Supporting information for: Prediction of Excited State Energies and Singlet-Triplet Gaps of Charge-Transfer States Using a Restricted Open-Shell Kohn-Sham Approach

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1 Molecules Tested

The effectiveness of the four devised protocols were determined by comparison to experimental data for the following compounds (structures given in Figure S1): 2CzPN,[S1] 4CzPN,[S1] 4CzTPN-Me,[S1] 4CzTPN,[S1] PIC-TRZ,[S1] ACRFLCN,[S1] α-NPD,[S1] PXZ-TAZ,[S2] DPA-DPS,[S1] PXZ-OXD,[S2] DTC-DPS,[S1,S3] CBP,[S1] CC2TA,[S1] DMAC-DPS,[S4] 2PXZ-OXD,[S2] DTPA-DPS,[S1] NPh_3,[S1] PhCz,[S1] 4CzIPN,[S1] 2PXZ-TAZ,[S2] PXZ-DPS,[S4] PPZ-4TPT,[S4] DMOC-DPS,[S3] PPZ-DPS,[S4] PXZ-TRZ,[S1] PPZ-DPO[S4] and PPZ-3TPT.[S4] The calculated equilibrium geometries are provided in the associated geometry.zip file. Convergence failure prevented a couple of

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S_1 optimizations with the LC-ωPBE functional (specific instances are noted in the data tables below), and thus the provided geometry corresponds to the final structure before the calculations crashed.

2 Structures of tested molecules

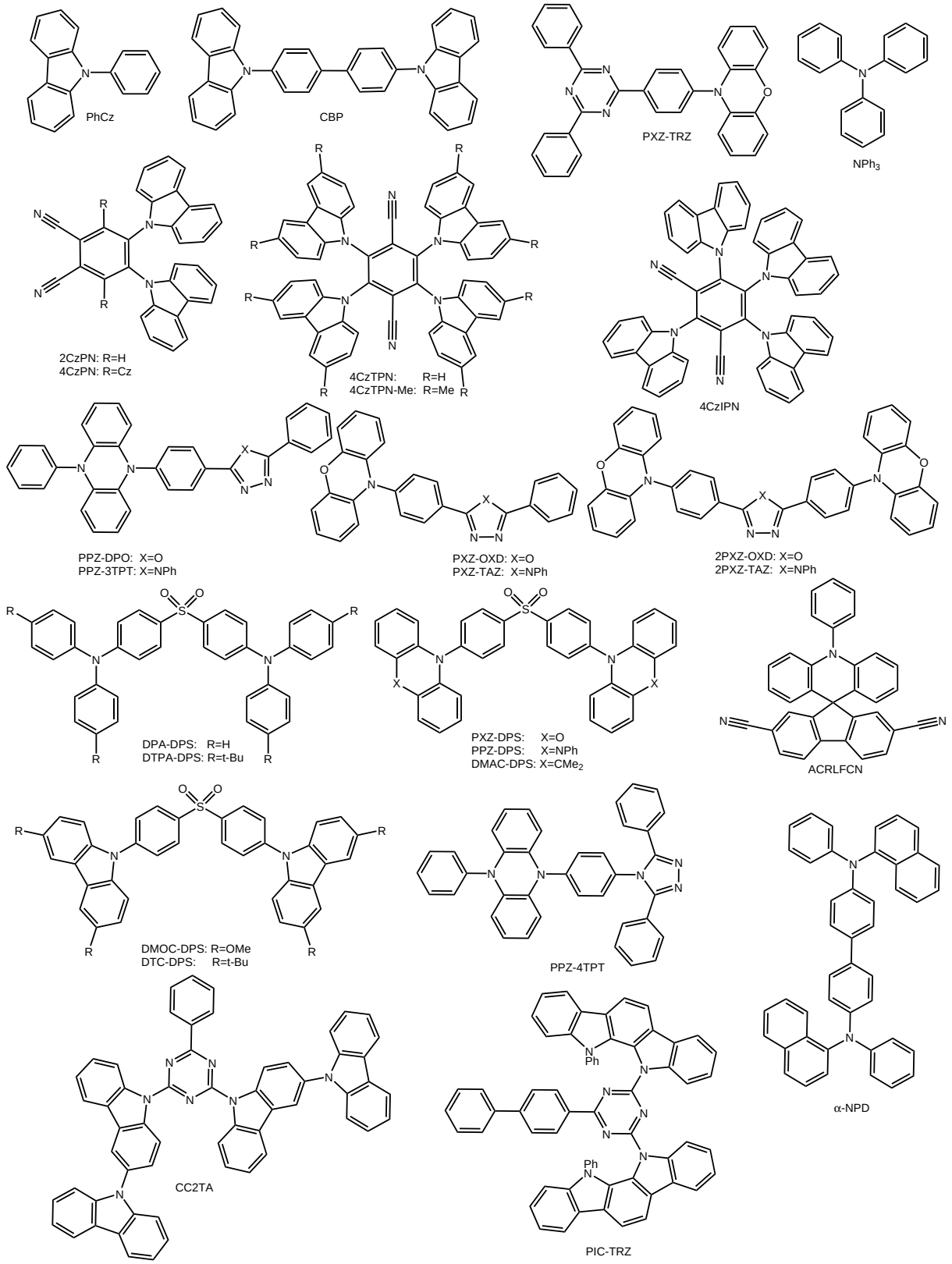

Figure S1: Structures of all the molecules in the test-set.[S1–S4]

3 Qualitative Comparison with Experiment

Table S1: Coefficient of correlation (r) between experimental values and calculated numbers. * Protocol C with LC-ωPBE originally had abnormally small $r = 0.38$ due to a single outlier data point (NPh_3). Deleting it increases r to 0.89.

