Supporting information for

Chemical Annealing of Zinc Tetraphenylporphyrin Films: Effects on Film Morphology and Organic Photovoltaic Performance

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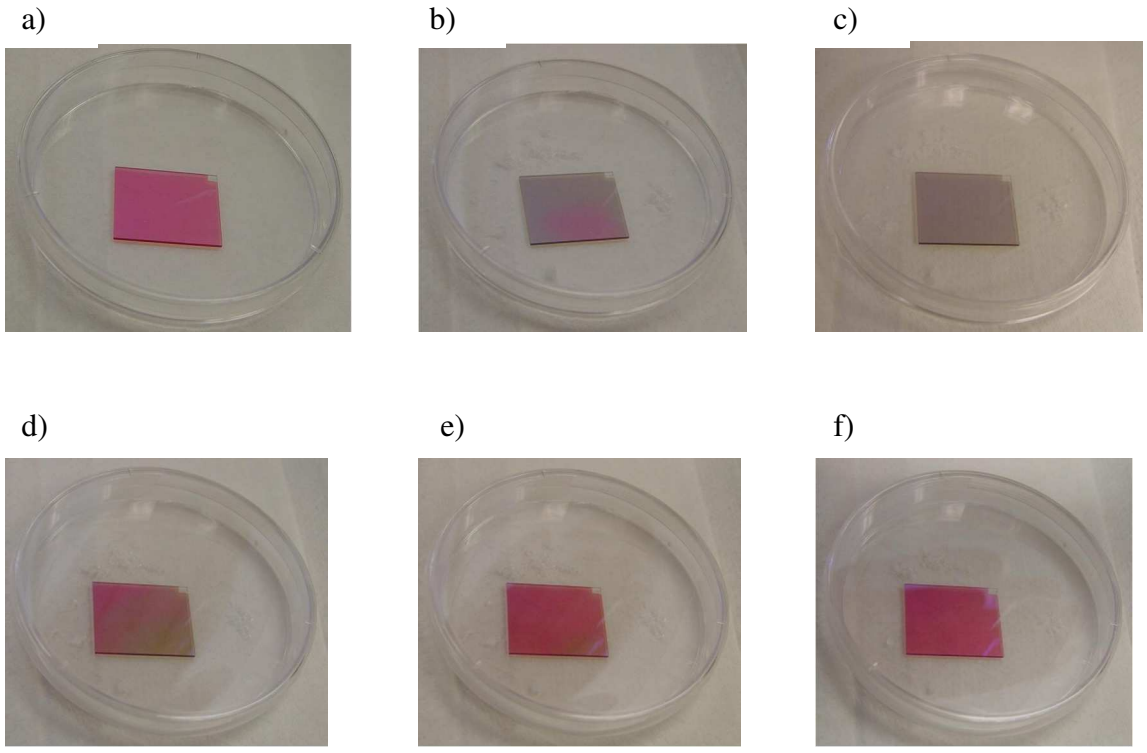


Figure S1. Digital images of the ZnTPP film (1300 Å) treated with pyz over time: a) ZnTPP; b) ZnTPP-pyz, 3 min; c) ZnTPP-pyz, 5min; d) ZnTPP-pyz, 7min; e) ZnTPP-pyz, 8min; f) ZnTPP-pyz, 15 min

