532 | -4.44182 |
| C | 4 | 0.97240 | 1.23465 | -2.40628 | C | 34 | -9.13833 | 5.76067 | -3.42869 | H | 64 | 1.32896 | 3.81399 | -3.01840 |
| O | 5 | 1.41300 | 1.79607 | -3.57916 | C | 35 | -8.48462 | 4.77596 | -2.62981 | H | 65 | 2.91834 | 3.02945 | -2.80136 |
| C | 6 | 3.70204 | -0.75486 | -0.90512 | C | 36 | -7.13682 | 4.68992 | -2.86127 | H | 66 | 8.71348 | -2.60062 | -0.98692 |
| C | 7 | 3.17747 | 0.06454 | -1.86485 | S | 37 | -6.59483 | 5.83838 | -4.10344 | H | 67 | 6.97459 | -3.86507 | 0.24419 |
| S | 8 | 2.54200 | -1.12162 | 0.37695 | O | 38 | -11.43246 | 5.49966 | -2.64807 | H | 68 | 4.61431 | -3.05553 | 0.29170 |
| C | 9 | -0.33485 | 1.40815 | -1.97450 | C | 39 | -7.43929 | 2.57054 | -0.20992 | H | 69 | 5.82874 | 0.25819 | -1.94914 |
| C | 10 | -0.83918 | 0.81743 | -0.77986 | C | 40 | -5.50600 | 1.38192 | 0.38705 | H | 70 | -10.13139 | 9.36545 | -6.71871 |
| C | 11 | -2.19778 | 1.17681 | -0.53449 | N | 41 | -6.86078 | 1.63508 | 0.66033 | H | 71 | -8.98513 | 4.14504 | -1.90940 |
| C | 12 | -2.73502 | 1.98159 | -1.50470 | O | 42 | -8.59877 | 2.92359 | -0.14647 | H | 72 | -6.91227 | 0.32152 | 2.24815 |
| S | 13 | -1.56860 | 2.34769 | -2.79382 | O | 43 | -4.81524 | 0.61026 | 1.01955 | H | 73 | -7.97699 | 1.74152 | 2.43544 |
| O | 14 | -0.39558 | -0.56158 | 1.17985 | C | 44 | -6.19866 | 3.80979 | -2.21180 | H | 74 | -8.44241 | 0.43018 | 1.33492 |
| C | 15 | -4.07702 | 2.50415 | -1.55664 | C | 45 | -6.35099 | 2.95997 | -1.13656 | H | 75 | -12.24997 | 5.33958 | -0.79937 |
| C | 16 | -1.28681 | -1.68582 | 1.06700 | C | 46 | -5.18259 | 2.24281 | -0.77434 | H | 76 | -10.47994 | 5.51706 | -0.77495 |
| C | 17 | 2.03012 | 3.08667 | -3.43828 | S | 47 | -4.53285 | 3.69172 | -2.77787 | H | 77 | -11.51538 | 6.93325 | -1.12707 |
| C | 18 | 7.68766 | -2.26022 | -0.94312 | C | 48 | -7.59823 | 0.99386 | 1.73624 | H | 78 | -6.83760 | 8.02410 | -7.85769 |
| C | 19 | 6.72120 | -2.94172 | -0.26599 | C | 49 | -11.40343 | 5.85215 | -1.25308 | H | 79 | -7.21896 | 6.39042 | -7.25163 |
| C | 20 | 5.37753 | -2.48294 | -0.21500 | C | 50 | -7.57841 | 7.42029 | -7.33572 | H | 80 | -8.52037 | 7.43148 | -7.89292 |
| C | 21 | 5.04892 | -1.31567 | -0.85743 | C | 51 | -14.63133 | 11.52941 | -7.75929 | H | 81 | -15.26096 | 12.22124 | -8.30247 |
| N | 22 | 6.03642 | -0.63576 | -1.52432 | C | 52 | -14.95767 | 11.06427 | -6.52069 | H | 82 | -15.87469 | 11.39906 | -6.04733 |
| C | 23 | 7.39106 | -1.01986 | -1.63480 | C | 53 | -14.12247 | 10.15444 | -5.81841 | H | 83 | -14.37470 | 9.82640 | -4.82046 |
| O | 24 | 8.17257 | -0.31721 | -2.25485 | C | 54 | -12.96097 | 9.72583 | -6.41037 | H | 84 | -11.83578 | 9.84162 | -8.14171 |
| C | 25 | -10.50172 | 6.11250 | -3.44227 | N | 55 | -12.65343 | 10.19459 | -7.66251 | | | | | |
| C | 26 | -10.90481 | 7.08919 | -4.34250 | C | 56 | -13.41654 | 11.10337 | -8.42837 | | | | | |
| C | 27 | -10.00523 | 7.73427 | -5.23541 | O | 57 | -13.03122 | 11.43558 | -9.53748 | | | | | |
| C | 28 | -8.64357 | 7.38836 | -5.21957 | H | 58 | 3.70927 | 0.36554 | -2.75750 | | | | | |
| O | 29 | -7.73970 | 8.01858 | -6.03867 | H | 59 | -2.76540 | 0.86027 | 0.32860 | | | | | |
| C | 30 | -12.00537 | 8.81787 | -5.78324 | H | 60 | -1.43520 | -2.05064 | 2.08194 | | | | | |