Parameter	PBE	B3LYP	PBE0	LC-ωPBE
E_{abs} (Protocols A and B)	0.77	0.83	0.83	0.87
E_{abs} (Protocols C and D)	0.78	0.90	0.83	0.85
E_{em} (Protocol A)	0.95	0.97	0.96	0.89
E_{em} (Protocol B)	0.92	0.96	0.96	0.86
E_{em} (Protocol C)	0.87	0.90	0.92	0.89*
E_{em} (Protocol D)	0.87	0.84	0.89	0.88
$E_{\text{0-0}}$(Protocol A)	0.93	0.97	0.97	0.94
$E_{\text{0-0}}$(Protocol B)	0.91	0.96	0.96	0.95
$E_{\text{0-0}}$(Protocol C)	0.92	0.95	0.96	0.93
$E_{\text{0-0}}$(Protocol D)	0.92	0.91	0.94	0.92
$\log(\Delta E_{\mathrm{ST}})$ (Protocol A)	0.67	0.70	0.80	0.82
$\log(\Delta E_{\mathrm{ST}})$ (Protocol B)	0.57	0.78	0.71	0.70
$\log(\Delta E_{\mathrm{ST}})$ (Protocol C)	0.64	0.71	0.78	0.65
$\log(\Delta E_{\mathrm{ST}})$ (Protocol D)	0.54	0.67	0.72	0.58

4 PBE Functional Calculations

Table S2: E_{abs} from PBE functional in eV. For Protocols A/B, RMS error is 1.38 eV and mean error −1.31 eV, while Protocols C/D have RMS error 0.69 eV and mean error −0.64 eV.

Compound	Expt.	Prot. A/B	Prot. C/D
2CzPN	3.19	2.01	2.68
4CzPN	2.82	1.61	2.23
4CzTPN-Me	2.49	1.40	2.09
4CzTPN	2.61	1.49	1.97
PIC-TRZ	3.35	1.90	2.54
ACRFLCN	3.05	1.71	3.01
a-NPD	3.31	2.26	2.46
PXZ-TAZ	3.33	1.85	2.73
DPA-DPS	3.53	2.80	2.78
PXZ-OXD	3.18	1.36	2.59
DTC-DPS	3.62	2.47	2.87
CBP	3.80	2.70	3.54
CC2TA	3.64	1.79	2.76
DMAC-DPS	3.38	1.88	2.61
2PXZ-OXD	3.12	1.19	2.05
DTPA-DPS	3.47	2.75	2.71
NPh_3	3.74	3.30	3.36
PhCz	3.66	3.39	3.49
4CzIPN	2.85	1.66	2.16
2PXZ-TAZ	3.30	1.70	2.64
PXZ-DPS	3.13	1.54	2.29
PPZ-4TPT	3.34	1.68	2.42
DMOC-DPS	3.35	2.20	2.60
PPZ-DPS	2.76	1.20	1.92
PXZ-TRZ	2.73	1.13	2.65
PPZ-DPO	2.78	0.96	2.17
PPZ-3TPT	3.34	1.47	2.33

Table S3: E_{em} from PBE functional in eV. Protocol A has RMS error 0.81 eV and mean error −0.75 eV; Protocol B has RMS error 1.48 eV and mean error −1.45 eV; Protocol C has RMS error 0.53 eV and mean error −0.49 eV; and Protocol D has RMS error 0.52 eV and mean error −0.48 eV.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	2.63	2.01	1.06	2.35	2.38
4CzPN	2.38	1.61	0.80	1.81	1.81
4CzTPN-Me	2.22	1.40	0.77	1.56	1.80
4CzTPN	2.32	1.49	0.85	1.55	1.56
PIC-TRZ	2.52	1.90	1.14	2.12	2.14
ACRFLCN	2.55	1.71	1.42	2.49	2.35
a-NPD	2.87	2.26	1.44	2.10	2.09
PXZ-TAZ	2.72	1.85	1.19	2.18	2.15
DPA-DPS	3.09	2.80	1.62	2.50	2.50
PXZ-OXD	2.50	1.36	0.97	2.09	2.07
DTC-DPS	3.07	2.47	1.49	2.62	2.59
CBP	3.40	2.70	2.09	2.50	2.47
CC2TA	2.63	1.79	1.13	2.30	2.35
DMAC-DPS	2.70	1.88	1.26	2.28	2.29
2PXZ-OXD	2.47	1.19	0.81	1.78	1.77
DTPA-DPS	2.96	2.75	1.52	2.41	2.41
NPh_3	3.46	3.30	2.43	3.05	3.14
PhCz	3.43	3.39	3.18	3.26	3.21
4CzIPN	2.48	1.66	1.00	1.81	1.80
2PXZ-TAZ	2.68	1.70	1.05	1.91	1.89
PXZ-DPS	2.45	1.54	0.81	1.96	1.97
PPZ-4TPT	2.50	1.68	0.97	2.05	2.05
DMOC-DPS	2.79	2.20	1.04	2.42	2.42
PPZ-DPS	2.15	1.20	0.46	1.61	1.61
PXZ-TRZ	2.27	1.13	0.79	2.11	2.12
PPZ-DPO	2.15	0.96	0.56	1.84	1.83
PPZ-3TPT	2.35	1.47	0.77	1.97	1.96