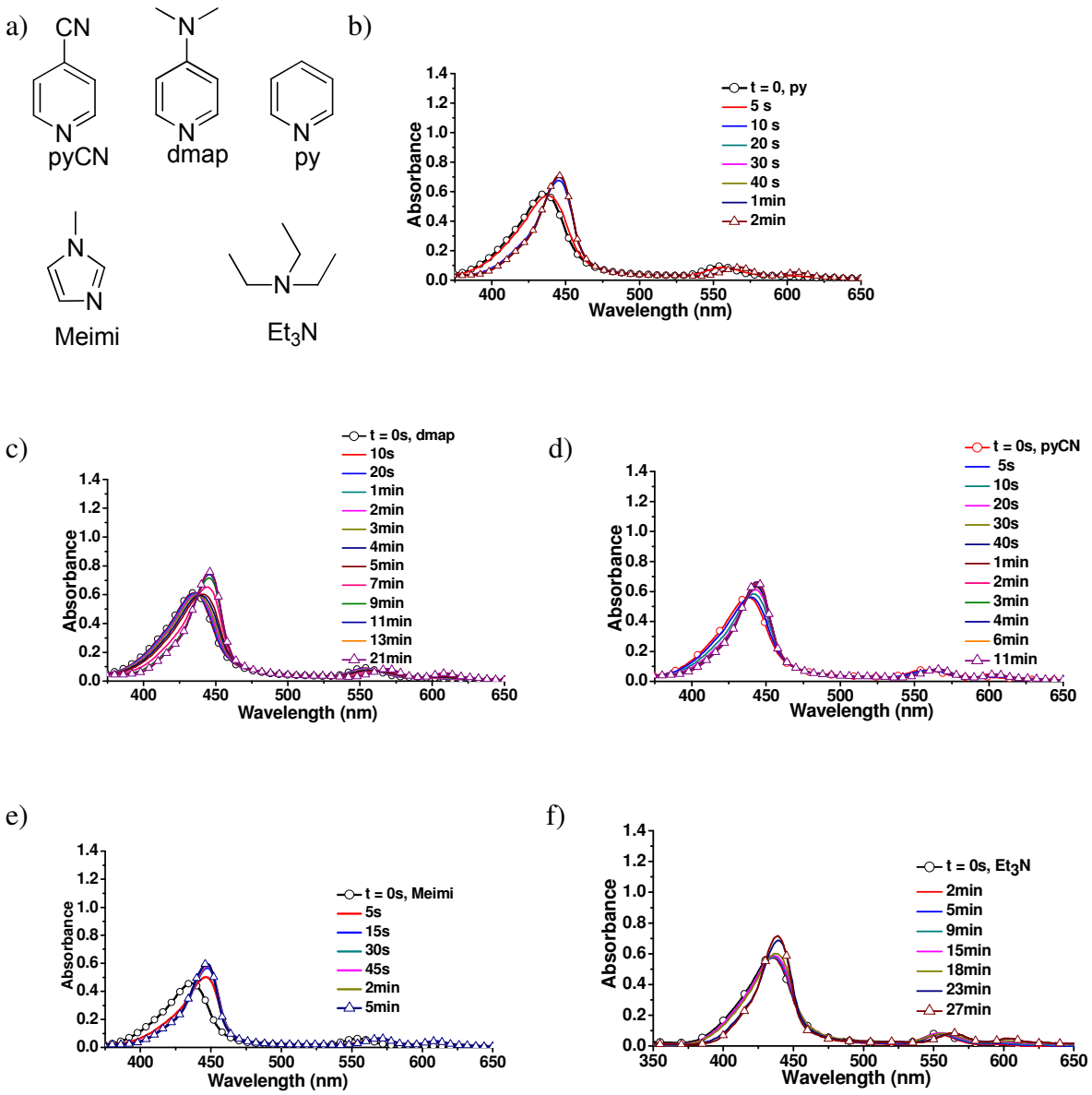
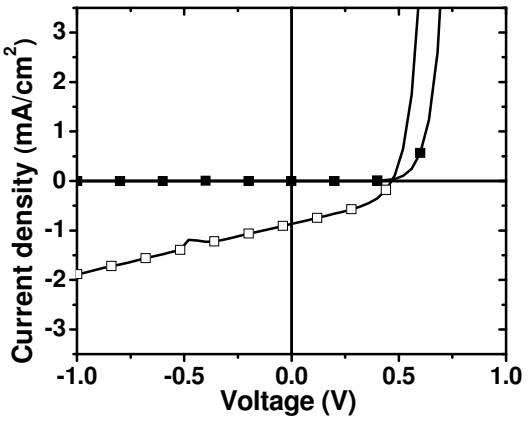


Figure S2: UV-vis spectra of ZnTPP film during chemical annealing process with different ligands. a) Abbreviations of the ligands, b) Pyridine, c) Dimethylamino Pyridine, d) Cyanopyridine, e) Methyl Imidazole and f) Triethylamine.



J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
0.87±0.02	0.46±0.01	0.41±0.01	0.17 ±0.01

Figure S3. Characteristics of device ITO/C_{60} (40 nm)/BCP (10 nm)/Al under AM 1.5G illumination.