**Table S7.** Cartesian coordinates (Å) of the DFT optimized structure of the compound **5**.

| **5** | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 0.02066 | 0.03062 | 0.14452 | C | 31 | 2.58878 | 12.25885 | -1.11490 | N | 61 | -2.90640 | -5.47061 | 0.69582 |
| C | 2 | -0.64252 | -1.16788 | 0.36982 | C | 32 | -3.63154 | 13.32629 | 2.61659 | C | 62 | -1.63286 | -4.96022 | 0.69226 |
| C | 3 | -1.95763 | -1.22698 | 0.90723 | S | 33 | 2.48576 | 6.23417 | -0.30217 | C | 63 | -0.57772 | -5.83637 | 0.74598 |
| C | 4 | -2.62877 | -0.03652 | 1.23491 | N | 34 | 1.39941 | 5.04998 | 0.00825 | C | 64 | -0.84306 | -7.23066 | 0.80471 |
| O | 5 | -3.88423 | -0.06421 | 1.79127 | N | 35 | 1.54469 | 7.53998 | -0.00523 | C | 65 | -2.11489 | -7.72014 | 0.81969 |
| C | 6 | -1.49515 | -3.50783 | 0.65691 | C | 36 | 0.25436 | 5.63757 | 0.35572 | O | 66 | -4.44043 | -7.15636 | 0.74916 |
| C | 7 | -2.40557 | -2.57581 | 1.06877 | C | 37 | 0.34025 | 7.09328 | 0.35103 | C | 67 | -1.43010 | 19.88346 | 1.53020 |
| S | 8 | -0.01621 | -2.77108 | 0.02703 | C | 38 | -0.79419 | 7.91066 | 0.70367 | N | 68 | -1.24856 | 18.48628 | 1.43385 |
| C | 9 | -1.96498 | 1.16187 | 1.01244 | C | 39 | -1.93840 | 7.20633 | 1.03560 | C | 69 | -0.24669 | 17.83944 | 0.75540 |
| C | 10 | -0.65197 | 1.22237 | 0.46700 | C | 40 | -2.02281 | 5.79772 | 1.03583 | C | 70 | 0.69474 | 18.59584 | 0.10318 |
| C | 11 | -0.19754 | 2.56746 | 0.30706 | C | 41 | -0.96931 | 4.96160 | 0.70944 | C | 71 | 0.59544 | 20.01200 | 0.15365 |
| C | 12 | -1.09447 | 3.51239 | 0.72681 | H | 42 | -3.35347 | -2.82055 | 1.52907 | C | 72 | -0.41355 | 20.63826 | 0.82229 |
| S | 13 | -2.58375 | 2.76523 | 1.35829 | H | 43 | 0.75873 | 2.82809 | -0.11675 | O | 73 | -2.36480 | 20.33098 | 2.17475 |
| O | 14 | 1.27455 | 0.03277 | -0.41215 | H | 44 | 3.27014 | 0.17386 | -0.07226 | H | 74 | -3.69548 | -4.84646 | 0.59309 |
| C | 15 | 2.35558 | 0.21113 | 0.51781 | H | 45 | 2.28569 | 1.17802 | 1.02430 | H | 75 | 0.43548 | -5.46265 | 0.77523 |
| C | 16 | -4.96453 | -0.04423 | 0.84399 | H | 46 | 2.36580 | -0.59110 | 1.26213 | H | 76 | -0.00439 | -7.91770 | 0.84659 |
| C | 17 | 0.87717 | 12.68205 | 0.47099 | H | 47 | -5.88225 | -0.06684 | 1.42994 | H | 77 | -2.32717 | -8.77993 | 0.86308 |
| C | 18 | 0.33524 | 13.95282 | 0.60681 | H | 48 | -4.93905 | 0.86584 | 0.23729 | H | 78 | -1.91488 | 17.94941 | 1.97287 |
| C | 19 | -1.04328 | 14.17345 | 0.87660 | H | 49 | -4.92648 | -0.91907 | 0.18711 | H | 79 | 1.47775 | 18.11439 | -0.46445 |
| C | 20 | -1.90996 | 13.07520 | 1.00978 | H | 50 | -2.36672 | 15.93010 | 1.06961 | H | 80 | 1.34316 | 20.60390 | -0.36378 |
| O | 21 | -3.25286 | 13.25871 | 1.23209 | H | 51 | 1.32553 | 9.81344 | 0.37681 | H | 81 | -0.49715 | 21.71579 | 0.86750 |
| C | 22 | -0.27242 | 16.38033 | 0.75726 | H | 52 | 3.67463 | 12.17619 | -1.12430 | | | | | |
| C | 23 | -1.35530 | 15.56785 | 0.94277 | H | 53 | 2.14718 | 11.32261 | -1.46808 | | | | | |
| S | 24 | 1.21830 | 15.46550 | 0.49726 | H | 54 | 2.27724 | 13.07911 | -1.76898 | | | | | |
| C | 25 | -1.36907 | 11.80458 | 0.87126 | H | 55 | -4.71118 | 13.46867 | 2.62918 | | | | | |
| C | 26 | 0.01197 | 11.58252 | 0.60938 | H | 56 | -3.37766 | 12.39949 | 3.13962 | | | | | |
| C | 27 | 0.32890 | 10.19117 | 0.53821 | H | 57 | -3.14396 | 14.16964 | 3.11589 | | | | | |
| C | 28 | -0.74852 | 9.36464 | 0.71013 | H | 58 | -2.83062 | 7.75287 | 1.31691 | | | | | |
| S | 29 | -2.24757 | 10.29100 | 0.97416 | H | 59 | -2.97682 | 5.36190 | 1.30752 | | | | | |
| O | 30 | 2.22175 | 12.52409 | 0.24898 | C | 60 | -3.26301 | -6.83552 | 0.76070 | | | | | |

**Table S8.** Cartesian coordinates (Å) of the DFT optimized structure of the compound **6**.

| **6** | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) | | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | 0.02900 | 0.00256 | 0.09338 | C | 31 | 2.54041 | 12.06543 | -1.21906 | N | 61 | -2.65826 | -5.62800 | 0.53993 |
| C | 2 | -0.58146 | -1.22578 | 0.29690 | C | 32 | -3.59001 | 13.41171 | 2.57228 | C | 62 | -1.40886 | -5.06173 | 0.56574 |
| C | 3 | -1.90297 | -1.34883 | 0.81066 | S | 33 | 2.31396 | 6.17355 | -0.31341 | C | 63 | -0.31678 | -5.89038 | 0.63234 |
| C | 4 | -2.63360 | -0.19530 | 1.13699 | N | 34 | 1.22268 | 4.99252 | -0.00868 | C | 64 | -0.52056 | -7.29566 | 0.67401 |
| O | 5 | -3.89460 | -0.28937 | 1.67188 | N | 35 | 1.37000 | 7.47666 | -0.01445 | C | 65 | -1.76926 | -7.84122 | 0.65950 |
| C | 6 | -1.33511 | -3.60430 | 0.54689 | C | 36 | 0.07873 | 5.57610 | 0.33656 | O | 66 | -4.11580 | -7.38120 | 0.54749 |
| C | 7 | -2.29313 | -2.71815 | 0.95066 | C | 37 | 0.16623 | 7.03392 | 0.33672 | C | 67 | -1.11028 | 19.87668 | 1.36631 |
| S | 8 | 0.12147 | -2.79689 | -0.04937 | C | 38 | -0.95930 | 7.87345 | 0.68668 | N | 68 | -0.99064 | 18.47161 | 1.28843 |
| C | 9 | -2.02240 | 1.03677 | 0.93643 | C | 39 | -2.08630 | 7.14797 | 1.00727 | C | 69 | -0.02715 | 17.77260 | 0.60624 |
| C | 10 | -0.70575 | 1.15935 | 0.41381 | C | 40 | -2.17279 | 5.73225 | 1.00202 | C | 70 | 0.93657 | 18.47794 | -0.07013 |
| C | 11 | -0.31021 | 2.52159 | 0.27391 | C | 41 | -1.14041 | 4.87724 | 0.68209 | C | 71 | 0.89879 | 19.89771 | -0.04015 |
| C | 12 | -1.25682 | 3.42542 | 0.68582 | F | 42 | -3.22395 | 7.77125 | 1.35339 | C | 72 | -0.07255 | 20.57644 | 0.63285 |
| S | 13 | -2.72674 | 2.60178 | 1.27554 | F | 43 | -3.37615 | 5.24942 | 1.35029 | O | 73 | -2.01505 | 20.37369 | 2.01705 |
| O | 14 | 1.29131 | 0.07190 | -0.43993 | H | 44 | -3.23796 | -3.00871 | 1.39006 | H | 74 | -3.47236 | -5.03859 | 0.42741 |
| C | 15 | 2.34708 | 0.26613 | 0.51547 | H | 45 | 0.64283 | 2.82287 | -0.12717 | H | 75 | 0.67789 | -5.47207 | 0.68468 |
| C | 16 | -4.96312 | -0.27389 | 0.71062 | H | 46 | 3.27337 | 0.27981 | -0.05712 | H | 76 | 0.34700 | -7.94505 | 0.72663 |
| C | 17 | 0.86960 | 12.56827 | 0.38613 | H | 47 | 2.22995 | 1.21578 | 1.04561 | H | 77 | -1.93480 | -8.90977 | 0.68952 |
| C | 18 | 0.38596 | 13.86225 | 0.50714 | H | 48 | 2.37485 | -0.55470 | 1.23870 | H | 78 | -1.67177 | 17.97189 | 1.84446 |
| C | 19 | -0.97952 | 14.14647 | 0.79033 | H | 49 | -5.88627 | -0.35269 | 1.28282 | H | 79 | 1.68994 | 17.95478 | -0.64097 |
| C | 20 | -1.89167 | 13.09148 | 0.95124 | H | 50 | -4.96539 | 0.65863 | 0.13875 | H | 80 | 1.66355 | 20.44919 | -0.57694 |
| O | 21 | -3.22146 | 13.34094 | 1.18478 | H | 51 | -4.88291 | -1.12189 | 0.02302 | H | 81 | -0.10920 | 21.65712 | 0.66281 |
| C | 22 | -0.11570 | 16.31606 | 0.62948 | H | 52 | -2.22297 | 15.96102 | 0.97571 | | | | | |
| C | 23 | -1.22980 | 15.55421 | 0.84030 | H | 53 | 1.19032 | 9.69191 | 0.32947 | | | | | |
| S | 24 | 1.33180 | 15.33446 | 0.36440 | H | 54 | 3.62095 | 11.93136 | -1.24169 | | | | | |
| C | 25 | -1.40944 | 11.79382 | 0.82748 | H | 55 | 2.05045 | 11.15218 | -1.56913 | | | | | |
| C | 26 | -0.04315 | 11.51031 | 0.55434 | H | 56 | 2.26071 | 12.90135 | -1.86757 | | | | | |
| C | 27 | 0.21234 | 10.10902 | 0.50113 | H | 57 | -4.66058 | 13.61009 | 2.59141 | | | | | |
| C | 28 | -0.89865 | 9.32861 | 0.69949 | H | 58 | -3.38360 | 12.46696 | 3.08363 | | | | | |
| S | 29 | -2.35190 | 10.32760 | 0.97678 | H | 59 | -3.05640 | 14.22291 | 3.07778 | | | | | |
| O | 30 | 2.20231 | 12.34328 | 0.14976 | C | 60 | -2.95457 | -7.00812 | 0.58542 | | | | | |