Table S4: E_{0-0} from PBE functional in eV. Experimental data was unavailable for a few of the molecules, and thus the corresponding slots have been left blank. Protocol A has RMS error 1.00 eV and mean error −0.95 eV; Protocol B has RMS error 1.30 eV and mean error −1.25 eV; Protocol C has RMS error 0.56 eV and mean error −0.54 eV; and Protocol D has RMS error 0.55 eV and mean error −0.52 eV.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	2.94	2.01	1.55	2.54	2.57
4CzPN	2.60	1.61	1.40	2.03	2.02
4CzTPN-Me	2.33	1.40	1.13	1.72	1.96
4CzTPN	2.43	1.49	1.26	1.75	1.75
PIC-TRZ	2.91	1.90	1.55	2.36	2.39
ACRFLCN	2.83	1.71	1.59	2.67	2.55
a-NPD	3.10	2.26	1.84	2.29	2.30
PXZ-TAZ		1.85	1.48	2.42	2.42
DPA-DPS	3.28	2.80	2.28	2.64	2.65
PXZ-OXD		1.36	1.18	2.26	2.27
DTC-DPS	3.34	2.47	2.08	2.75	2.74
CBP	3.54	2.70	2.43	2.73	2.76
CC2TA	3.15	1.79	1.52	2.55	2.57
DMAC-DPS	3.00	1.88	1.63	2.45	2.47
2PXZ-OXD		1.19	1.04	1.92	1.93
DTPA-DPS	3.19	2.75	2.18	2.56	2.56
NPh_3	3.60	3.30	2.96	3.20	3.35
PhCz	3.58	3.39	3.40	3.36	3.45
4CzIPN	2.63	1.66	1.48	2.00	1.97
2PXZ-TAZ		1.70	1.34	2.11	2.11
PXZ-DPS	2.73	1.54	1.26	2.15	2.15
PPZ-4TPT	2.80	1.68	1.31	2.23	2.24
DMOC-DPS	3.12	2.20	1.69	2.52	2.51
PPZ-DPS	2.40	1.20	0.87	1.77	1.76
PXZ-TRZ	2.53	1.13	0.97	2.23	2.25
PPZ-DPO	2.40	0.96	0.77	2.00	2.00
PPZ-3TPT	2.65	1.47	1.07	2.14	2.15
r^2		0.87	0.83	0.85	0.84

Table S5: ΔE_{ST} from PBE functional in meV. Experimental data was unavailable for a few of the molecules, and thus the corresponding slots have been left blank. Some of the calculated numbers were negative, and thus were excluded from the log error calculation. Protocol A has log RMS error is 0.92 and log mean error -0.74; Protocol B has log RMS error 1.45 and log mean error -1.34; Protocol C has log RMS error 0.73 and log mean error -0.55; and Protocol D has log RMS error 0.49 and log mean error -0.34.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	310	163	9	202	225
4CzPN	150	81	8	13	-1
4CzTPN-Me	90	50	9	-18	223
4CzTPN	90	71	11	-10	-8
PIC-TRZ	180	34	26	64	92
ACRFLCN	240	6	8	342	228
a-NPD	730	140	15	124	136
PXZ-TAZ		6	4	167	173
DPA-DPS	520	295	26	114	117
PXZ-OXD		5	4	178	192
DTC-DPS	360	119	2	81	76
CBP	710	177	118	248	276
CC2TA	200	13	23	62	81
DMAC-DPS	90	6	2	1	25
2PXZ-OXD		4	3	80	95
DTPA-DPS	460	278	32	80	83
NPh_3	570	400	171	228	383
PhCz	550	402	466	291	382
4CzIPN	100	69	11	14	-16
2PXZ-TAZ		4	3	76	77
PXZ-DPS	80	5	2	6	10
PPZ-4TPT	420	10	3	142	149
DMOC-DPS	240	109	1	63	57
PPZ-DPS	90	5	2	-5	-17
PXZ-TRZ	60	4	4	94	109
PPZ-DPO	90	4	3	106	108
PPZ-3TPT	270	5	3	122	126

5 B3LYP Functional Calculations

Table S6: E_{abs} from B3LYP functional in eV. The numbers in brackets for Protocols C/D are from the cc-pVTZ basis set (some calculations crashed for a few of the larger molecules, leading to blanks). The larger basis introduces an RMS red-shift of about 0.08 eV for both protocols, which however does not affect the overall conclusions. For Protocols A/B, RMS error is 0.57 eV and mean error −0.45 eV, while Protocols C/D have RMS error 0.18 eV and mean error −0.06 eV. All the reported errors correspond to the 6-31G* calculations alone.

Compound	Expt.	Prot. A/B	Prot. C/D
2CzPN	3.19	2.84	3.16 (3.14)
4CzPN	2.82	2.47	2.74 (2.72)
4CzTPN-Me	2.49	2.21	2.44 (2.40)
4CzTPN	2.61	2.26	2.47 (2.43)
PIC-TRZ	3.35	2.82	3.24
ACRFLCN	3.05	2.55	3.25 (3.17)
a-NPD	3.31	3.07	3.22 (3.14)
PXZ-TAZ	3.33	2.74	3.33 (3.27)
DPA-DPS	3.53	3.53	3.52 (3.42)
PXZ-OXD	3.18	2.31	3.12 (3.07)
DTC-DPS	3.62	3.31	3.55
CBP	3.80	3.56	3.68 (3.60)
CC2TA	3.64	2.92	3.45
DMAC-DPS	3.38	2.75	3.27 (3.19)
2PXZ-OXD	3.12	2.21	2.79 (2.77)
DTPA-DPS	3.47	3.47	3.48
NPh_3	3.74	3.93	3.92 (3.69)
PhCz	3.66	4.04	4.02 (3.89)
4CzIPN	2.85	2.50	2.65 (2.64)
2PXZ-TAZ	3.30	2.63	3.28 (3.22)
PXZ-DPS	3.13	2.46	2.96 (2.89)
PPZ-4TPT	3.34	2.53	2.95 (2.85)
DMOC-DPS	3.35	3.10	3.34 (3.26)
PPZ-DPS	2.76	2.05	2.75
PXZ-TRZ	2.73	2.10	2.97 (2.93)
PPZ-DPO	2.78	1.90	2.68 (2.63)
PPZ-3TPT	3.34	2.34	2.89 (2.81)