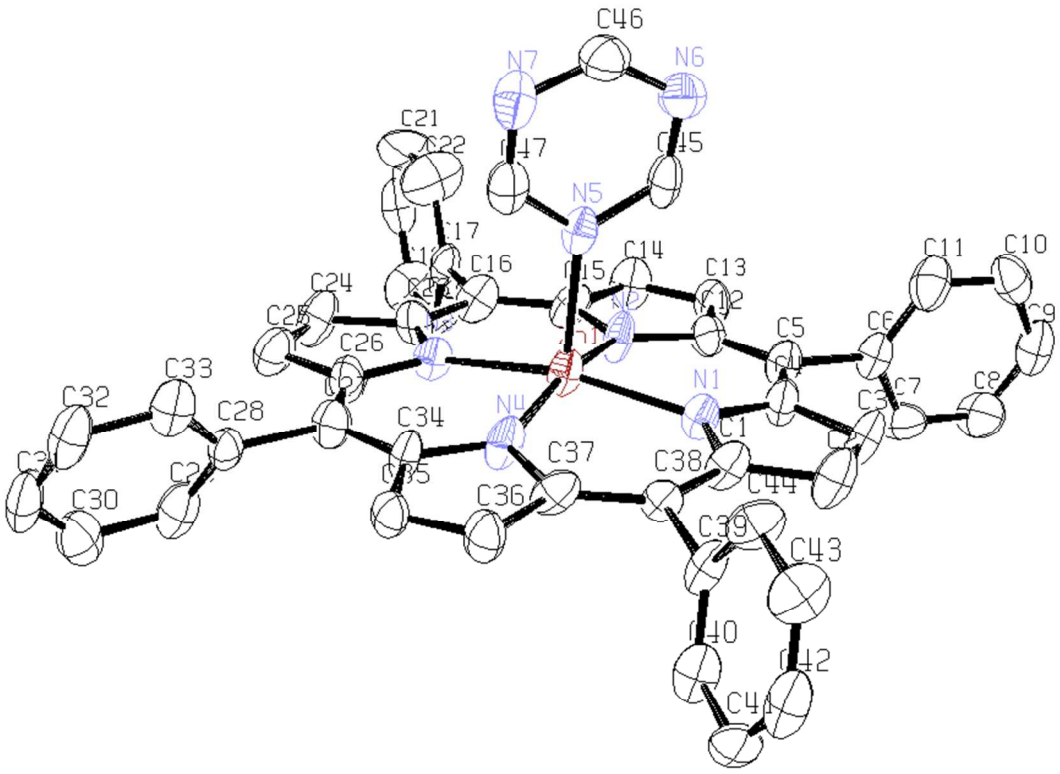


Figure S4. ORTEP diagram of ZnTPP•tz. H atoms are omitted for clarity.

Table S1. Crystallographic data for compound ZnTPP•tz.

Empirical formula	$C_{47}H_{31}N_7Zn$
Formula weight	759.16
Temperature, K	128(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	10.959(7)
b (Å)	13.245(9)
c (Å)	14.329(10)
α (deg)	87.302(12)
β (deg)	71.284(12)
γ (deg)	67.699(12)
V ($Å^3$)	1816(2)
Z	2
D_{calcd} (g/cm^3)	1.388
μ (mm^{-1})	0.722
F(000)	784
θ range	1.51 to 27.54
Reflections collected	7817
Independent reflections	2680 [R(int) = 0.0801]
Refinement method	Full-matrix least-squares on F^2
Data/restraints / parameters	7817 / 0 / 496
GOF on F^2	0.915
Final R indices[I>2σ(I)]	R1 = 0.0752, wR2 = 0.1560
R indices (all data)	R1 = 0.1778, wR2 = 0.1844

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for ZnTPP•tz. U (eq) is defined as one third of the trace of the orthogonal U^{ij} tensor.

