# Benzo[c][1,2,5]thiadiazole Donor-Acceptor Dyes: A Synthetic, Spectroscopic and Computational Study

## SUPPORTING INFORMATION

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**Table S1: Electrochemical data for investigated compounds, recorded in $CH_2Cl_2$ with $Bu_4NPF_6$ electrolyte and referenced against $(Fc^*)^+/Fc^*$.**

| Compound | $E_{red}$ / V vs SCE | $E_{ox}$ / V vs SCE | $E_{ox}$-$E_{red}$ / V vs SCE | $E_{HOMO}$ / eV | $E_{LUMO}$ / ev | Bandgap / eV |
|---|---|---|---|---|---|---|
| BTD | -1.52 | - | - | - | -2.88 | - |
| BTD-TPA | -1.45 | 1.03 | 2.48 | -5.48 | -2.9 | 2.58 |
| BTD-$(OMe)_2$TPA | -1.57 | 1.02 | 2.59 | -5.48 | -2.76 | 2.73 |
| BTDMe-TPA | -1.53 | 1.04 | 2.57 | -5.51 | -2.81 | 2.7 |
| BTD-$TPA_2$ | -1.43 | 1.04 | 2.47 | -5.53 | -2.92 | 2.61 |
| BTD-$NMe_2$ | -1.51 | 0.93 | 2.44 | -5.41 | -2.81 | 2.6 |
| BTD-TRZTPA | -1.3 | 1.00 | 2.3 | -5.45 | -3.06 | 2.39 |
| BTD-$(OMe)_2$Ph | -1.57 | - | - | - | -2.74 | - |

**Table S2: Mean absolute deviations (MADs) for calculated Raman frequencies in toluene.**

| | Mean Absolute Deviation of Raman Modes / $cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | M06L | B3LYP | PBE0 | M06 | CAM-B3LYP | wB97XD |
| BTD-TPA | 16.45 | 8.21 | 25.29 | 14.67 | 33.05 | 31.33 |
| BTD-$(OMe)_2$TPA | 13.58 | 9.95 | 21.79 | 46.65 | 37.28 | 39.39 |
| BTDMe-TPA | 15.54 | 9.01 | 24.74 | 20.01 | 38.41 | 35.46 |
| BTD-$TPA_2$ | 13.01 | 9.22 | 22.57 | 13.4 | 35.77 | 31.68 |
| BTD-$NMe_2$ | 15.22 | 8.25 | 27.79 | 13.33 | 23.2 | 24.01 |
| BTD-TRZTPA | 11.74 | 7.44 | 20.74 | 15.51 | 40.53 | 28.67 |
| BTD-$(OMe)_2$Ph | 12.33 | 16.05 | 26.75 | 25.71 | 43.47 | 39.28 |
| Average | 13.98 | 9.73 | 24.28 | 21.33 | 35.96 | 32.83 |

**Table S3: Mean absolute deviations (MADs) for calculated Raman frequencies *in vacuo*.**

| | Mean Absolute Deviation of Raman Modes / $cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | M06L | B3LYP | PBE0 | M06 | CAM-B3LYP | wB97XD |
| BTD-TPA | 19.90 | 12.92 | 29.74 | 22.98 | 30.50 | 31.64 |
| BTD-$(OMe)_2$TPA | 12.61 | 10.38 | 27.36 | 21.80 | 32.01 | 33.39 |
| BTDMe-TPA | 16.93 | 10.14 | 36.42 | 26.06 | 46.05 | 41.76 |
| BTD-$TPA_2$ | 13.97 | 12.89 | 23.17 | 17.36 | 24.52 | 24.27 |
| BTD-$NMe_2$ | 15.56 | 10.29 | 18.87 | 12.13 | 20.72 | 23.00 |
| BTD-TRZTPA | 16.86 | 20.69 | 25.52 | 16.84 | 29.87 | 27.51 |
| BTD-$(OMe)_2$Ph | 16.61 | 13.84 | 29.34 | 20.93 | 39.26 | 36.19 |
| Average | 16.06 | 13.02 | 27.20 | 19.73 | 31.85 | 31.11 |