Table S7: E_{em} from B3LYP functional in eV. The labels R and U for Protocol D describes whether the triplet geometries were obtained via RODFT or UODFT respectively. The numbers in brackets for Protocols C and D are from the cc-pVTZ basis set (some calculations crashed for a few of the larger molecules, leading to blanks). The larger basis introduces an RMS red-shift of about 0.07 eV for both protocols, which however does not affect the overall conclusions. Protocol A has RMS error 0.25 eV and mean error 0.11 eV; Protocol B has RMS error 0.65 eV and mean error −0.62 eV; Protocol C has RMS error 0.19 eV and mean error −0.001 eV; and Protocol D has RMS error 0.22 eV and mean error 0.02 eV with RODFT; and RMS error 0.23 eV with mean error 0.01 eV when used with UODFT. All the reported errors correspond to the 6-31G* calculations alone.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D (R)	Prot. D (U)
2CzPN	2.63	2.84	1.85	2.66 (2.65)	2.79 (2.76)	2.78
4CzPN	2.38	2.47	1.55	2.11 (2.10)	2.25 (2.24)	2.25
4CzTPN-Me	2.22	2.21	1.41	1.87	2.07 (2.03)	2.00
4CzTPN	2.32	2.26	1.50	1.98 (1.96)	2.01 (1.99)	2.00
PIC-TRZ	2.52	2.82	1.79	2.54 (2.52)	2.70	2.72
ACRFLCN	2.55	2.55	2.12	2.77 (2.71)	2.83 (2.76)	2.82
a-NPD	2.87	3.07	2.19	2.72 (2.64)	2.62 (2.55)	2.62
PXZ-TAZ	2.72	2.74	2.10	2.72 (2.66)	2.63 (2.57)	2.62
DPA-DPS	3.09	3.53	2.59	3.11 (3.02)	3.10 (3.01)	3.10
PXZ-OXD	2.5	2.31	1.82	2.58 (2.53)	2.49 (2.44)	2.47
DTC-DPS	3.07	3.31	2.52	3.21	3.17	3.17
CBP	3.40	3.56	2.87	2.99 (2.91)	2.87 (2.79)	2.85
CC2TA	2.63	2.92	1.87	2.66	2.74	2.69
DMAC-DPS	2.70	2.75	2.27	2.90 (2.84)	3.27 (3.18)	3.29
2PXZ-OXD	2.47	2.21	1.70	2.37 (2.35)	2.28 (2.26)	2.26
DTPA-DPS	2.96	3.47	2.46	3.03	3.04	3.04
NPh_3	3.46	3.93	3.13	3.56 (3.39)	3.51 (3.40)	3.51
PhCz	3.43	4.04	3.74	3.75 (3.65)	3.75 (3.64)	3.68
4CzIPN	2.48	2.50	1.70	2.20 (2.19)	2.26 (2.25)	2.25
2PXZ-TAZ	2.68	2.63	1.99	2.54 (2.51)	2.47 (2.43)	2.46
PXZ-DPS	2.45	2.46	1.81	2.52 (2.46)	2.53 (2.46)	2.53
PPZ-4TPT	2.50	2.53	1.88	2.50 (2.42)	2.49 (2.40)	2.49
DMOC-DPS	2.79	3.10	2.16	3.00 (2.91)	3.00 (2.92)	3.00
PPZ-DPS	2.15	2.05	1.45	2.23	2.29	2.29
PXZ-TRZ	2.27	2.10	1.62	2.51 (2.47)	2.51 (2.46)	2.50
PPZ-DPO	2.15	1.90	1.38	2.25 (2.21)	2.25 (2.21)	2.25
PPZ-3TPT	2.35	2.34	1.66	2.43 (2.37)	2.43 (2.37)	2.43