atoms	x	y	z	U (eq)
Zn1	0.60767(10)	0.81044(7)	0.68787(6)	0.0229(3)
N1	0.5616(6)	0.6716(4)	0.7148(4)	0.0213(15)
N2	0.7179(6)	0.7491(4)	0.5441(4)	0.0243(15)
N3	0.6145(6)	0.9614(4)	0.6510(4)	0.0213(15)
N4	0.4563(6)	0.8854(4)	0.8215(4)	0.0250(15)
N5	0.7823(6)	0.7465(4)	0.7480(4)	0.0223(14)
N6	0.9688(7)	0.5951(5)	0.7741(4)	0.0286(16)
N7	0.9004(7)	0.7707(5)	0.8523(4)	0.0315(17)
C1	0.4725(8)	0.6538(5)	0.8011(4)	0.0234(18)
C2	0.4783(8)	0.5430(6)	0.7915(5)	0.030(2)
H2	0.4282	0.5091	0.8402	0.036
C3	0.5672(8)	0.4974(5)	0.7014(5)	0.028(2)
H3	0.5926	0.4249	0.6755	0.033
C4	0.6182(8)	0.5788(5)	0.6504(5)	0.0242(18)
C5	0.7083(8)	0.5658(5)	0.5523(5)	0.0245(18)
C6	0.7572(8)	0.4579(6)	0.4926(4)	0.0214(18)
C7	0.6870(8)	0.4462(6)	0.4320(5)	0.0314(19)
H7	0.6076	0.5065	0.4276	0.038
C8	0.7309(9)	0.3473(6)	0.3772(5)	0.037(2)
H8	0.6826	0.3409	0.3348	0.045
C9	0.8401(9)	0.2621(6)	0.3842(5)	0.033(2)
H9	0.8682	0.1938	0.3487	0.04
C10	0.9135(8)	0.2728(6)	0.4438(5)	0.031(2)
H10	0.9935	0.2124	0.447	0.037
C11	0.8709(9)	0.3707(6)	0.4982(5)	0.033(2)
H11	0.9208	0.3772	0.5394	0.039
C12	0.7516(8)	0.6461(5)	0.5024(5)	0.0234(18)

C13	0.8401(8)	0.6330(5)	0.4006(5)	0.0252(18)
H13	0.8782	0.5695	0.3561	0.03
C14	0.8589(8)	0.7274(5)	0.3806(5)	0.029(2)
H14	0.913	0.7427	0.3194	0.035
C15	0.7815(8)	0.8011(6)	0.4692(5)	0.0259(19)
C16	0.7709(8)	0.9106(6)	0.4779(5)	0.0259(19)
C17	0.8504(8)	0.9494(5)	0.3859(5)	0.0237(18)
C18	0.7915(9)	0.9902(6)	0.3131(5)	0.040(2)
H18	0.6991	0.9967	0.322	0.048
C19	0.8665(10)	1.0222(6)	0.2266(5)	0.040(2)
H19	0.8232	1.0523	0.1784	0.047
C20	1.0002(10)	1.0109(6)	0.2103(5)	0.035(2)
H20	1.0508	1.0313	0.1505	0.042
C21	1.0614(9)	0.9699(6)	0.2806(6)	0.049(2)
H21	1.1545	0.9627	0.2701	0.059
C22	0.9869(10)	0.9382(7)	0.3683(5)	0.050(3)
H22	1.0309	0.9088	0.4163	0.06
C23	0.6928(8)	0.9836(5)	0.5622(5)	0.0218(18)
C24	0.6782(9)	1.0963(6)	0.5693(5)	0.033(2)
H24	0.722	1.1322	0.5186	0.04
C25	0.5910(8)	1.1414(6)	0.6608(5)	0.030(2)
H25	0.5628	1.2145	0.6865	0.037
C26	0.5483(8)	1.0571(5)	0.7126(5)	0.0262(19)
C27	0.4533(8)	1.0721(5)	0.8087(5)	0.0242(19)
C28	0.3856(8)	1.1867(5)	0.8583(5)	0.0199(17)
C29	0.3035(8)	1.2692(6)	0.8165(5)	0.032(2)
H29	0.292	1.2524	0.7569	0.039
C30	0.2370(8)	1.3763(6)	0.8594(5)	0.035(2)
H30	0.18	1.4319	0.8299	0.042
C31	0.2550(9)	1.4007(6)	0.9456(5)	0.035(2)
H31	0.21	1.4734	0.976	0.043