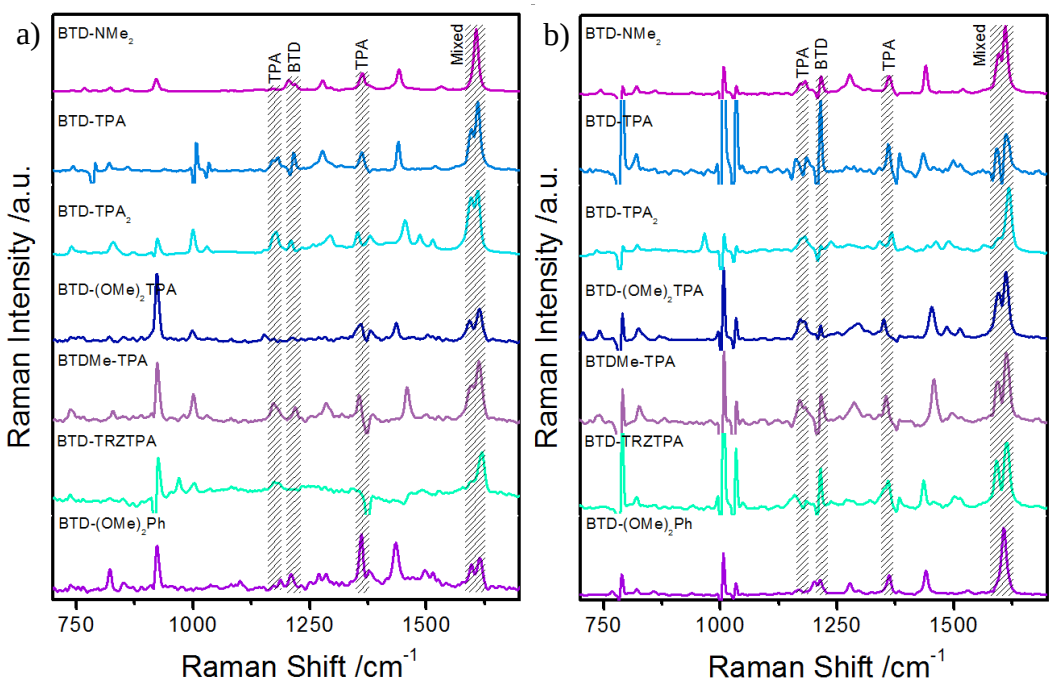



**Figure S1: Liquid FT-Raman spectra for the compound series in a) acetonitrile and b) toluene.**

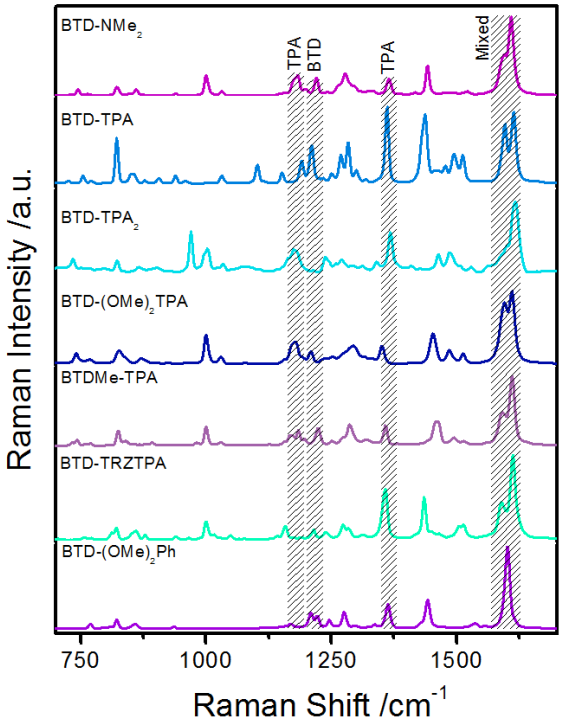



**Figure S2: Solid FT-Raman spectra for the compound series.**

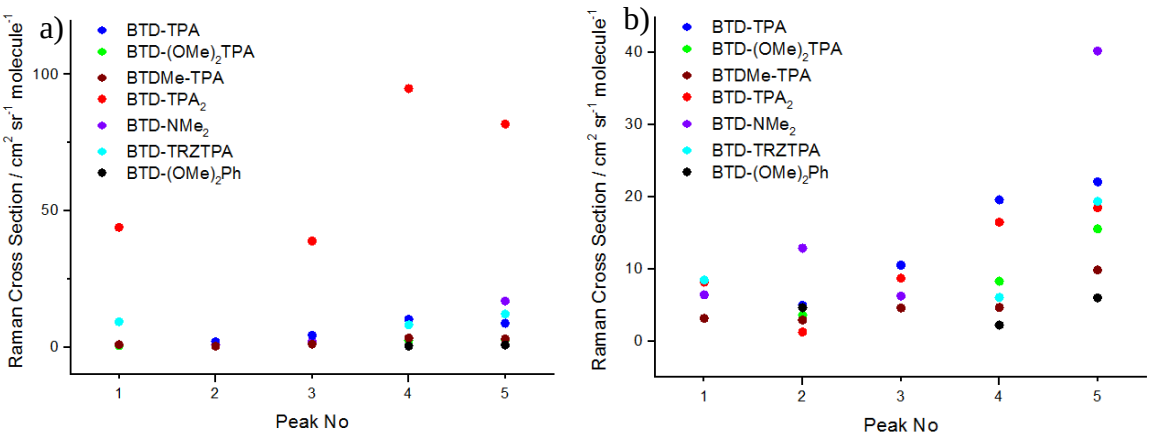



**Figure S3: Experimental Raman cross sections for the compound series in a) acetonitrile and b) toluene.**

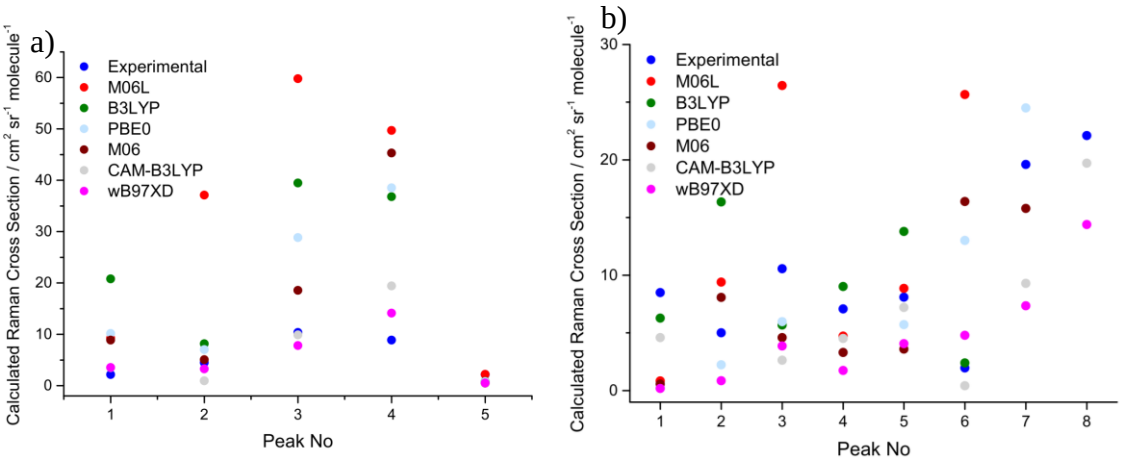



**Figure S4: Raman cross sections for BTD-TPA in a) acetonitrile and b) toluene.**

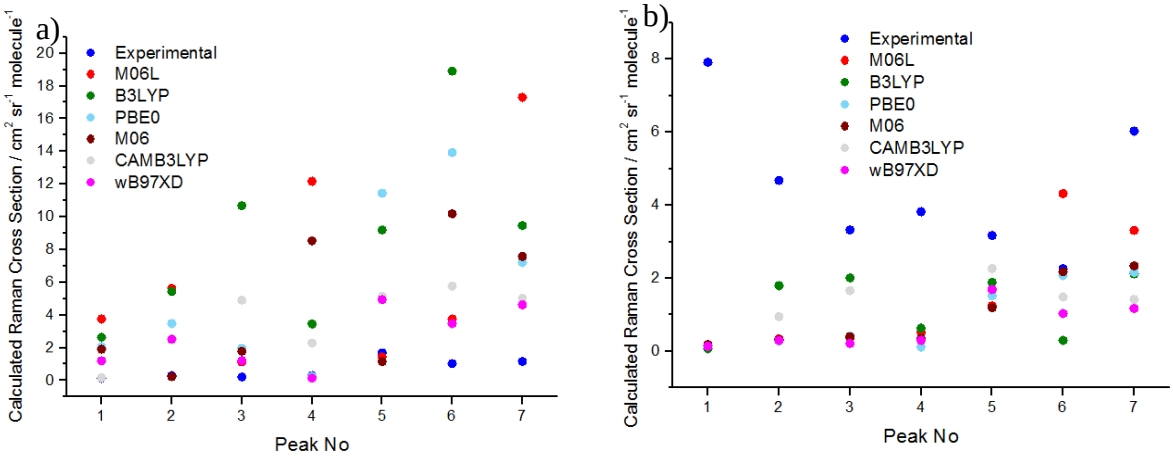



**Figure S5. Raman cross sections for BTD-(OMe)$_2$TPA in (a) acetonitrile and (b) toluene.**

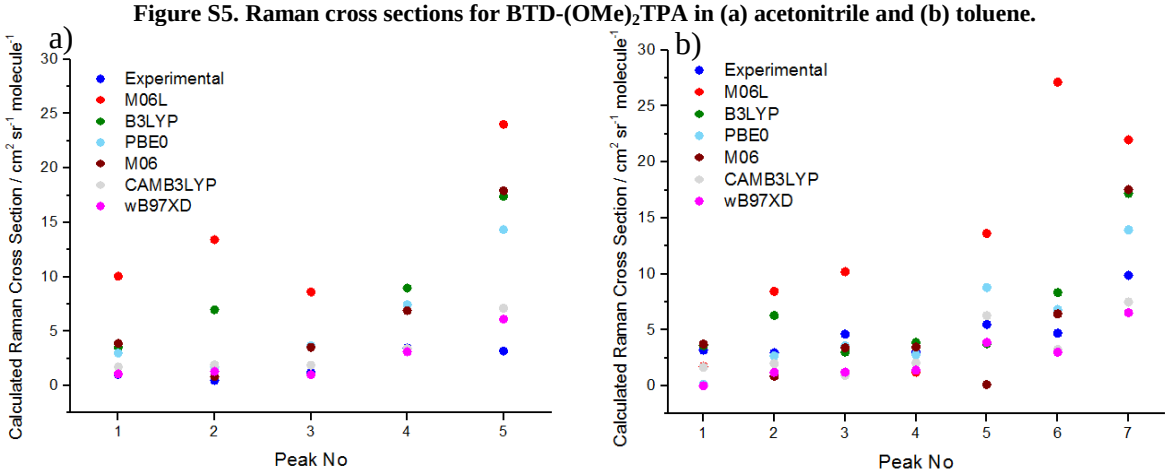



**Figure S6: Raman cross sections for BTDMe-TPA in a) acetonitrile and b) toluene.**

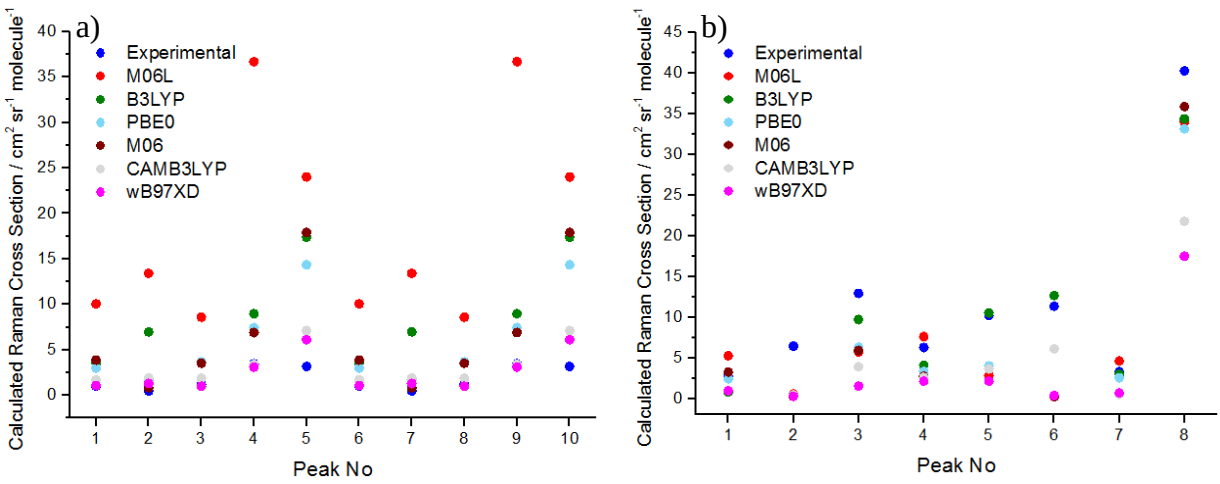



**Figure S7: Raman cross sections for BTD-NMe$_2$ in a) acetonitrile and b) toluene.**

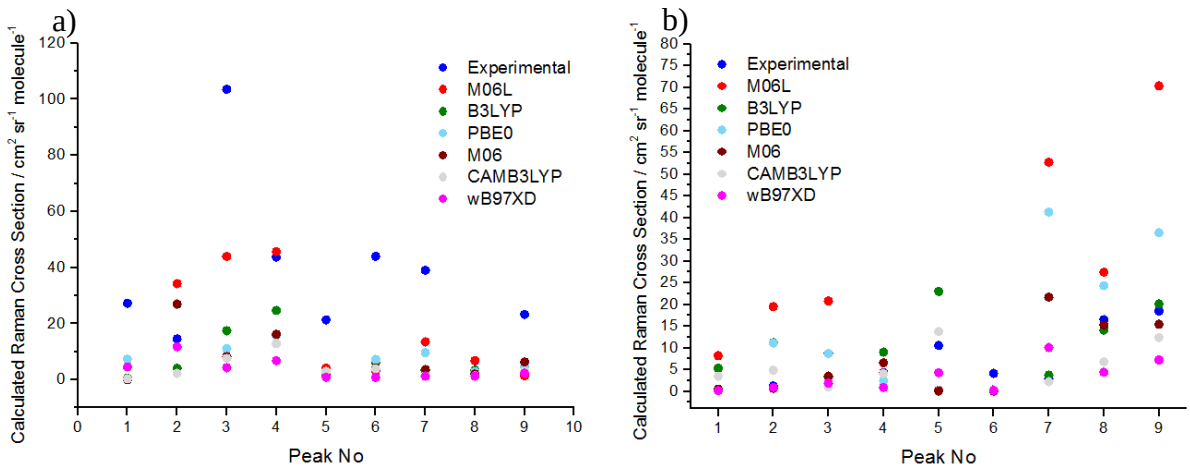



**Figure S8: Raman cross sections for BTD-TPA$_2$ in a) acetonitrile and b) toluene.**

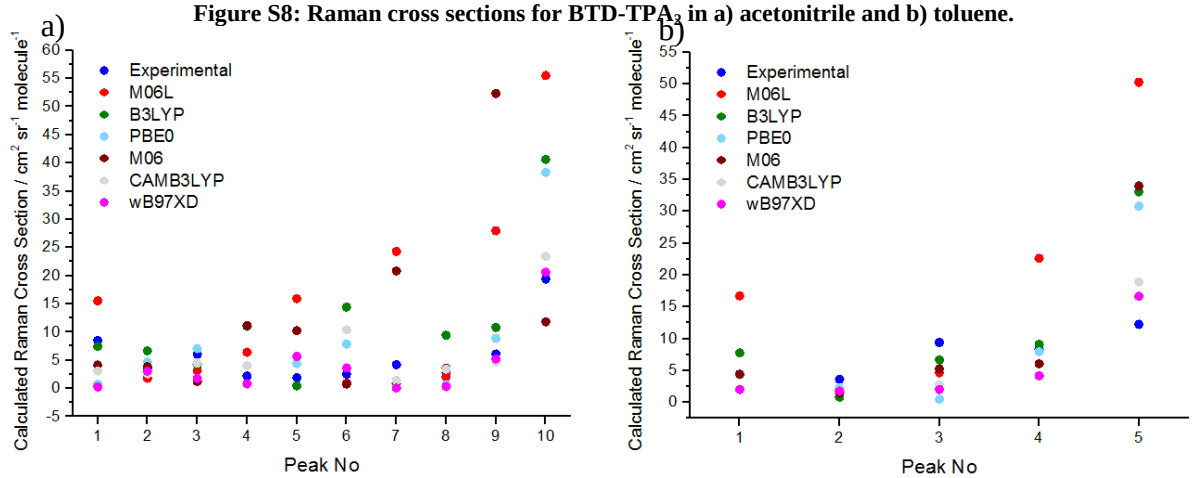