Table S8: E_{0-0} from B3LYP functional in eV. Experimental data was unavailable for a few of the molecules, and thus the corresponding slots have been left blank. The labels R and U for Protocol D describes whether the triplet geometries were obtained via RODFT or UODFT respectively. The numbers in brackets for Protocols C and D are from the cc-pVTZ basis set (some calculations crashed for a few of the larger molecules, leading to blanks). The larger basis introduces an RMS shift of about 0.05 eV for both protocols, which however does not affect the overall conclusions. Protocol A has RMS error 0.26 eV and mean error −0.10 eV; Protocol B has RMS error 0.52 eV and mean error −0.46 eV; Protocol C has RMS error 0.14 eV and mean error 0.02 eV; Protocol D has RMS error 0.23 eV and mean error 0.10 eV with RODFT; and RMS error 0.24 eV with mean error 0.09 eV when used with UODFT. All the reported errors correspond to the 6-31G* calculations alone.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D (R)	Prot. D (U)
2CzPN	2.94	2.84	2.28	2.95 (2.96)	3.03 (3.04)	3.04
4CzPN	2.60	2.47	2.04	2.46 (2.45)	2.49 (2.51)	2.49
4CzTPN-Me	2.33	2.21	1.81	2.20	2.26	2.22
4CzTPN	2.43	2.26	1.9	2.24 (2.23)	2.24 (2.25)	2.24
PIC-TRZ	2.91	2.82	2.35	2.91	3.09	3.16
ACRFLCN	2.83	2.55	2.34	3.02 (2.97)	3.17 (3.12)	3.19
a-NPD	3.10	3.07	2.65	2.97 (2.90)	3.01 (2.94)	3.02
PXZ-TAZ		2.74	2.41	3.03 (3.01)	3.06 (3.05)	3.07
DPA-DPS	3.28	3.53	3.11	3.33 (3.26)	3.39 (3.33)	3.39
PXZ-OXD		2.31	2.07	2.82 (2.81)	2.85 (2.85)	2.86
DTC-DPS	3.34	3.31	2.91	3.41	3.48	3.49
CBP	3.54	3.56	3.24	3.30 (3.24)	3.41 (3.26)	3.32
CC2TA	3.15	2.92	2.43	3.09	3.09	3.08
DMAC-DPS	3.00	2.75	2.54	3.11 (3.06)	3.66 (3.63)	3.69
2PXZ-OXD		2.21	1.95	2.58 (2.59)	2.61 (2.63)	2.61
DTPA-DPS	3.19	3.47	3.02	3.27	3.32	3.33
NPh_3	3.60	3.93	3.65	3.74 (3.60)	3.86 (3.78)	3.86
PhCz	3.58	4.04	3.9	3.88 (3.81)	4.14 (4.05)	4.08
4CzIPN	2.63	2.5	2.12	2.46 (2.45)	2.46 (2.47)	2.45
2PXZ-TAZ		2.63	2.31	2.84 (2.85)	2.88 (2.89)	2.89
PXZ-DPS	2.73	2.46	2.17	2.78 (2.75)	2.78 (2.76)	2.78
PPZ-4TPT	2.80	2.53	2.22	2.73 (2.66)	2.74 (2.66)	2.74
DMOC-DPS	3.12	3.1	2.59	3.21 (3.13)	3.27 (3.21)	3.27
PPZ-DPS	2.40	2.05	1.78	2.51	2.52	2.52
PXZ-TRZ	2.53	2.1	1.87	2.73 (2.71)	2.76 (2.75)	2.76
PPZ-DPO	2.40	1.9	1.65	2.47 (2.44)	2.47 (2.44)	2.47
PPZ-3TPT	2.65	2.34	1.99	2.66 (2.61)	2.67 (2.62)	2.67

Table S9: ΔE_{ST} from B3LYP functional in eV. The labels R and U for Protocols C and D describes whether the T_1 state was obtained via RODFT or UODFT respectively. Experimental data was unavailable for a few of the molecules, and thus the corresponding slots have been left blank. Some of the calculated numbers were negative, and thus were excluded from the log error calculation. The numbers in brackets for Restricted calculations with Protocols C and D are from the cc-pVTZ basis set (some calculations crashed for a few of the larger molecules, leading to blanks). The larger basis introduces some shift which however does not affect the overall conclusions. Protocol A has log RMS error is 0.68 and log mean error -0.37; Protocol B has log RMS error 1.04 and log mean error -0.85; Protocol C has log RMS error 0.35 and log mean error -0.20 with RODFT; and log RMS error 0.16 and log mean error 0.00 with UODFT. Finally, Protocol D has log RMS error 0.35 and log mean error -0.03 with RODFT, and log RMS error 0.31 and log mean error 0.12 with UODFT. All the reported errors correspond to the 6-31G* calculations alone.

Compound	Expt.	Prot. A	Prot. B	Prot. C (R)	Prot. C (U)	Prot. D (R)	Prot. D (U)
2CzPN	310	340	10	284 (274)	394	357 (352)	477
4CzPN	150	179	10	13 (-26)	71	48 (41)	105
4CzTPN-Me	90	107	10	-13	49	47	64
4CzTPN	90	129	-3	52 (50)	108	44 (67)	99
PIC-TRZ	180	78	28	129	198	308	448
ACRFLCN	240	8	10	354 (313)	439	500 (468)	613
a-NPD	730	582	513	370 (365)	430	411 (408)	479
PXZ-TAZ		11	7	353 (333)	413	382 (372)	447
DPA-DPS	520	636	395	341 (320)	403	407 (397)	472
PXZ-OXD		8	6	324 (304)	387	356 (347)	424
DTC-DPS	360	337	80	265	324	341	404
CBP	710	596	753	497 (487)	570	610 (505)	597
CC2TA	200	66	55	53	139	53	135
DMAC-DPS	90	9	9	79 (53)	146	631 (614)	727
2PXZ-OXD		20	6	175 (167)	224	202 (208)	259
DTPA-DPS	460	606	338	307	369	363	428
NPh_3	570	745	699	460 (359)	540	582 (536)	661
PhCz	550	852	1007	599 (571)	702	863 (813)	908
4CzIPN	100	126	10	35 (23)	92	27 (42)	83
2PXZ-TAZ		9	6	215 (211)	267	247 (255)	315
PXZ-DPS	80	38	8	20 (-21)	66	18 (-11)	62
PPZ-4TPT	420	57	6	239 (244)	289	254 (244)	306
DMOC-DPS	240	280	6	177 (162)	232	239 (244)	301
PPZ-DPS	90	7	7	131	178	134	181
PXZ-TRZ	60	6	5	197 (176)	255	228 (220)	287
PPZ-DPO	90	6	5	135 (132)	179	141 (140)	185
PPZ-3TPT	270	8	5	195 (196)	241	207 (205)	255

6 PBE0 Functional Calculations

Table S10: E_{abs} from PBE0 functional in eV. For Protocols A/B, RMS error is 0.43 eV and mean error −0.28 eV, while Protocols C/D have RMS error 0.28 eV and mean error 0.11 eV.