**Table S9.** Cartesian coordinates (Å) of the DFT optimized structure of the compound **7**.

| **7** | | x (Å) | y (Å) | z (Å) | | x (Å) | y (Å) | z (Å) | | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 1 | -0.29734 | 0.06331 | -0.10140 | C 31 | -1.34389 | -7.97441 | 0.04401 | C 61 | -2.77345 | -13.92292 | 1.71789 |
| N | 2 | -0.56915 | -1.31164 | 0.07179 | C 32 | -1.74919 | -8.14793 | 1.39499 | C 62 | -2.51944 | -12.52555 | 1.70540 |
| C | 3 | -0.52653 | -2.00829 | 1.25299 | C 33 | -2.09630 | -9.50015 | 1.67524 | C 63 | -2.19914 | -11.78981 | 0.58461 |
| C | 4 | -0.20095 | -1.32951 | 2.40069 | C 34 | -1.94983 | -10.35356 | 0.60628 | F 64 | -3.08285 | -14.40800 | 2.93190 |
| C | 5 | 0.08058 | 0.06057 | 2.32176 | S 35 | -1.37322 | -9.48578 | -0.84112 | F 65 | -2.62221 | -11.94390 | 2.91204 |
| C | 6 | 0.04561 | 0.73477 | 1.13787 | O 36 | -2.19263 | -7.16414 | 3.56986 | H 66 | -0.27712 | -3.95829 | -0.83863 |
| O | 7 | -0.37868 | 0.56294 | -1.21187 | C 37 | -1.17998 | -7.60348 | 4.49006 | H 67 | -2.45683 | -9.81132 | 2.64051 |
| C | 8 | -4.43853 | -26.64223 | 0.25876 | C 38 | -1.61412 | -6.32755 | -2.71561 | H 68 | -1.65537 | -7.63687 | 5.46928 |
| N | 9 | -4.22139 | -25.25450 | 0.40505 | C 39 | -3.73167 | -19.35471 | 2.42526 | H 69 | -0.81321 | -8.60002 | 4.22659 |
| C | 10 | -4.64435 | -24.46889 | 1.44730 | C 40 | -3.92169 | -20.63059 | 1.91720 | H 70 | -0.34120 | -6.90104 | 4.51290 |
| C | 11 | -5.34133 | -25.06081 | 2.47094 | C 41 | -3.84829 | -20.91852 | 0.52505 | H 71 | -1.13089 | -6.24112 | -3.68780 |
| C | 12 | -5.59911 | -26.45644 | 2.41122 | C 42 | -3.58024 | -19.88546 | -0.38691 | H 72 | -2.33928 | -7.14631 | -2.73868 |
| C | 13 | -5.18217 | -27.21998 | 1.36216 | O 43 | -3.54367 | -20.13471 | -1.73728 | H 73 | -2.13016 | -5.39190 | -2.47741 |
| O | 14 | -3.99986 | -27.22543 | -0.71942 | C 44 | -4.34177 | -23.04315 | 1.37507 | H 74 | -4.15930 | -22.69064 | -0.75321 |
| H | 15 | -0.86852 | -1.77888 | -0.77369 | C 45 | -4.10467 | -22.29956 | 0.25393 | H 75 | -3.18095 | -16.55670 | 2.78663 |
| H | 16 | -0.13002 | -1.85776 | 3.34038 | S 46 | -4.25034 | -22.07840 | 2.85515 | H 76 | -4.90478 | -18.51537 | 5.34866 |
| H | 17 | 0.33734 | 0.59109 | 3.23269 | C 47 | -3.39293 | -18.60429 | 0.11885 | H 77 | -5.27411 | -17.66327 | 3.82594 |
| H | 18 | 0.25705 | 1.79330 | 1.06777 | C 48 | -3.45688 | -18.32102 | 1.50996 | H 78 | -5.83646 | -19.34112 | 4.07068 |
| H | 19 | -3.65224 | -24.85037 | -0.32674 | C 49 | -3.20462 | -16.94662 | 1.78366 | H 79 | -2.37790 | -20.62455 | -3.32553 |
| H | 20 | -5.71307 | -24.46221 | 3.28983 | C 50 | -2.97659 | -16.18078 | 0.66386 | H 80 | -1.54138 | -19.63226 | -2.10242 |
| H | 21 | -6.15063 | -26.91801 | 3.22358 | S 51 | -3.05149 | -17.16593 | -0.82088 | H 81 | -1.84829 | -21.36378 | -1.79002 |
| H | 22 | -5.37237 | -28.28347 | 1.30826 | O 52 | -3.77372 | -19.12696 | 3.77813 | | | | |
| C | 23 | -1.78013 | -7.04273 | 2.26641 | C 53 | -5.02858 | -18.63124 | 4.27292 | | | | |
| C | 24 | -1.41525 | -5.80775 | 1.75281 | C 54 | -2.24372 | -20.45647 | -2.25788 | | | | |
| C | 25 | -1.01846 | -5.62979 | 0.39735 | Se 55 | -1.84324 | -13.41235 | -3.00275 | | | | |
| C | 26 | -0.98227 | -6.73401 | -0.46874 | N 56 | -1.82242 | -12.07812 | -1.79561 | | | | |
| O | 27 | -0.56516 | -6.59091 | -1.76970 | N 57 | -2.27949 | -14.64927 | -1.77089 | | | | |
| C | 28 | -0.80691 | -3.43922 | 1.19532 | C 58 | -2.12273 | -12.59218 | -0.61998 | | | | |
| C | 29 | -0.66823 | -4.27069 | 0.12038 | C 59 | -2.37822 | -14.04177 | -0.60566 | | | | |
| S | 30 | -1.39737 | -4.28726 | 2.63127 | C 60 | -2.71505 | -14.74738 | 0.61474 | | | | |

**S3. Solvent effects on the DFT calculations**

The solvent effect of $CHCl_3$ on the structure and the TDDFT transition energy of the compounds **0**-**7** is considered by carrying out the same implicit-solvation-model calculations as done in our previous work on similar systems (J. Ku, Y. Gim, Y. Lansac, Y. H. Jang, Phys. Chem. Chem. Phys. 2016, 18, 1017): the conductor-like polarizable continuum model (CPCM) (V. Barone, M. Cossi, J. Phys. Chem. A 1998, 102, 1995; M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 2003, 24, 669) of $CHCl_3$ with a dielectric constant ($\varepsilon$) of 4.7113 and the Universal Force Field (UFF) radii (Å) of H (1.443), C (1.925), N (1.83), O (1.75), F (1.682), Si (2.147), S (2.018), and Se (2.103) (A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skiff, J. Am. Chem. Soc. 1992, 114, 10024) as well as a scaling factor ($\alpha$) of 1.1 to build the cavity of the solute **0**-**7**, as implemented in Gaussian09.