**Figure S9: Raman cross sections for BTD-TRZTPA in a) acetonitrile and b) toluene.**

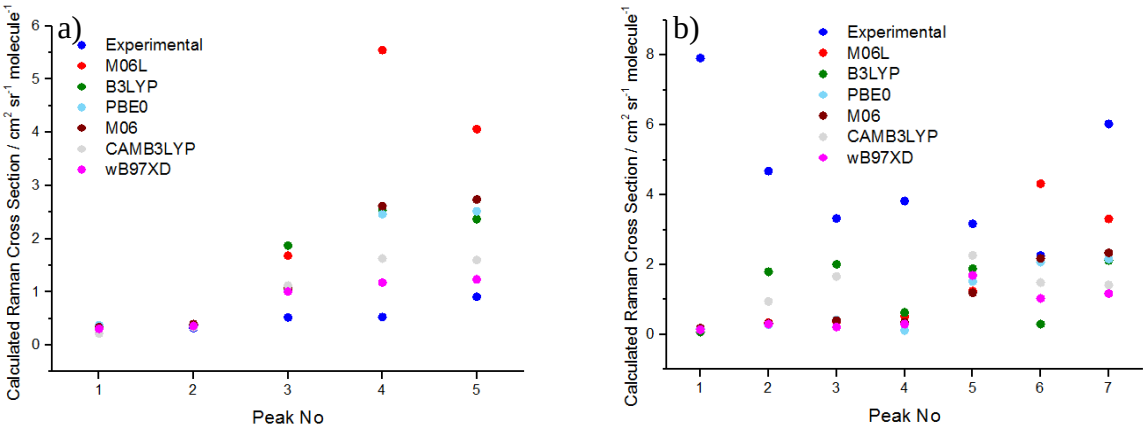



**Figure S10: Raman cross sections for BTD-$(OMe)_2$Ph in a) acetonitrile and b) toluene.**

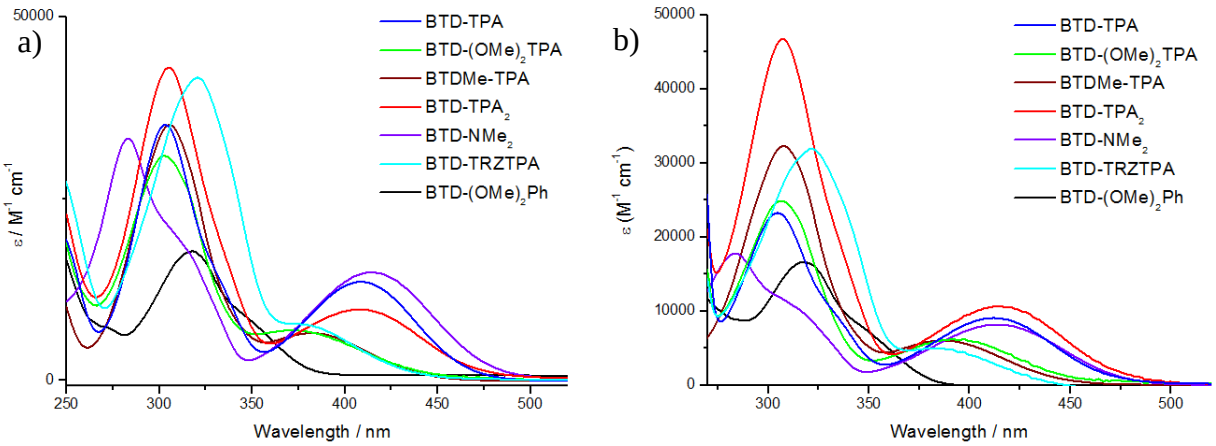



**Figure S11: UV-Vis data for all compounds in a) dichloromethane and b) chloroform.**

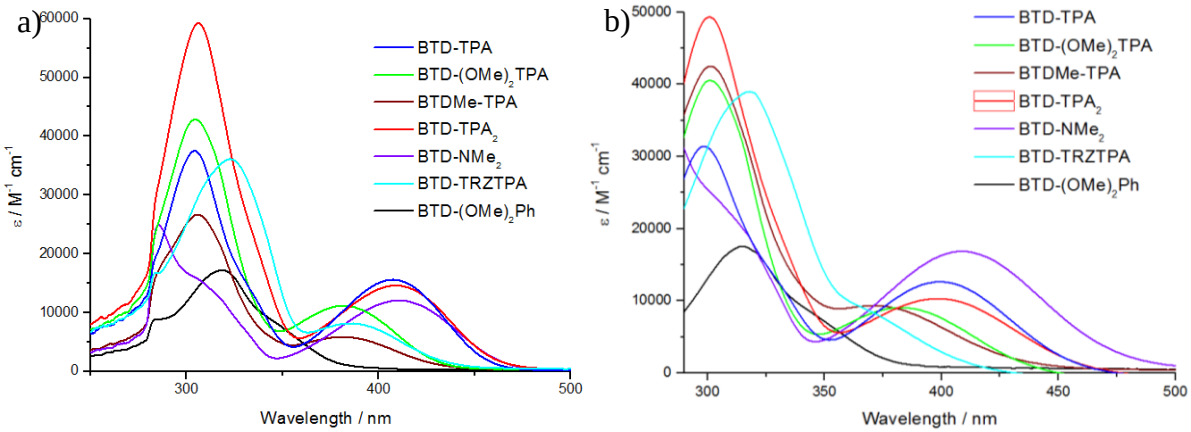



**Figure S12: UV-Vis data for all compounds in a) toluene and b) acetonitrile.**

**Table 4: Raman Cross-Sections for compounds in vacuo, acetonitrile and toluene. Orange denotes bands used for MPE analysis and PCA.**

| | Raman Shift / $cm^{-1}$ (Calculated Raman Cross Section / $10^{30}$ $cm^2$ $sr^{-1}$ $molecule^{-1}$) | |
|---|---|---|
| | Acetonitrile | Toluene |
| BTD-TPA | 669 (2) | 1179 (8) |
| | 1217 (4) | 1217 (5) |
| | 1278 (10) | 1278 (10) |
| | 1597 (9) | 1362 (7) |
| | 1611 (2) | 1440 (8) |
| | | 1519 (2) |
| | | 1597 (20) |
| | | 1612 (20) |
| BTD-$(OMe)_2$TPA | 1000 (0.1) | 1215 (8) |
| | 1153 (0.3) | 1357 (5) |
| | 1359 (0.2) | 1383 (3) |
| | 1382 (0.3) | 1436 (4) |
| | 1436 (2) | 1508 (3) |
| | 1593 (1) | 1592 (2) |