C32	0.3372(8)	1.3203(6)	0.9863(5)	0.031(2)
H32	0.3487	1.338	1.0456	0.038
C33	0.4057(8)	1.2123(5)	0.9440(4)	0.0272(19)
H33	0.4646	1.1576	0.9729	0.033
C34	0.4100(8)	0.9917(5)	0.8590(5)	0.0230(18)
C35	0.3039(7)	1.0104(5)	0.9546(4)	0.0231(18)
H35	0.2546	1.0773	0.9955	0.028
C36	0.2880(8)	0.9147(5)	0.9748(5)	0.0263(19)
H36	0.2269	0.9011	1.0335	0.032
C37	0.3793(8)	0.8380(6)	0.8922(5)	0.0247(19)
C38	0.3907(7)	0.7285(5)	0.8831(4)	0.0204(17)
C39	0.2900(9)	0.6966(5)	0.9671(4)	0.0228(18)
C40	0.1520(9)	0.7355(6)	0.9734(5)	0.0286(19)
H40	0.1228	0.7797	0.9243	0.034
C41	0.0541(8)	0.7113(6)	1.0501(5)	0.0302(19)
H41	-0.0414	0.7388	1.0545	0.036
C42	0.1007(9)	0.6456(6)	1.1201(5)	0.032(2)
H42	0.0355	0.6277	1.1729	0.038
C43	0.2361(9)	0.6064(6)	1.1154(5)	0.032(2)
H43	0.2653	0.5613	1.1639	0.039
C44	0.3326(8)	0.6328(6)	1.0386(5)	0.0287(19)
H44	0.4275	0.6068	1.0354	0.034
C45	0.8701(8)	0.6398(5)	0.7343(5)	0.0257(19)
H45	0.8594	0.593	0.692	0.031
C46	0.9776(8)	0.6651(6)	0.8338(5)	0.031(2)
H46	1.0457	0.6358	0.8658	0.037
C47	0.8043(8)	0.8071(6)	0.8079(5)	0.0273(19)
H47	0.7461	0.8828	0.8198	0.033

Table S3. Bond length (Å) for ZnTPP•tz.

Zn1	N2	2.044(5)
Zn1	N3	2.067(5)
Zn1	N4	2.072(5)
Zn1	N1	2.073(5)
Zn1	N5	2.209(6)
N1	C4	1.381(7)
N1	C1	1.383(8)
N2	C12	1.381(7)
N2	C15	1.388(7)
N3	C23	1.377(7)
N3	C26	1.381(8)
N4	C34	1.372(7)
N4	C37	1.388(8)
N5	C47	1.336(7)
N5	C45	1.354(8)
N6	C45	1.312(8)
N6	C46	1.340(8)
N7	C46	1.317(8)
N7	C47	1.327(9)
C1	C38	1.387(8)
C1	C2	1.455(8)
C2	C3	1.341(8)
C2	H2	0.95
C3	C4	1.459(8)
C3	H3	0.95
C4	C5	1.409(9)
C5	C12	1.401(8)
C5	C6	1.516(8)
C6	C11	1.362(10)

C6	C7	1.380(9)
C7	C8	1.393(9)
C7	H7	0.95
C8	C9	1.326(10)
C8	H8	0.95
C9	C10	1.390(9)
C9	H9	0.95
C10	C11	1.382(8)
C10	H10	0.95
C11	H11	0.95
C12	C13	1.444(9)
C13	C14	1.346(8)
C13	H13	0.95
C14	C15	1.443(8)
C14	H14	0.95
C15	C16	1.419(8)
C16	C23	1.395(8)
C16	C17	1.517(9)
C17	C18	1.383(9)
C17	C22	1.384(10)
C18	C19	1.396(9)
C18	H18	0.95
C19	C20	1.357(10)
C19	H19	0.95
C20	C21	1.365(10)
C20	H20	0.95
C21	C22	1.405(9)
C21	H21	0.95
C22	H22	0.95
C23	C24	1.445(8)
C24	C25	1.352(9)
C24	H24	0.95

C25	C26	1.453(8)
C25	H25	0.95
C26	C27	1.403(9)
C27	C34	1.403(8)
C27	C28	1.506(9)
C28	C29	1.379(9)
C28	C33	1.392(8)
C29	C30	1.389(9)
C29	H29	0.95
C30	C31	1.382(9)
C30	H30	0.95
C31	C32	1.355(10)
C31	H31	0.95
C32	C33	1.398(9)
C32	H32	0.95
C33	H33	0.95
C34	C35	1.443(9)
C35	C36	1.350(8)
C35	H35	0.95
C36	C37	1.420(8)
C36	H36	0.95
C37	C38	1.416(8)
C38	C39	1.516(9)
C39	C40	1.374(10)
C39	C44	1.381(9)
C40	C41	1.390(9)
C40	H40	0.95
C41	C42	1.391(9)
C41	H41	0.95
C42	C43	1.353(10)
C42	H42	0.95
C43	C44	1.396(9)