The solvent effect of $CHCl_3$ on the optimized structure is evaluated by a root-mean square deviation (RMSD; Å) between all the corresponding atoms in the two superimposed structures, one optimized in gas (gray, Fig. S2) and the other optimized in $CHCl_3$ (blue, Fig. S2), as summarized in Table S1. Only a marginal RMSD (< 0.2 Å) is obtained as a solvent effect. For **1**, which shows a higher RMSD of 0.73 Å due to the low-energy-barrier twisting of the benzene moiety in each SA unit, the RMSD excluding the benzene ring is listed in Table S1

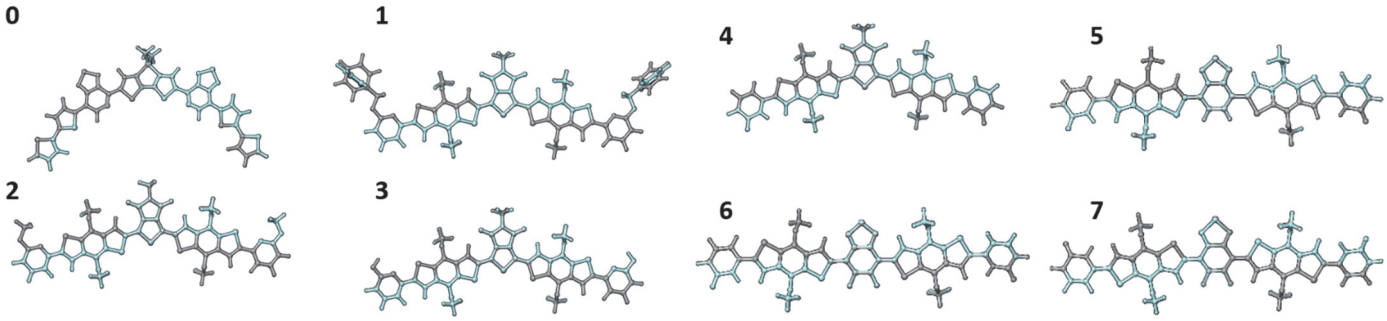



**Figure S2.** Two superimposed structures of the compounds **0**-**7**, one optimized in the gas phase (gray) and the other optimized in the $CHCl_3$ solution (blue), which are used to evaluate the RMSD between all the corresponding atoms as a barometer of the solvation effect of $CHCl_3$ on the structure (Table S1).

**Table S1**. RMSD between all the corresponding atoms in the two superimposed structures, one optimized in gas (gray, Fig. S2) and the other optimized in $CHCl_3$ (blue, Fig. S2).

| | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|---|
| **RMSD (Å)** | 0.07 | 0.73 (0.15) | 0.18 | 0.17 | 0.20 | 0.06 | 0.13 | 0.11 |

The solvent effect of $CHCl_3$ on the optical properties of **0-7** such as the lowest TDDFT transition energy ($E_g$) is represented by the shift (nm or eV) between the two lowest-energy (first from the right side, Fig. S3) peaks in the TDDFT absorption spectra of each compound, one calculated in gas (black curve) and the other calculated in $CHCl_3$ (red and blue curves depending on whether optimized in gas or in $CHCl_3$, which completely overlap each other within 0.5 nm or 0.003 eV), as summarized in Table S2. Only a marginal peak shift (< 0.08 eV or 30 nm) is obtained as a solvent effect.

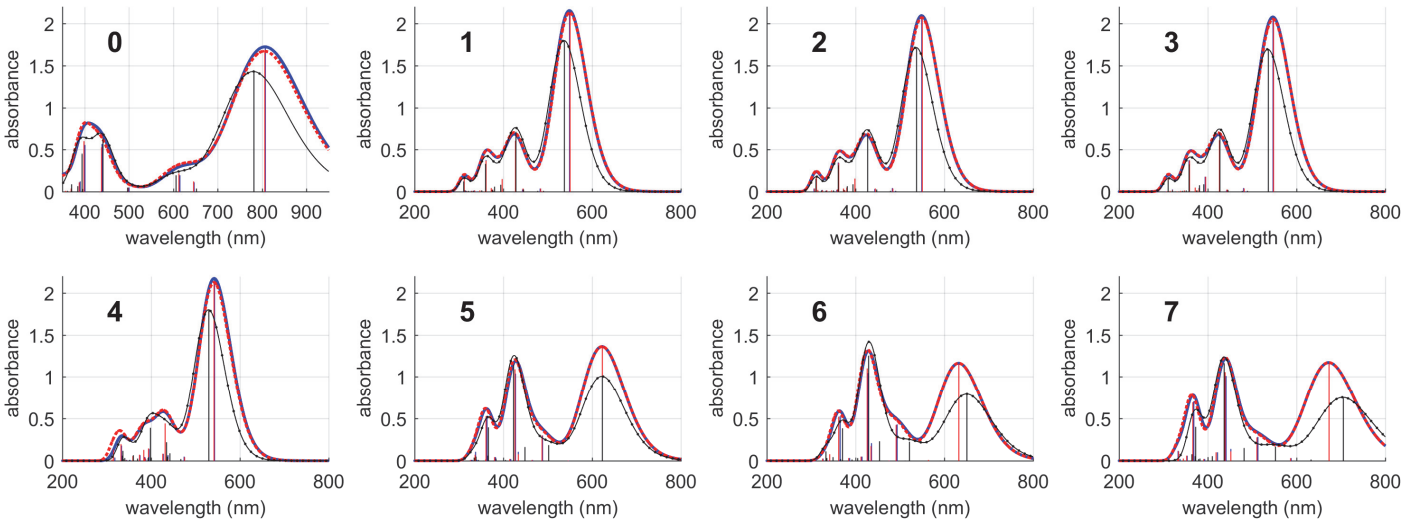



**Figure S3.** TDDFT absorption spectra simulated (with a Gaussian broadening of 0.03 eV) for the compounds **0-7**. (Black bars and curves) those calculated in the gas phase; (red bars and curves) those calculated in $CHCl_3$ at the geometries optimized in the gas phase; (blue bars and curves) those calculated in $CHCl_3$ at the geometries optimized in $CHCl_3$. Whether the geometry is optimized in gas (red) or in solution (blue), there is essentially no effect on TDDFT absorption spectra. On the other hand, whether the TDDFT transition energy (the first peak maximum position from the right side) is calculated in gas (black) or in solution (red, blue) makes a marginal (< 30 nm or 0.08 eV) effect on the lowest TDDFT transition energy (the first peak maximum position).