| | 1614 (1) | 1614 (6) |
| BTDMe-TPA | 1174 (1) | 1171 (3) |
| | 1219 (0.5) | 1216 (3) |
| | 1286 (1) | 1287 (5) |
| | 1598 (3) | 1355 (3) |
| | 1615 (3) | 1458 (5) |
| | | 1593 (5) |
| | | 1613 (10) |
| BTD-$TPA_2$ | 665(30) | 1176 (8) |
| | 829 (20) | 1215 (1) |
| | 1000 (100) | 1295 (9) |
| | 1177 (40) | 1351 (4) |
| | 1293 (20) | 1453 (10) |
| | 1486 (40) | 1485 (4) |
| | 1514 (40) | 1514 (3) |
| | 1596 (7) | 1595 (20) |
| | 1611 (20) | 1613 (20) |
| BTD-$NMe_2$ | 523 (1) | 858 (3) |
| | 664 (0.5) | 1169 (6) |
| | 823 (1) | 1208 (13) |
| | 859 (3) | 1278 (3) |
| | 1206 (3) | 1362 (10) |
| | 1220 (1) | 1441 (10) |
| | 1278 (0.5) | 1531 (3) |
| | 1296 (1) | 1609 (40) |
| | 1533 (3) | |
| | 1607 (3) | |
| BTD-TRZTPA | 971 (5) | 1178 (9) |
| | 1003 (4) | 1342 (4) |
| | 1177 (9) | 1367 (6) |
| | 1598 (8) | 1401 (2) |
| | 1617 (10) | 1444 (2) |
| | | 1462 (2) |
| | | 1489 (4) |
| | | 1565 (3) |
| | | 1598 (7) |
| | | 1618 (20) |
| BTD-$(OMe)_2$Ph | 664 (0.3) | 1034 (8) |
| | 684 (0.3) | 1215 (5) |
| | 823 (0.5) | 1360 (3) |
| | 1597 (0.5) | 1382 (4) |
| | 1614 (0.9) | 1436 (3) |
| | | 1593 (2) |
| | | 1613 (6) |