C43	H43	0.95
C44	H44	0.95
C45	H45	0.95
C46	H46	0.95
C47	H47	0.95
Zn1	N2	2.044(5)

Table S4. Angles (°) for ZnTPP•tz.

N2	Zn1	N3	89.7(2)
N2	Zn1	N4	166.5(2)
N3	Zn1	N4	88.6(2)
N2	Zn1	N1	89.3(2)
N3	Zn1	N1	167.1(2)
N4	Zn1	N1	89.3(2)
N2	Zn1	N5	98.1(2)
N3	Zn1	N5	99.8(2)
N4	Zn1	N5	95.4(2)
N1	Zn1	N5	93.0(2)
C4	N1	C1	107.7(5)
C4	N1	Zn1	125.9(4)
C1	N1	Zn1	126.3(4)
C12	N2	C15	105.6(5)
C12	N2	Zn1	127.7(4)
C15	N2	Zn1	126.6(4)
C23	N3	C26	107.3(5)
C23	N3	Zn1	126.1(4)
C26	N3	Zn1	126.4(4)
C34	N4	C37	105.3(5)
C34	N4	Zn1	127.8(4)
C37	N4	Zn1	126.9(4)
C47	N5	C45	113.5(6)
C47	N5	Zn1	123.2(5)
C45	N5	Zn1	123.1(5)
C45	N6	C46	114.1(6)
C46	N7	C47	114.7(6)
N1	C1	C38	126.1(6)
N1	C1	C2	108.4(6)
C38	C1	C2	125.5(6)

C3	C2	C1	107.7(6)
C3	C2	H2	126.2
C1	C2	H2	126.2
C2	C3	C4	107.9(6)
C2	C3	H3	126
C4	C3	H3	126
N1	C4	C5	125.7(6)
N1	C4	C3	108.1(6)
C5	C4	C3	126.1(6)
C12	C5	C4	125.8(6)
C12	C5	C6	116.4(6)
C4	C5	C6	117.8(6)
C11	C6	C7	118.8(6)
C11	C6	C5	120.7(6)
C7	C6	C5	120.6(7)
C6	C7	C8	121.0(7)
C6	C7	H7	119.5
C8	C7	H7	119.5
C9	C8	C7	120.0(7)
C9	C8	H8	120
C7	C8	H8	120
C8	C9	C10	119.8(7)
C8	C9	H9	120.1
C10	C9	H9	120.1
C11	C10	C9	120.5(7)
C11	C10	H10	119.7
C9	C10	H10	119.7
C6	C11	C10	119.9(7)
C6	C11	H11	120.1
C10	C11	H11	120.1
N2	C12	C5	124.8(6)
N2	C12	C13	109.9(6)

C5	C12	C13	125.2(6)
C14	C13	C12	107.3(6)
C14	C13	H13	126.3
C12	C13	H13	126.3
C13	C14	C15	107.3(6)
C13	C14	H14	126.3
C15	C14	H14	126.3
N2	C15	C16	125.2(6)
N2	C15	C14	109.8(5)
C16	C15	C14	125.0(6)
C23	C16	C15	125.4(6)
C23	C16	C17	118.9(5)
C15	C16	C17	115.7(6)
C18	C17	C22	117.6(7)
C18	C17	C16	120.5(7)
C22	C17	C16	121.7(7)
C17	C18	C19	120.7(8)
C17	C18	H18	119.7
C19	C18	H18	119.7
C20	C19	C18	121.1(7)
C20	C19	H19	119.5
C18	C19	H19	119.5
C19	C20	C21	119.5(8)
C19	C20	H20	120.2
C21	C20	H20	120.2
C20	C21	C22	120.1(8)
C20	C21	H21	120
C22	C21	H21	120
C17	C22	C21	121.1(8)
C17	C22	H22	119.5
C21	C22	H22	119.5
N3	C23	C16	126.0(6)