**Table S2**. The solvent effect on the lowest TDDFT transition energies of **0-7**

| $E_g$ | **0** | | **1** | | **2** | | **3** | | **4** | | **5** | | **6** | | **7** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **geometry/energy** | (nm) | (eV) | (nm) | (eV) | (nm) | (eV) | (nm) | (eV) | (nm) | (eV) | (nm) | (eV) | (nm) | (eV) | (nm) | (eV) |
| **1. gas/gas** | 781 | 1.59 | 537 | 2.31 | 537 | 2.31 | 535 | 2.32 | 530 | 2.34 | 622 | 1.99 | 651 | 1.91 | 705 | 1.76 |
| **2. gas/$CHCl_3$** | 806 | 1.54 | 550 | 2.26 | 549 | 2.26 | 547 | 2.27 | 542 | 2.29 | 622 | 1.99 | 632 | 1.96 | 673 | 1.84 |
| **Δ(2-1)** | 25 | -0.05 | 13 | -0.05 | 12 | -0.05 | 12 | -0.05 | 12 | -0.05 | 0 | 0.00 | -19 | 0.05 | -32 | 0.08 |
| **3. $CHCl_3$/$CHCl_3$** | 807 | 1.54 | 549 | 2.26 | 549 | 2.26 | 547 | 2.29 | 542 | 2.29 | 622 | 1.99 | 632 | 1.96 | 673 | 1.84 |
| **Δ(3-2)** | 1 | 0.00 | -1 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 | 0 | 0.00 |

**S4. Electrochemical and spectroscopic analysis**

Cyclic voltammetry was conducted with Eco Chemie Autolab PGSTAT 30 through three-electrode system consisting of ITO as the working electrode, Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode in acetonitrile with 0.1 M $Bu_4NClO_4$ as the supporting electrolyte at a scan rate of 50 mV/s. UV/VIS spectroscopy was performed with Perkin Elmer Lambda 750.

**S5. Device fabrication and characterization**

**a. Solar Cell**: The inverted small molecule (SM) solar cells consisting of ITO/ZnO/**SM**:$PC_{70}BM$/$MoO_3$/Ag were fabricated as follows: the ITO-coated glass substrate was carefully cleaned with detergent and then ultrasonicated in deionized water, acetone and isopropyl alcohol for 30 min each. The cleaned ITO substrate was dried overnight in an oven at 80 °C. The dried ITO substrate was treated with UV/ozone for 15 min before casting ZnO layer. The ZnO precursor solutions diluted in 2-methoxyethanol were spin-cast in air on top of ITO. Then, the ZnO-coated substrate was annealed at 200 °C for 10 min in air and then transferred into a glove box. The SM:$PC_{70}BM$ blend (1:0.8) in chloroform was spin-coated at 3000 rpm for 60 sec and then was annealed at 70 °C for 10 min. Certain volume of diiodooctane (DIO) as a processing additive was added to the blend solutions when needed. The blend solution was spin-cast on top of ZnO layer. Final devices were transferred into a metal deposition chamber. The hole transport layer $MoO_3$ (10 nm thickness) and anode electrode (Ag, 100 nm thickness) were deposited by thermal evaporation under high vacuum (5 x $10^{-7}$ Torr). The current density-voltage (*J-V*) characteristics were measured under air mass 1.5 global (AM 1.5G) illumination from a calibrated solar simulator with an irradiation intensity of 100 mW/$cm^2$ using a Keithley 236 source measure unit (SMU). The spectral mismatch factor was verified with the incident photon to charge carrier efficiency (IPCE) spectrum. IPCE (or external quantum efficiency, EQE) spectra were obtained using a solar cell spectral response/QE/incident photon-to-current efficiency (IPCE) measurement system (PV Measurements, Inc., Boulder, CO, USA).

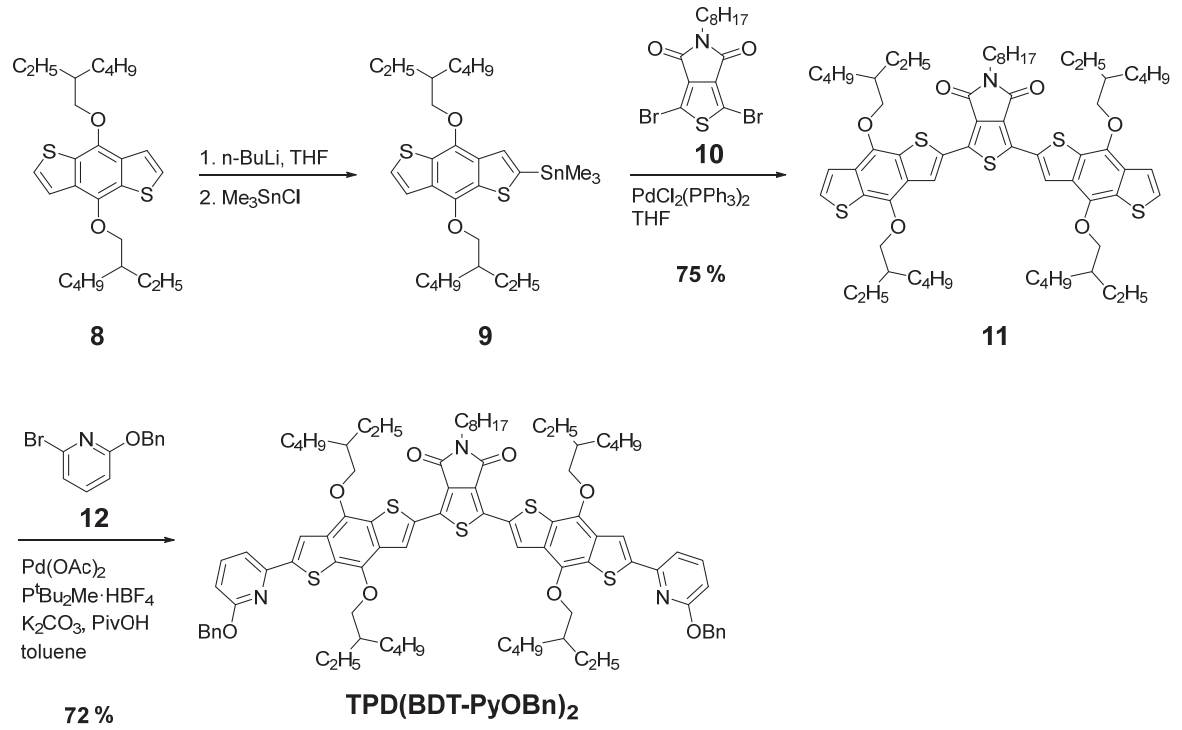
**b. Organic Field-Effect Transistor:** To make the TPD(BDT-PyOBn)$_2$ (**1**) solution (5 wt%), 5 mg of TPD(BDT-PyOBn)$_2$ (**1**) was added into 1 ml of chloroform solvent. The resulting mixture was stirred at room temperature until the TPD(BDT-PyOBn)$_2$ (**1**) was completely dissolved in the solvent. Before the deposition

of the TPD(BDT-PyOBn)$_2$ (**1**) solution, heavily n-type-doped silicon substrates with 200-nm-thick $SiO_2$ were cleaned with acetone and isopropyl alcohol, respectively, for 10 min and dried at 100°C for 15 min. UV/ozone treatment for 30 minutes was used to clean the surface of substrates. The clean substrates were modified with octadecyltrichloro silane (OTS) self-assembled monolayer (SAM). The TPD(BDT-PyOBn)$_2$ (**1**) solution was deposited onto the substrates via spin casting procedure with 2000 rpm for 30 seconds under ambient/$N_2$ conditions. The final thickness of the TPD(BDT-PyOBn)$_2$ (**1**) was approximately 70 nm, as measured using a Surf Corder ET 3000. Then, top-contact and bottom-gate (TC/BG) field-effect transistors were finalized with Molybdenum trioxide ($t \sim 5$ nm) as a hole injection layer (HIL) and an Ag source and drain electrode (70 nm) with a channel length of 100 μm and a width of 1000 μm. The transfer and output characteristics were determined in a $N_2$-filled glove box using a Keithley 4200 source meter (internal impedance > $10^{10}$ Ω). The saturation-regime mobility of the transistor was determined using the following equation: $I_{ds} = (WC_i/2L)\ \mu_{sat}(V_g - V_{th})^2$, where $I_{ds}$ is the source-drain current, $C_i$ (17.2 nF·cm$^{-2}$) is the capacitance per unit area, $L$ is the channel length, $W$ is the channel width, and $V_g$ and $V_{th}$ are the gate and threshold voltages, respectively.