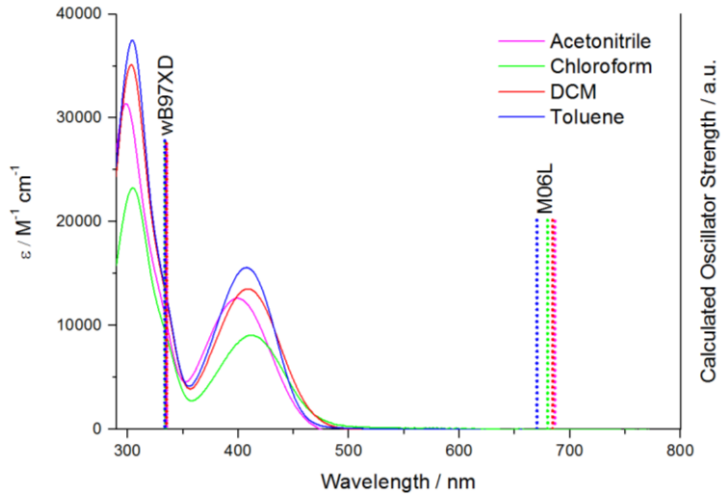



**Figure 13: UV-Vis data for BTD-TPA in a variety of solvents with M06L/wB97XD calculated transitions overlaid.**

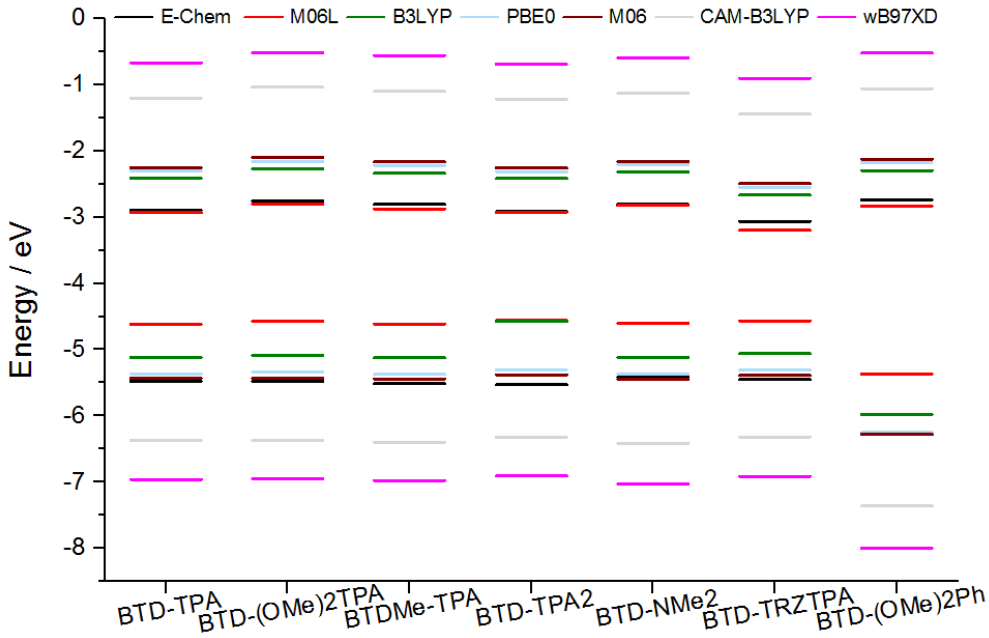



**Figure S14: Calculated frontier molecular orbital energies for experimental and computational data. UV-Vis HOMO and LUMO energies are calculated from $\lambda_{max}$ (eV) centred on the mean of all other data. All data was collected or modelled in dichloromethane.**

$$E_{HOMO} = -(E_{pa} + 4.4) \qquad Equation\ S1.$$

$$E_{LUMO} = -(E_{pc} + 4.4) \qquad Equation\ S2.$$

The previously established method for estimating HOMO and LUMO energies from cyclic voltammetry data.[41] Where $E_{pa}$ is the anodic peak of the oxidation process and $E_{pc}$ the cathodic peak of the reduction process.

**Table S5: Experimental and calculated absorption properties for the lowest energy transition. All data was collected in dichloromethane.**

| | λmax / nm (ε /$M^{-1}$ $cm^{-1}$) | Absorption Max λmax / nm (Oscillator Strength) | | | | | |
|---|---|---|---|---|---|---|---|
| | EXPERIMENTAL | M06L | B3LYP | PBE0 | M06 | CAM-B3LYP | wB97XD |
| BTD-TPA | 399(12600) | 683(0.19) | 526(0.24) | 480(0.27) | 469(0.27) | 354(0.53) | 335(0.57) |
| BTD-$(OMe)_2$TPA | 382(9000) | 669(0.13) | 511(0.15) | 467(0.18) | 454(0.19) | 347(0.37) | 330(0.38) |
| BTDMe-TPA | 371(9330) | 683(0.09) | 514(0.09) | 465(0.101) | 454(0.14) | 329(0.28) | 312(0.28) |
| BTD-$TPA_2$ | 398(10300) | 714(0.21) | 539(0.20) | 492(0.24) | 479(0.25) | 350(0.61) | 329(0.64) |
| BTD-$NMe_2$ | 408(16800) | 615(0.22) | 506(0.25) | 468(0.28) | 460(0.28) | 361(0.40) | 344(0.40) |
| BTD-TRZTPA | 366(9100) | 897(0.03) | 587(0.04) | 518(0.04) | 497(0.04) | 331(0.30) | 309(0.71) |
| BTD-$(OMe)_2$Ph | 315(10900) | 453(0.11) | 393(0.08) | 369(0.13) | 371(0.13) | 316(0.16) | 309(0.13) |