N3	C23	C24	108.9(6)
C16	C23	C24	125.1(6)
C25	C24	C23	107.8(6)
C25	C24	H24	126.1
C23	C24	H24	126.1
C24	C25	C26	107.2(6)
C24	C25	H25	126.4
C26	C25	H25	126.4
N3	C26	C27	126.1(6)
N3	C26	C25	108.8(6)
C27	C26	C25	125.1(6)
C26	C27	C34	125.6(6)
C26	C27	C28	116.3(6)
C34	C27	C28	117.9(6)
C29	C28	C33	119.0(6)
C29	C28	C27	118.9(6)
C33	C28	C27	122.1(6)
C28	C29	C30	121.7(7)
C28	C29	H29	119.2
C30	C29	H29	119.2
C31	C30	C29	119.1(7)
C31	C30	H30	120.5
C29	C30	H30	120.5
C32	C31	C30	119.6(7)
C32	C31	H31	120.2
C30	C31	H31	120.2
C31	C32	C33	122.2(7)
C31	C32	H32	118.9
C33	C32	H32	118.9
C28	C33	C32	118.5(7)
C28	C33	H33	120.8
C32	C33	H33	120.8

N4	C34	C27	124.8(6)
N4	C34	C35	110.1(5)
C27	C34	C35	125.0(6)
C36	C35	C34	106.9(6)
C36	C35	H35	126.6
C34	C35	H35	126.6
C35	C36	C37	107.3(6)
C35	C36	H36	126.3
C37	C36	H36	126.3
N4	C37	C38	124.7(6)
N4	C37	C36	110.4(6)
C38	C37	C36	124.9(6)
C1	C38	C37	126.3(6)
C1	C38	C39	118.0(5)
C37	C38	C39	115.3(6)
C40	C39	C44	119.5(7)
C40	C39	C38	118.6(6)
C44	C39	C38	121.8(7)
C39	C40	C41	121.3(7)
C39	C40	H40	119.3
C41	C40	H40	119.3
C40	C41	C42	117.8(8)
C40	C41	H41	121.1
C42	C41	H41	121.1
C43	C42	C41	121.9(7)
C43	C42	H42	119
C41	C42	H42	119
C42	C43	C44	119.5(7)
C42	C43	H43	120.2
C44	C43	H43	120.2
C39	C44	C43	120.0(8)
C39	C44	H44	120

C43	C44	H44	120
N6	C45	N5	126.0(6)
N6	C45	H45	117
N5	C45	H45	117
N7	C46	N6	126.1(7)
N7	C46	H46	117
N6	C46	H46	117
N7	C47	N5	125.6(7)
N7	C47	H47	117.2
N5	C47	H47	117.2