**S6. Materials**

All reactions were performed in flame-dried glassware under inert atmosphere of argon. THF was purified through solvent purification column (Flinn Scientific). Toluene was distilled before using in reactions. $Pd(OAc)_2$ was purchased from Strem Chemicals. $PdCl_2(PPh_3)_2$, n-BuLi, $K_2CO_3$, $P^tBu_2Me{\bullet}HBF_4$, 1,3-Dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione were purchased from Sigma Aldrich. Pivalic acid, oxalyl chloride, diethylamine were purchased from Acros Organics. Trimethyltin chloride, 4,7-dibromo-2,1,3-benzothiadiazole, thiophene-3-carboxylic acid were purchased from Alfa Aesar. 2-Bromo-6-benzyloxypyridine (BnOPy) was purchased from TCI. Silica gel (230~400 mesh) was purchased from Merck. All reagents were used without further purification. 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene was synthesized following the literature procedure[1].

**S7. Synthesis**




**Scheme S1.** Synthesis of TPD(BDT-PyOBn)$_2$

*(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)trimethylstannane (**9**)*

Compound **8** (536 mg, 1.20 mmol) was dissolved in THF (22 ml) under inert atmosphere and the mixture was cooled down to -78 °C using a dry ice-acetone bath. 0.48 ml of n-BuLi (2.5 M in hexane,  mmol) was added dropwise and the solution was stirred at the same temperature for 1 h. Then the solution was slowly warmed up to room temperature and stirred for 30 min. The cloudy mixture was cooled again and trimethyltin chloride (319 mg, 1.60 mmol) was added in one portion. The reaction mixture was stirred for 2 h at room temperature, was then poured into ice water, and was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. It was used for the next step without any further purification.

*1,3-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**11**)*[2]

To a Schlenk flask filled with compound **9** (731 mg, 1.20 mmol), $PdCl_2(PPh_3)_2$ (19 mg, 0.0271 mmol, 6 mol%) was added in a glove box, followed by adding compound **10** (186 mg, 0.440 mmol) and THF (18 ml). The solution was refluxed for 24 h, then cooled and poured into water. The mixture was extracted with $CH_2Cl_2$. The organic combined phase was washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: hexane/$CH_2Cl_2$, 2:1, v/v) to provide red solid (381 mg, 0.330 mmol, 75 %). $^1$H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.68 (s, 2H), 7.39 (dd, *J* = 12, 6, 4H), 4.24 (dd, *J* = 36, 6, 8H), 3.70 (t, *J* = 9, 2H), 1.92-1.30 (m, 48H), 1.10-0.89 (m, 27H). $^{13}$C NMR ($CDCl_3$, 75 MHz), δ (ppm): 152.8, 145.4, 144.3, 138.4, 132.6, 132.5, 130.4, 129.1, 127.0, 126.5, 126.4, 122.6, 120.5, 76.2, 76.0, 40.9, 40.8, 30.8, 30.6, 29.5, 29.4, 24.1, 24.0, 23.3, 23.3, 14.3, 14.3, 11.6, 11.5.

*1,3-bis(6-(6-(benzyloxy)pyridin-2-yl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**TPD(BDT-PyOBn)$_2$**)*

$Pd(OAc)_2$ (1.7 mg, 7.57*10$^{-3}$ mmol, 3 mol%), $P^tBu_2Me$•$HBF_4$ (11.4 mg, 0.0460 mmol, 20 mol%), pivalic acid (23 mg, 0.225 mmol), potassium carbonate (95 mg, 0.687 mmol), compound **11** (263 mg, 0.228 mmol), and compound **12** (143 mg, 0.541 mmol) were added into a Schlenk flask, and then toluene (2 mL) was poured into the flask. The reactant was refluxed with stirring under an argon for 24 h. The solution was cooled and filtered over Celite®. The crude product was purified by column chromatography (eluent: hexane/$CH_2Cl_2$, 1:1, v/v) to afford red solid (248 mg, 0.163 mmol, 72 %). $^1$H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.59 (s, 2H), 7.74 (s, 2H), 7.55 (d, *J* = 6, 4H), 7.47 (t, *J* = 9, 2H), 7.41-7.32 (m, 6H), 7.22 (d, *J* = 6, 2H), 6.61 (d, *J* = 6, 2H), 5.46 (s, 4H), 4.25 (dd, *J* = 36, 6, 8H), 3.72 (t, *J* = 9, 2H), 1.92-1.31 (m, 48H), 1.09-0.90 (m, 27H). $^{13}$C NMR ($CDCl_3$, 100 MHz), δ (ppm): 163.0, 162.4, 149.6, 145.8, 145.6, 144.3, 139.2, 137.5, 137.1, 134.0, 132.0, 131.2, 130.8, 130.6, 129.9, 128.5, 128.5, 128.0, 117.1, 112.6, 110.6, 76.6, 76.2, 67.8, 65.4, 42.1, 40.8, 40.8, 32.0, 30.6, 30.6, 30.2, 29.8, 29.4, 29.4, 29.3, 29.3, 29.2, 28.6, 27.1, 24.0, 23.9, 23.4, 23.3, 23.3, 23.2, 22.7, 14.3, 14.3, 14.2, 11.5, 11.5, 11.2. MALDI-TOF MS (m/z): calcd for $C_{90}H_{109}N_3O_8S_5$: 1519.7 ($M^+$, 100 %). Found: 1519.8 ($M^+$, 100 %)