**Table S6: Experimental and calculated absorption properties for the lowest energy transition. All data was collected in chloroform.**

| | λmax / nm (ε /$M^{-1}$ $cm^{-1}$) | Absorption Max λmax / nm (Oscillator Strength) | | | | | |
|---|---|---|---|---|---|---|---|
| | EXPERIMENTAL | M06L | B3LYP | PBE0 | M06 | CAM-B3LYP | wB97XD |
| BTD-TPA | 399(12600) | 679(0.19) | 523(0.23) | 478(0.27) | 468(0.28) | 353(0.54) | 334(0.58) |
| BTD-$(OMe)_2$TPA | 382(9000) | 657(0.13) | 504(0.15) | 461(0.19) | 449(0.19) | 346(0.38) | 330(0.39) |
| BTDMe-TPA | 371(9330) | 678(0.11) | 511(0.09) | 464(0.11) | 452(0.14) | 329(0.28) | 312(0.30) |
| BTD-$TPA_2$ | 398(10300) | 705(0.22) | 537(0.20) | 490(0.24) | 477(0.25) | 349(0.62) | 328(0.84) |
| BTD-$NMe_2$ | 408(16800) | 606(0.21) | 500(0.25) | 464(0.28) | 455(0.28) | 359(0.41) | 342(0.41) |
| BTD-TRZTPA | 366(9100) | 907(0.03) | 592(0.04) | 523(0.04) | 502(0.05) | 33(0.30) | 310(0.70) |
| BTD-$(OMe)_2$Ph | 315(10900) | 449(0.11) | 390(0.09) | 366(0.13) | 370(0.13) | 315(0.15) | 309(0.13) |

**Table S7: Experimental and calculated absorption properties for the lowest energy transition. All data was collected in toluene.**

| | λmax / nm (ε /$M^{-1}$ $cm^{-1}$) | Absorption Max λmax / nm (Oscillator Strength) | | | | | |
|---|---|---|---|---|---|---|---|
| | EXPERIMENTAL | M06L | B3LYP | PBE0 | M06 | CAM-B3LYP | wB97XD |
| BTD-TPA | 407(15600) | 669(0.19) | 517(0.24) | 475(0.27) | 464(0.28) | 352(0.55) | 333(0.59) |
| BTD-$(OMe)_2$TPA | 381(11100) | 634(0.12) | 490(0.14) | 450(0.20) | 439(0.19) | 342(0.39) | 327(0.40) |
| BTDMe-TPA | 382(5800) | 667(0.11) | 504(0.09) | 458(0.11) | 447(0.14) | 327(0.29) | 310(0.30) |
| BTD-$TPA_2$ | 406(14600) | 683(0.22) | 531(0.20) | 486(0.25) | 473(0.26) | 348(0.65) | 328(0.66) |
| BTD-$NMe_2$ | 410(12000) | 589(0.21) | 489(0.25) | 454(0.28) | 447(0.28) | 355(0.41) | 339(0.41) |
| BTD-TRZTPA | 387(8100) | 923(0.03) | 600(0.04) | 530(0.05) | 508(0.05) | 337(0.30) | 312(0.68) |
| BTD-$(OMe)_2$Ph | 319(17200) | 441(0.11) | 384(0.10) | 362(0.13) | 365(0.13) | 313(0.15) | 309(0.13) |