Compound	Expt.	Prot. A/B	Prot. C/D
2CzPN	3.19	3.03	3.31
4CzPN	2.82	2.66	2.83
4CzTPN-Me	2.49	2.41	2.61
4CzTPN	2.61	2.45	3.31
PIC-TRZ	3.35	3.03	3.35
ACRFLCN	3.05	2.73	3.29
a-NPD	3.31	3.22	3.36
PXZ-TAZ	3.33	2.90	3.41
DPA-DPS	3.53	3.63	3.63
PXZ-OXD	3.18	2.50	3.20
DTC-DPS	3.62	3.47	3.67
CBP	3.80	3.73	4.73
CC2TA	3.64	3.16	3.66
DMAC-DPS	3.38	2.91	3.35
2PXZ-OXD	3.12	2.39	3.12
DTPA-DPS	3.47	3.57	3.56
NPh_3	3.74	4.05	4.04
PhCz	3.66	4.16	4.16
4CzIPN	2.85	2.70	2.78
2PXZ-TAZ	3.30	2.81	3.38
PXZ-DPS	3.13	2.65	3.04
PPZ-4TPT	3.34	2.69	3.04
DMOC-DPS	3.35	3.29	3.47
PPZ-DPS	2.76	2.20	2.80
PXZ-TRZ	2.73	2.28	3.02
PPZ-DPO	2.78	2.09	2.76
PPZ-3TPT	3.34	2.51	2.97

Table S11: E_{em} from PBE0 functional in eV. Protocol A has RMS error 0.35 eV and mean error 0.28 eV; Protocol B has RMS error 0.49 eV and mean error −0.44 eV; Protocol C has RMS error 0.20 eV and mean error 0.10 eV; and Protocol D has RMS error 0.23 eV and mean error 0.11 eV.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	2.63	3.03	2.00	2.73	2.89
4CzPN	2.38	2.66	1.80	2.36	2.45
4CzTPN-Me	2.22	2.41	1.57	2.09	2.13
4CzTPN	2.32	2.45	1.66	2.09	2.12
PIC-TRZ	2.52	3.03	2.03	2.62	2.88
ACRFLCN	2.55	2.73	2.28	2.94	2.84
a-NPD	2.87	3.22	2.40	2.83	2.74
PXZ-TAZ	2.72	2.90	2.29	2.84	2.74
DPA-DPS	3.09	3.63	2.77	3.21	3.20
PXZ-OXD	2.50	2.50	2.01	2.68	2.59
DTC-DPS	3.07	3.47	2.63	3.32	3.29
CBP	3.40	3.73	3.10	3.13	2.99
CC2TA	2.63	3.16	2.11	2.83	2.83
DMAC-DPS	2.70	2.91	2.39	2.94	2.91
2PXZ-OXD	2.47	2.39	1.90	2.49	2.39
DTPA-DPS	2.96	3.57	2.57	3.11	3.13
NPh_3	3.46	4.05	3.32	3.51	3.62
PhCz	3.43	4.16	3.94	3.88	3.91
4CzIPN	2.48	2.70	1.86	2.37	2.43
2PXZ-TAZ	2.68	2.81	2.18	2.67	2.62
PXZ-DPS	2.45	2.65	1.95	2.59	2.60
PPZ-4TPT	2.50	2.69	2.05	2.57	2.57
DMOC-DPS	2.79	3.29	2.35	3.11	3.30
PPZ-DPS	2.15	2.20	1.55	2.21	2.18
PXZ-TRZ	2.27	2.28	1.79	2.55	2.57
PPZ-DPO	2.15	2.09	1.57	2.31	2.32
PPZ-3TPT	2.35	2.51	1.84	2.50	2.51

Table S12: E_{0-0} from PBE0 functional in eV. Experimental data was unavailable for a few of the molecules, and thus the corresponding slots have been left blank. Protocol A has RMS error 0.23 eV and mean error 0.07 eV; Protocol B has RMS error 0.37 eV and mean error −0.28 eV; Protocol C has RMS error 0.17 eV and mean error 0.11 eV; and Protocol D has RMS error 0.27 eV and mean error 0.19 eV.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	2.94	3.03	2.48	3.05	3.14
4CzPN	2.60	2.66	2.29	2.63	2.69
4CzTPN-Me	2.33	2.41	1.99	2.33	2.33
4CzTPN	2.43	2.45	2.10	2.34	2.36
PIC-TRZ	2.91	3.03	2.55	2.99	3.32
ACRFLCN	2.83	2.73	2.51	3.20	3.22
a-NPD	3.10	3.22	2.83	3.10	3.15
PXZ-TAZ		2.90	2.59	3.12	3.17
DPA-DPS	3.28	3.63	3.26	3.43	3.51
PXZ-OXD		2.50	2.26	2.90	2.96
DTC-DPS	3.34	3.47	3.09	3.51	3.64
CBP	3.54	3.73	3.46	3.44	3.46
CC2TA	3.15	3.16	2.66	3.21	3.21
DMAC-DPS	3.00	2.91	2.67	3.16	3.32
2PXZ-OXD		2.39	2.14	2.69	2.74
DTPA-DPS	3.19	3.57	3.15	3.35	3.43
NPh_3	3.60	4.05	3.84	3.84	3.99
PhCz	3.58	4.16	4.09	4.01	4.31
4CzIPN	2.63	2.70	2.35	2.60	2.62
2PXZ-TAZ		2.81	2.48	2.95	3.03
PXZ-DPS	2.73	2.65	2.30	2.84	2.85
PPZ-4TPT	2.80	2.69	2.37	2.80	2.83
DMOC-DPS	3.12	3.29	2.77	3.31	3.51
PPZ-DPS	2.40	2.20	1.90	2.45	2.44
PXZ-TRZ	2.53	2.28	2.04	2.76	2.81
PPZ-DPO	2.40	2.09	1.83	2.53	2.55
PPZ-3TPT	2.65	2.51	2.16	2.73	2.77