**S8. NMR spectra**

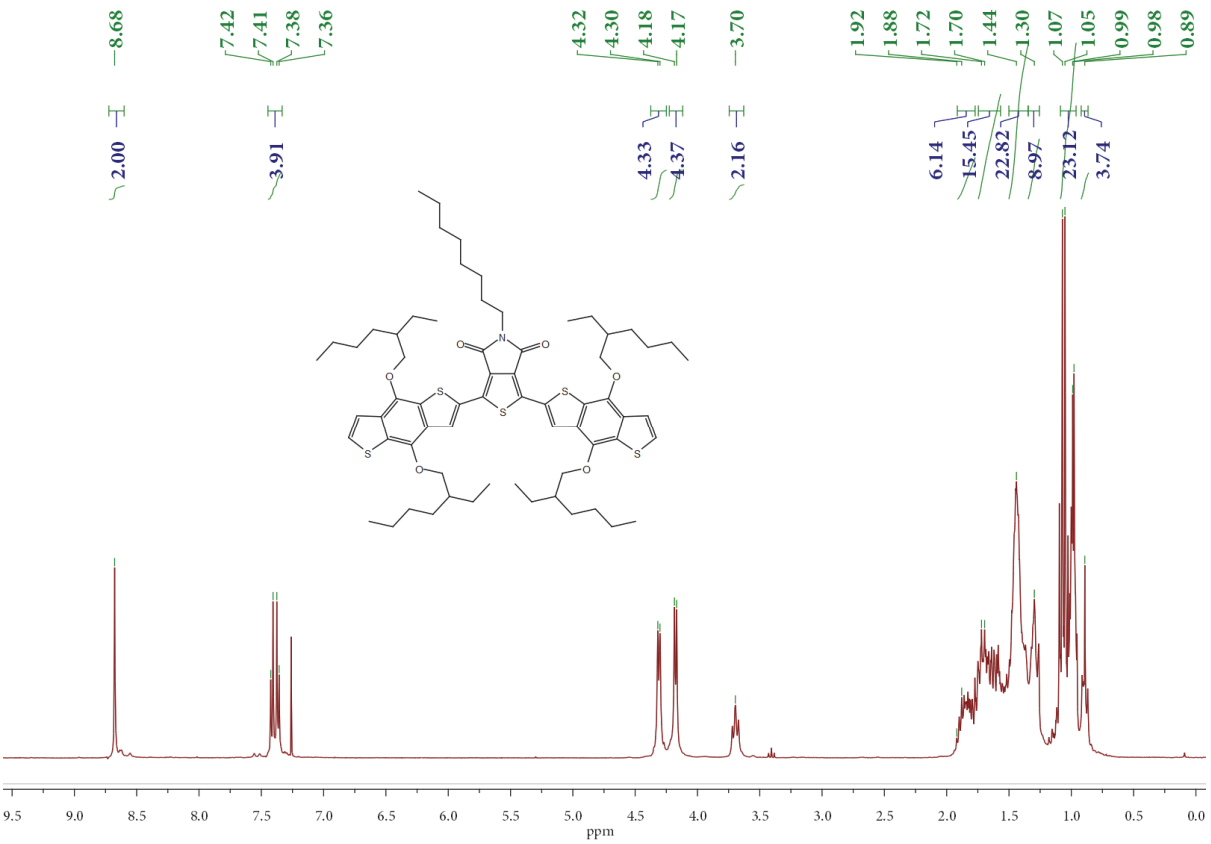



**Figure S4.** $^{1}$H NMR spectrum of **11** in $CDCl_3$

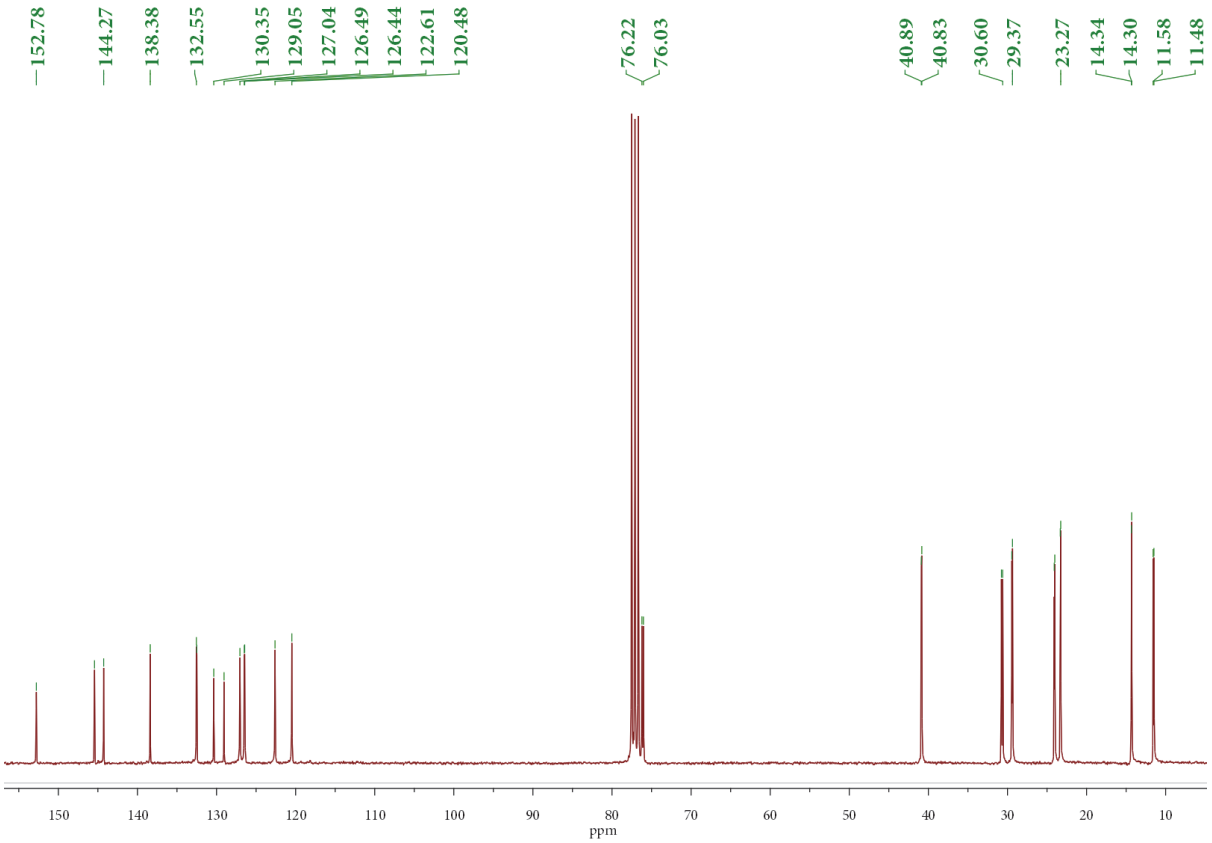



**Figure S5.** $^{13}C$ NMR spectrum of **11** in $CDCl_3$

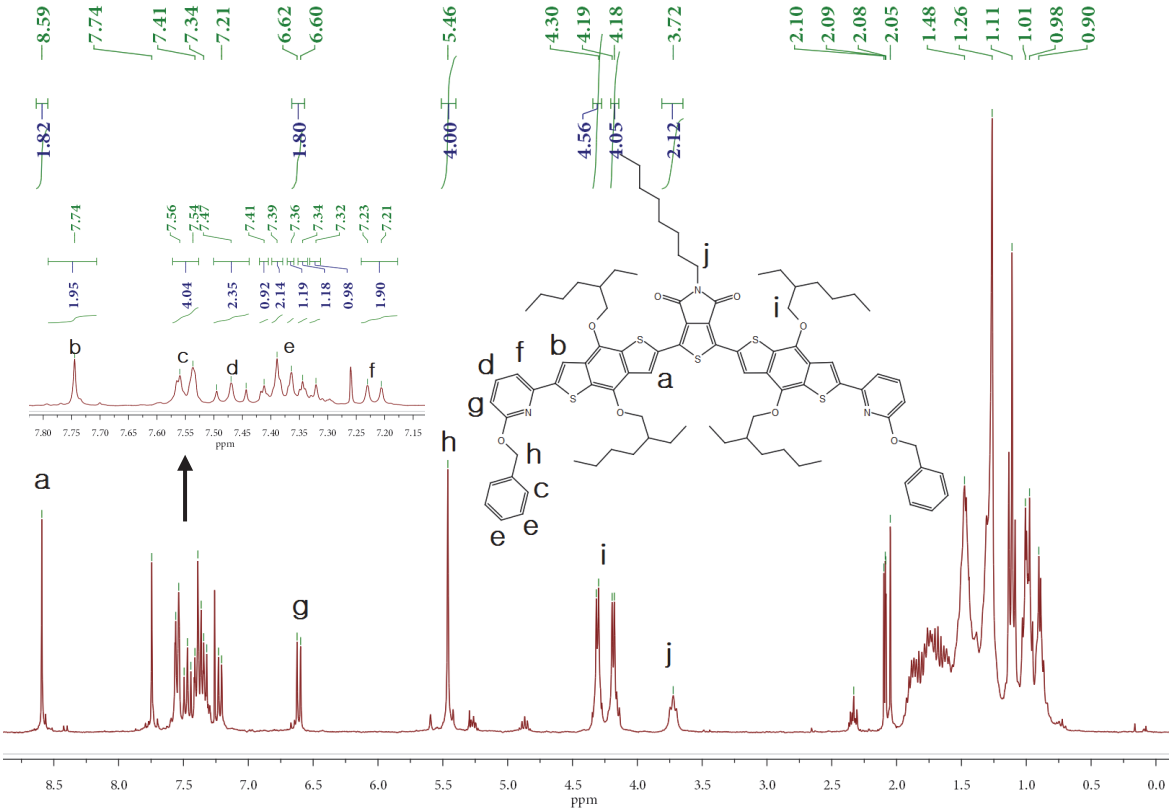



**Figure S6.** $^{1}H$ NMR spectrum of TPD(BDT-PyOBn)$_2$ in $CDCl_3$

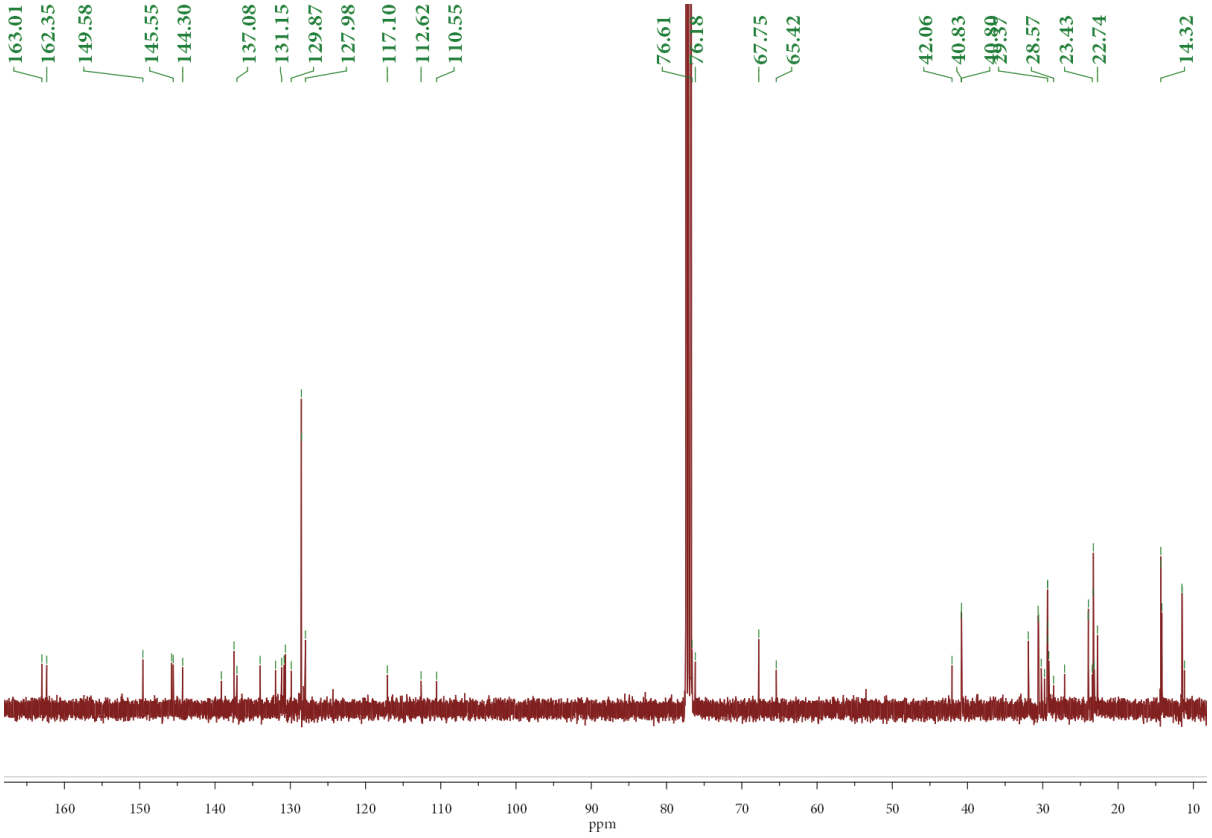
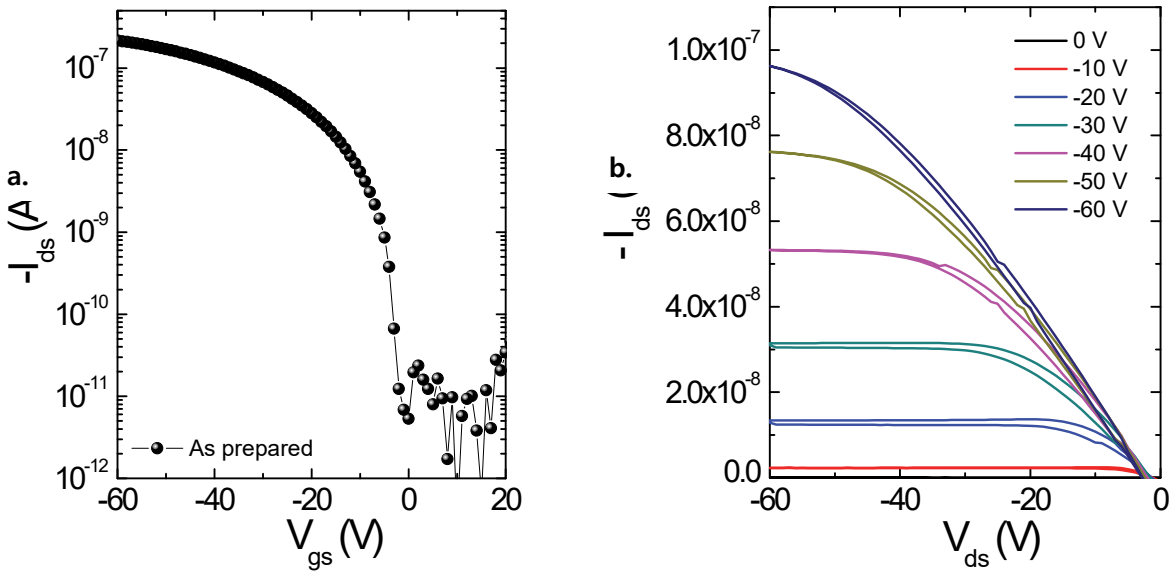



**Figure S7.** $^{13}C$ NMR spectrum of TPD(BDT-PyOBn)$_2$ in $CDCl_3$

**S9. Hole mobility measurement for 1, TPD(BDT-PyOBn)$_2$**




| Mobility ($cm^2/Vs$) | On/Off | $V_{Th}$ |
|---|---|---|
| $1.06 \times 10^{-3}$ | $>10^4$ | -1 V |

**Figure S8.** Hole mobility of **1**, TPD(BDT-PyOBn)$_2$. (a) transfer characteristics, (b) output characteristics

**S10. Reference**

1. J. Hou, M. Park, S. Zhang, Y. Yao, L. Chen, J. Li, and Y. Yang, *Macromolecules,* 2008, **41**, 6012

2. WO2011028827A2