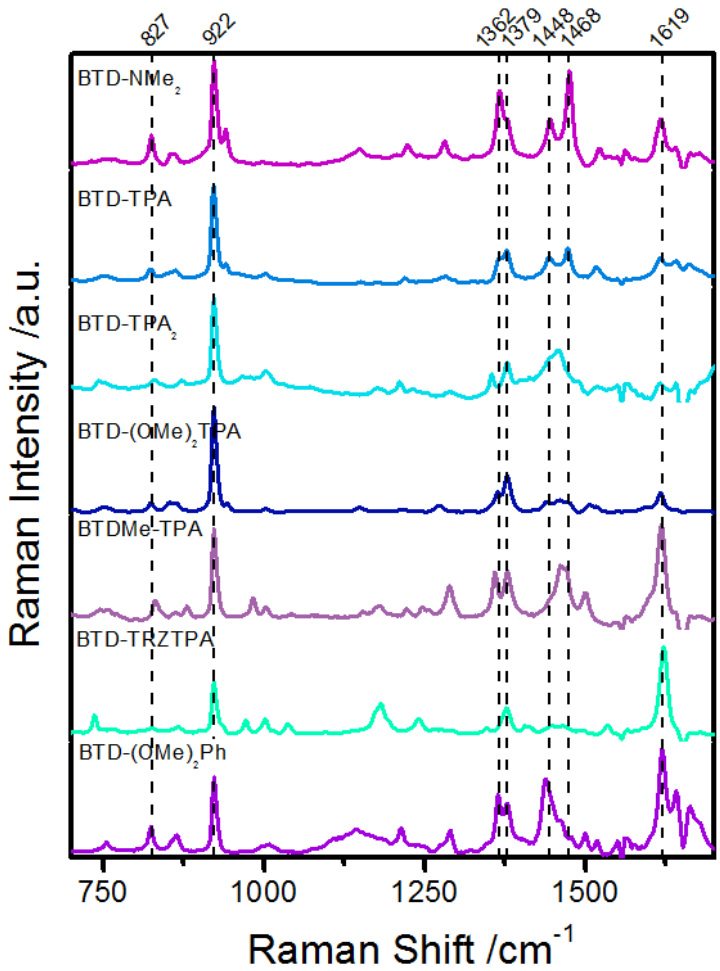



**Figure S15: Resonance Raman data for the compound series of interest. Data collected at 351nm excitation.**

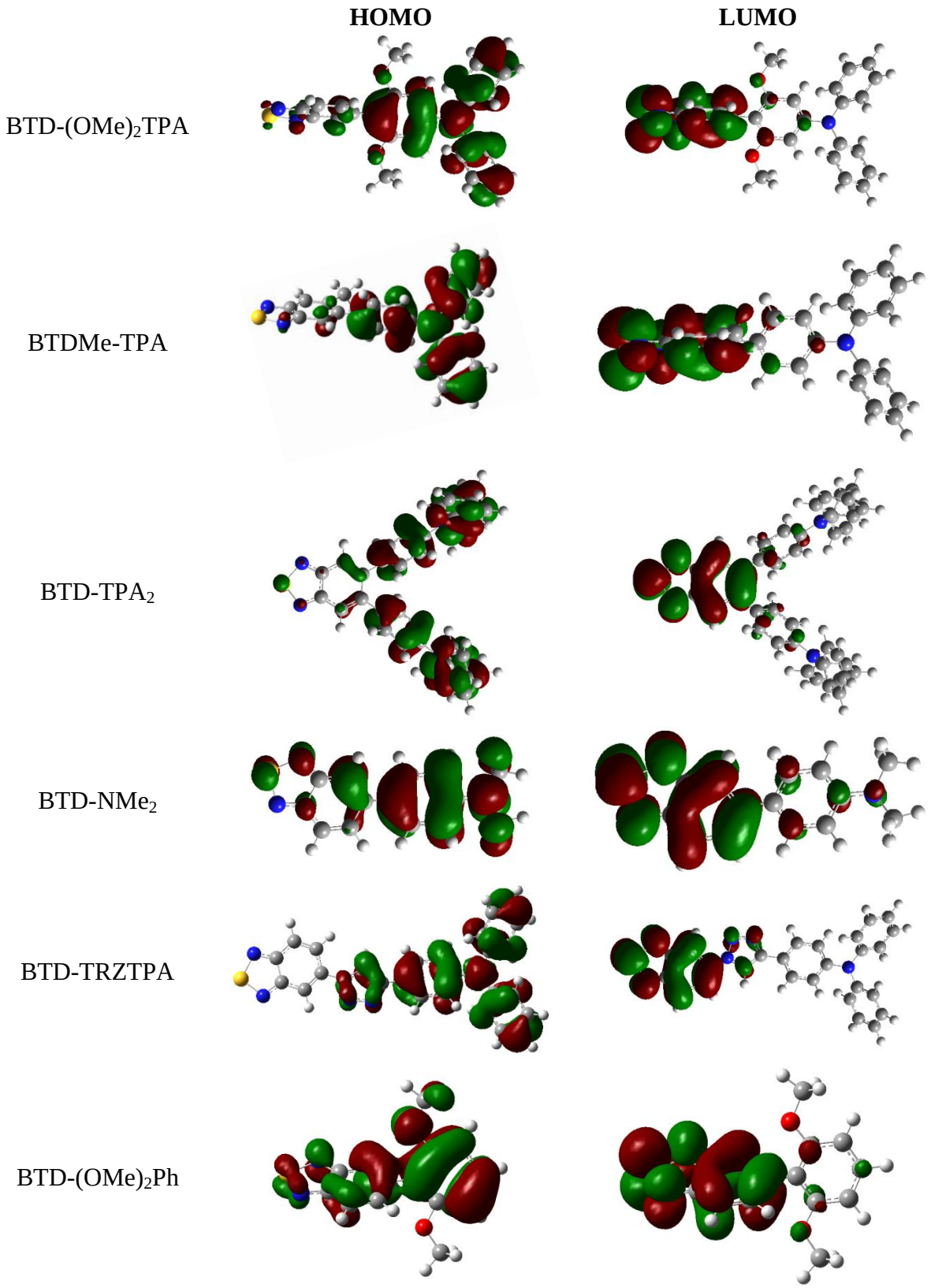
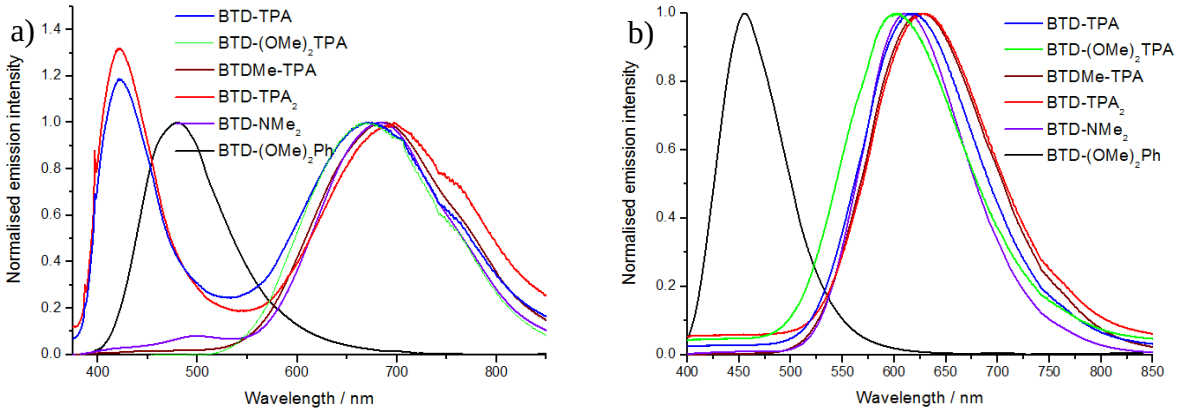
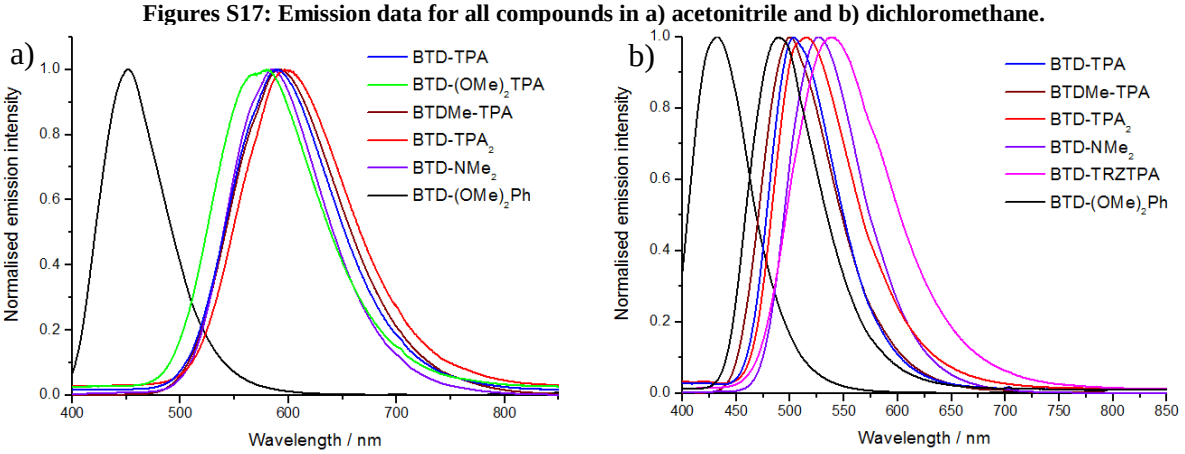



**Figure S16: DFT calculated HOMO and LUMO orbitals for the remaining compounds in acetonitrile using the B3LPY functional.**