Table S13: ΔE_{ST} from PBE0 functional in meV. Experimental data was unavailable for a few of the molecules, and thus the corresponding slots have been left blank. Protocol A has log RMS error is 0.45 and log mean error −0.09; Protocol B has log RMS error 0.85 and log mean error −0.60; Protocol C has log RMS error 0.27 and log mean error −0.07; and Protocol D has log RMS error 0.32 and log mean error 0.04.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	310	477	12	316	410
4CzPN	150	276	51	130	190
4CzTPN-Me	90	154	60	65	71
4CzTPN	90	177	58	92	105
PIC-TRZ	180	215	38	158	486
ACRFLCN	240	134	13	468	483
a-NPD	730	805	814	445	496
PXZ-TAZ		144	203	388	438
DPA-DPS	520	767	587	423	504
PXZ-OXD		11	9	349	403
DTC-DPS	360	460	255	332	457
CBP	710	785	1028	573	599
CC2TA	200	181	66	81	82
DMAC-DPS	90	13	14	141	294
2PXZ-OXD		10	8	204	249
DTPA-DPS	460	727	510	386	465
NPh_3	570	936	960	529	679
PhCz	550	1062	1278	676	980
4CzIPN	100	213	29	76	92
2PXZ-TAZ		45	9	261	344
PXZ-DPS	80	98	11	29	40
PPZ-4TPT	420	243	9	270	304
DMOC-DPS	240	397	9	318	517
PPZ-DPS	90	10	10	12	11
PXZ-TRZ	60	8	8	202	254
PPZ-DPO	90	9	7	136	153
PPZ-3TPT	270	51	8	213	245

7 LC-ωPBE Functional Calculations

Table S14: E_{abs} from LC-ωPBE functional in eV. For Protocols A/B, RMS error is 0.74 eV and mean error 0.72 eV, while Protocols C/D have RMS error 0.82 eV and mean error 0.75 eV.

Compound	Expt.	Prot. A/B	Prot. C/D
2CzPN	3.19	3.98	3.85
4CzPN	2.82	3.65	3.52
4CzTPN-Me	2.49	3.45	3.45
4CzTPN	2.61	3.36	3.44
PIC-TRZ	3.35	4.13	4.22
ACRFLCN	3.05	4.21	3.74
a-NPD	3.31	4.01	4.64
PXZ-TAZ	3.33	4.02	4.06
DPA-DPS	3.53	4.22	4.80
PXZ-OXD	3.18	3.80	3.54
DTC-DPS	3.62	4.34	4.35
CBP	3.80	4.47	4.93
CC2TA	3.64	4.34	4.38
DMAC-DPS	3.38	4.02	4.48
2PXZ-OXD	3.12	3.74	3.47
DTPA-DPS	3.47	4.19	4.76
NPh_3	3.74	4.59	4.81
PhCz	3.66	4.48	4.76
4CzIPN	2.85	3.58	3.58
2PXZ-TAZ	3.30	4.08	3.84
PXZ-DPS	3.13	3.81	3.59
PPZ-4TPT	3.34	3.58	3.58
DMOC-DPS	3.35	4.09	4.17
PPZ-DPS	2.76	3.47	3.16
PXZ-TRZ	2.73	3.71	3.34
PPZ-DPO	2.78	3.49	3.15
PPZ-3TPT	3.34	3.58	3.58

Table S15: E_{em} from LC-ωPBE functional in eV. A few of the S_1 optimizations for Protocol C failed to converge, and the corresponding spaces have been left blank. Protocol A has RMS error 1.28 eV and mean error 1.29 eV; Protocol B has RMS error 0.66 eV and mean error 0.63 eV; Protocol C has RMS error 0.79 eV and mean error 0.45 eV; and Protocol D has RMS error 0.85 eV and mean error 0.79 eV.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	2.63	3.98	3.32	3.10	3.43
4CzPN	2.38	3.65	3.15		3.10
4CzTPN-Me	2.22	3.45	2.82		2.87
4CzTPN	2.32	3.36	2.86		2.90
PIC-TRZ	2.52	4.13	3.75	2.91	2.99
ACRFLCN	2.55	4.21	3.56	3.17	3.13
a-NPD	2.87	4.01	3.49	3.75	3.52
PXZ-TAZ	2.72	4.02	3.19	3.24	3.34
DPA-DPS	3.09	4.22	3.82	3.67	3.85
PXZ-OXD	2.50	3.80	3.30	3.02	3.16
DTC-DPS	3.07	4.34	3.54	3.80	4.39
CBP	3.4	4.47	3.76	3.93	4.80
CC2TA	2.63	4.34	3.12		4.19
DMAC-DPS	2.70	4.02	3.30	3.14	3.77
2PXZ-OXD	2.47	3.74	3.24	3.63	3.46
DTPA-DPS	2.96	4.19	3.45	3.66	3.78
NPh_3	3.46	4.59	4.09	1.14	4.13
PhCz	3.43	4.48	4.23	4.43	4.43
4CzIPN	2.48	3.58	3.06	2.95	3.17
2PXZ-TAZ	2.68	4.08	3.17	3.83	3.30
PXZ-DPS	2.45	3.81	2.88	2.71	3.48
PPZ-4TPT	2.50	3.58	2.82	2.60	2.92
DMOC-DPS	2.79	4.09	3.31	3.53	4.08
PPZ-DPS	2.15	3.47	2.65	2.30	2.30
PXZ-TRZ	2.27	3.71	3.12	2.72	3.00
PPZ-DPO	2.15	3.49	2.93	2.53	2.53
PPZ-3TPT	2.35	3.58	2.93	2.75	2.92

Table S16: E_{0-0} from LC-ωPBE functional in eV. The blanks in the Experimental column correspond to cases where data was unavailable, while the blanks in column C resulted from convergence failure in S_1 optimization. Protocol A has RMS error 1.04 eV and mean error 1.03 eV; Protocol B has RMS error 0.82 eV and mean error 0.81 eV; Protocol C has RMS error 0.70 eV and mean error 0.66 eV; and Protocol D has RMS error 1.09 eV and mean error 1.03 eV.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	2.94	3.98	3.74	3.54	3.43
4CzPN	2.60	3.65	3.51		3.10
4CzTPN-Me	2.33	3.45	3.07		2.87
4CzTPN	2.43	3.36	3.13		2.90
PIC-TRZ	2.91	4.13	4.09	3.51	2.99
ACRFLCN	2.83	4.21	3.90	3.46	3.13
a-NPD	3.10	4.01	3.76	4.15	3.52
PXZ-TAZ		4.02	3.79	3.57	3.34
DPA-DPS	3.28	4.22	4.04	4.40	3.85
PXZ-OXD		3.80	3.56	3.29	3.16
DTC-DPS	3.34	4.34	4.19	4.09	4.39
CBP	3.54	4.47	4.17	4.37	4.80
CC2TA	3.15	4.34	3.96		4.19
DMAC-DPS	3.00	4.02	3.74	3.53	3.77
2PXZ-OXD		3.74	3.49	3.90	3.46
DTPA-DPS	3.19	4.19	4.03	3.98	3.78
NPh_3	3.60	4.59	4.58	4.16	4.13
PhCz	3.58	4.48	4.36	4.59	4.43
4CzIPN	2.63	3.58	3.42	3.31	3.17
2PXZ-TAZ		4.08	3.75	4.25	3.30
PXZ-DPS	2.73	3.81	3.44	3.19	3.48
PPZ-4TPT	2.80	3.58	3.44	3.15	2.92
DMOC-DPS	3.12	4.09	3.96	3.90	4.08
PPZ-DPS	2.40	3.47	3.12	2.78	2.30
PXZ-TRZ	2.53	3.71	3.42	3.03	3.00
PPZ-DPO	2.40	3.49	3.21	2.84	2.53
PPZ-3TPT	2.65	3.58	3.47	3.13	2.92

Table S17: ΔE_{ST} from LC-ωPBE functional in meV. The blanks in the Experimental column correspond to cases where data was unavailable, while the blanks in column C resulted from convergence failure in S_1 optimization. Some of the calculated numbers were negative, and thus were excluded from the log error calculation. Protocol A has log RMS error is 0.76 and log mean error 0.71; Protocol B has log RMS error 0.74 and log mean error 0.69; Protocol C has log RMS error 0.58 and log mean error -0.06; and Protocol D has log RMS error 0.65 and log mean error 0.25.

Compound	Expt.	Prot. A	Prot. B	Prot. C	Prot. D
2CzPN	310	1187	1292	-9	349
4CzPN	150	990	696		764
4CzTPN-Me	90	774	442		392
4CzTPN	90	698	443		496
PIC-TRZ	180	1290	1703	25	79
ACRFLCN	240	1538	1673	438	690
a-NPD	730	1562	1242	1118	1176
PXZ-TAZ		1229	1272	459	850
DPA-DPS	520	1235	1321	1204	1087
PXZ-OXD		1003	1030	324	730
DTC-DPS	360	1297	902	617	1478
CBP	710	1386	1725	1145	2123
CC2TA	200	1305	1174		1232
DMAC-DPS	90	857	512	220	1067
2PXZ-OXD		934	698	958	1014
DTPA-DPS	460	1215	1318	577	808
NPh_3	570	1432	1725	731	1200
PhCz	550	1396	1586	1053	1432
4CzIPN	100	879	976	346	688
2PXZ-TAZ		1235	1223	1142	805
PXZ-DPS	80	938	903	46	734
PPZ-4TPT	420	1040	1206	257	403
DMOC-DPS	240	1113	1305	559	1163
PPZ-DPS	90	917	883	2	6
PXZ-TRZ	60	910	900	-339	11
PPZ-DPO	90	947	974	7	7
PPZ-3TPT	270	1045	1244	252	408

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