**Figures S17: Emission data for all compounds in a) acetonitrile and b) dichloromethane.**




**Figures S18: Emission data for all compounds in a) chloroform and b) toluene.**

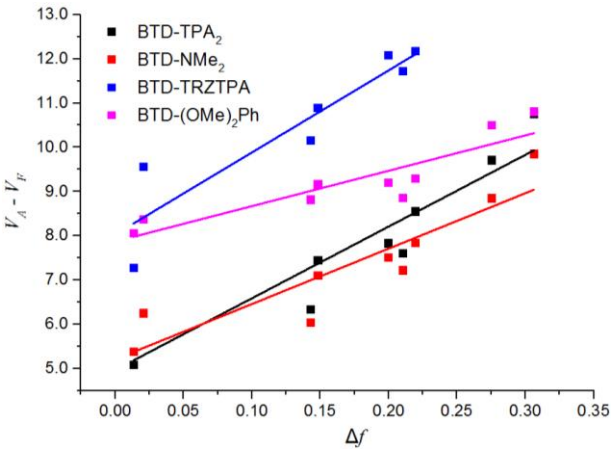



**Figure S19: Lippert-Mataga plot for the remaining compounds across solvent.**

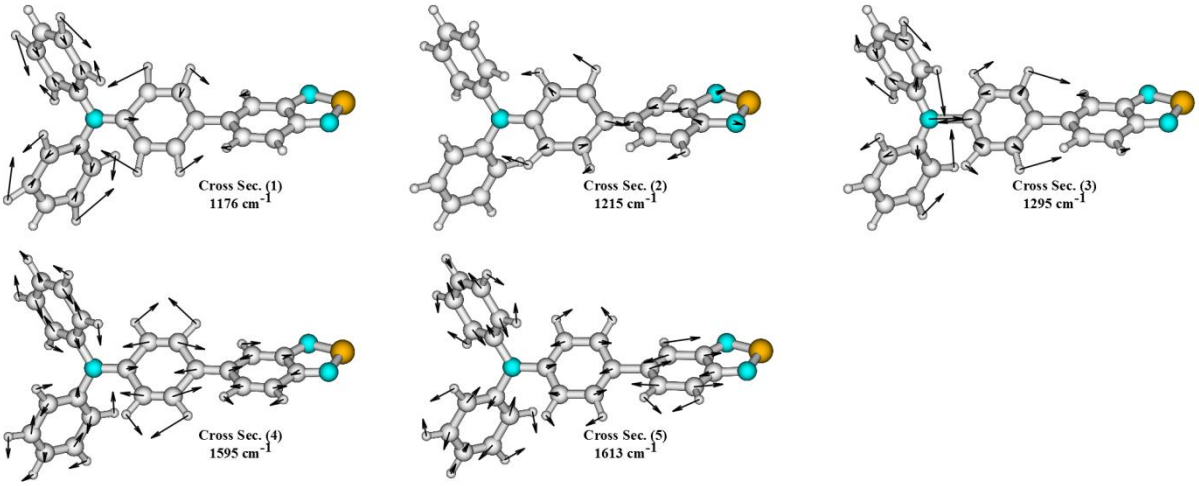



**Figure S20: Systematic eigenvector diagrams for vibrations chosen in MPE and PCA analysis. Eigenvectors were predicted generated from BTD-TPA data (B3LPY) in a dichloromethane solvent field.**

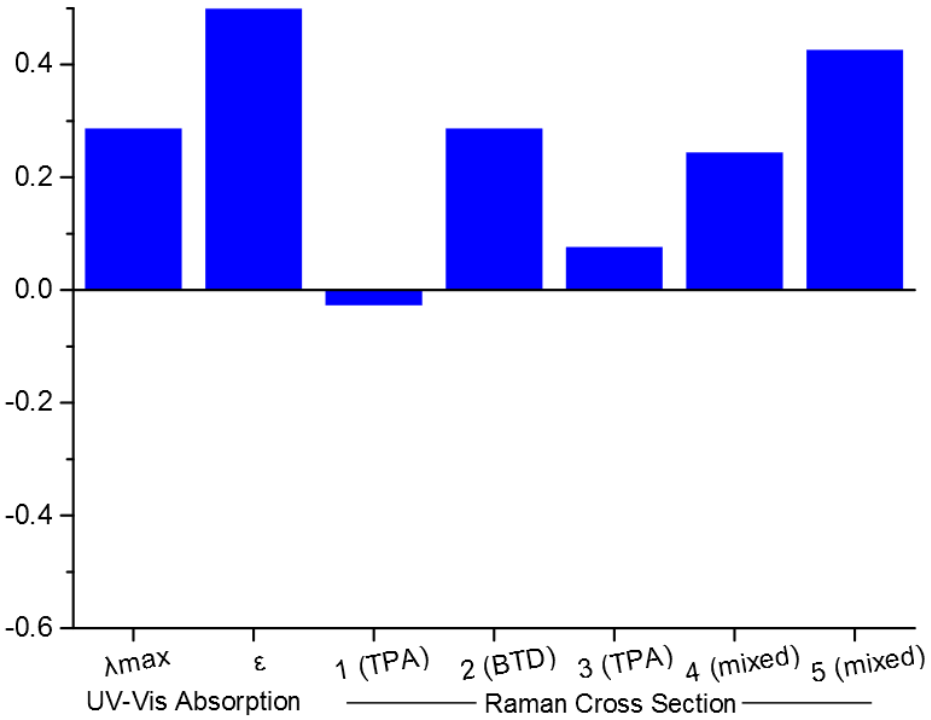



**Figure S21: PCA loadings plot for PC2 which describes 13% of variation within the data set.**

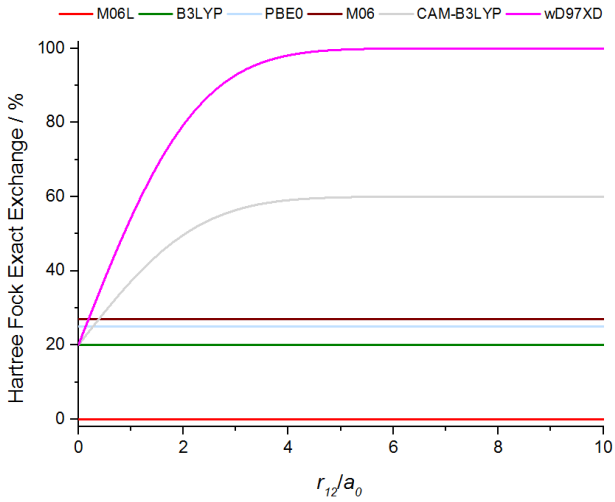



**Figure S22: The relationship of Hartree Fock and distance for the functionals investigated in this study.**

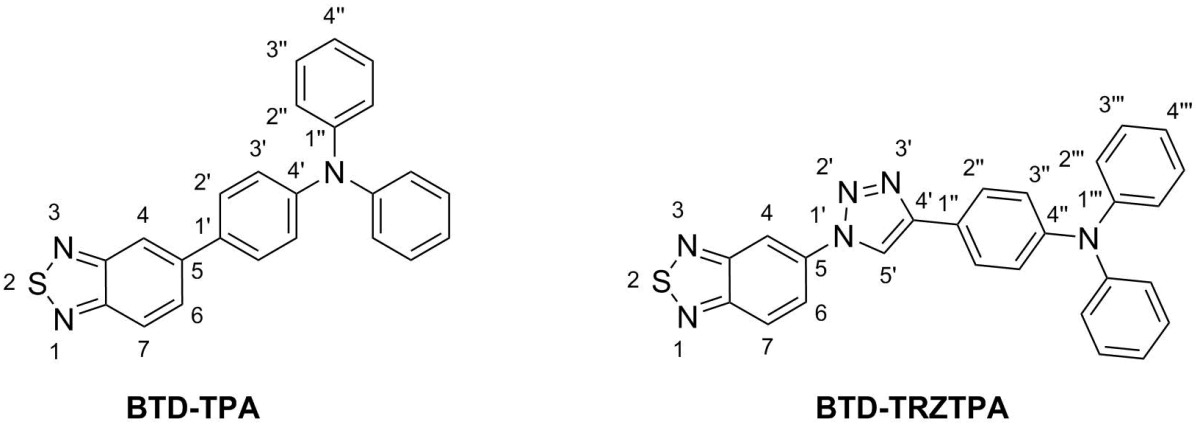



**Figure S23: Compound numbering scheme used for NMR assignments.**