Table S5. Anisotropic displacement parameters ($Å^2$) for ZnTPP•tz. The anisotropic displacement factor exponent takes the form: $-2\pi[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn1	0.0299(6)	0.0212(5)	0.0184(5)	-0.0009(3)	-0.0028(4)	-0.0144(4)
N1	0.025(4)	0.022(3)	0.015(3)	-0.004(3)	0.001(3)	-0.012(3)
N2	0.036(4)	0.021(3)	0.015(3)	-0.005(3)	0.002(3)	-0.018(3)
N3	0.022(4)	0.024(3)	0.014(3)	-0.001(3)	0.005(3)	-0.013(3)
N4	0.033(4)	0.026(3)	0.016(3)	0.002(3)	0.004(3)	-0.022(3)
N5	0.029(4)	0.020(3)	0.019(3)	0.001(3)	-0.004(3)	-0.014(3)
N6	0.027(5)	0.029(4)	0.030(4)	0.001(3)	-0.010(3)	-0.010(3)
N7	0.047(5)	0.025(4)	0.028(4)	0.003(3)	-0.015(4)	-0.017(4)
C1	0.028(5)	0.031(4)	0.013(4)	-0.002(3)	0.001(3)	-0.019(4)
C2	0.045(6)	0.034(4)	0.016(4)	0.002(3)	-0.002(4)	-0.028(4)
C3	0.044(6)	0.028(4)	0.024(4)	0.004(3)	-0.011(4)	-0.027(4)
C4	0.029(5)	0.018(4)	0.025(4)	-0.001(3)	-0.003(4)	-0.013(4)
C5	0.031(5)	0.022(4)	0.023(4)	0.000(3)	-0.007(4)	-0.014(4)
C6	0.031(5)	0.024(4)	0.010(4)	0.001(3)	-0.001(4)	-0.017(4)
C7	0.023(5)	0.041(5)	0.031(4)	-0.003(4)	-0.011(4)	-0.010(4)
C8	0.036(6)	0.037(5)	0.040(5)	-0.015(4)	-0.016(4)	-0.011(5)
C9	0.045(7)	0.027(5)	0.027(4)	-0.003(4)	-0.001(4)	-0.021(5)
C10	0.033(6)	0.022(4)	0.031(4)	0.008(4)	-0.007(4)	-0.007(4)
C11	0.051(7)	0.030(5)	0.030(4)	0.006(4)	-0.021(4)	-0.022(5)
C12	0.025(5)	0.019(4)	0.024(4)	-0.005(3)	-0.006(4)	-0.007(4)
C13	0.028(5)	0.022(4)	0.020(4)	-0.008(3)	-0.001(4)	-0.008(4)
C14	0.041(6)	0.031(4)	0.013(4)	0.001(3)	0.000(4)	-0.019(4)
C15	0.031(5)	0.033(4)	0.019(4)	0.001(3)	-0.005(4)	-0.021(4)
C16	0.036(6)	0.033(4)	0.015(4)	0.003(3)	-0.007(4)	-0.020(4)
C17	0.023(5)	0.020(4)	0.024(4)	-0.009(3)	0.003(4)	-0.012(4)
C18	0.047(7)	0.063(6)	0.039(5)	0.014(4)	-0.030(5)	-0.038(5)
C19	0.051(7)	0.047(5)	0.028(5)	0.016(4)	-0.015(5)	-0.026(5)

C20	0.049(7)	0.020(4)	0.027(5)	0.001(3)	-0.005(5)	-0.011(4)
C21	0.017(6)	0.054(6)	0.064(6)	0.022(5)	0.006(5)	-0.018(5)
C22	0.056(7)	0.066(6)	0.043(5)	0.027(5)	-0.022(5)	-0.039(6)
C23	0.024(5)	0.021(4)	0.014(4)	-0.003(3)	0.002(3)	-0.007(4)
C24	0.050(6)	0.032(5)	0.029(4)	0.011(4)	-0.012(4)	-0.030(5)
C25	0.033(6)	0.030(4)	0.031(4)	0.001(4)	-0.004(4)	-0.020(4)
C26	0.033(6)	0.016(4)	0.033(4)	0.005(3)	-0.014(4)	-0.011(4)
C27	0.031(5)	0.024(4)	0.017(4)	-0.004(3)	-0.006(4)	-0.011(4)
C28	0.021(5)	0.017(4)	0.021(4)	0.001(3)	-0.003(4)	-0.010(4)
C29	0.042(6)	0.033(5)	0.027(4)	-0.003(4)	-0.008(4)	-0.022(5)
C30	0.035(6)	0.024(4)	0.040(5)	0.006(4)	-0.002(4)	-0.014(4)
C31	0.044(6)	0.026(5)	0.035(5)	-0.006(4)	0.003(4)	-0.024(5)
C32	0.047(6)	0.033(5)	0.017(4)	-0.003(4)	0.000(4)	-0.027(5)
C33	0.036(6)	0.029(4)	0.016(4)	0.001(3)	0.002(4)	-0.020(4)
C34	0.032(5)	0.018(4)	0.024(4)	0.001(3)	-0.007(4)	-0.016(4)
C35	0.024(5)	0.020(4)	0.021(4)	-0.006(3)	-0.001(4)	-0.009(4)
C36	0.030(5)	0.023(4)	0.023(4)	-0.005(3)	-0.002(4)	-0.011(4)
C37	0.024(5)	0.035(5)	0.017(4)	-0.001(3)	-0.001(4)	-0.018(4)
C38	0.017(5)	0.023(4)	0.015(4)	-0.008(3)	0.004(3)	-0.008(4)
C39	0.031(6)	0.028(4)	0.011(4)	-0.006(3)	0.002(4)	-0.020(4)
C40	0.038(6)	0.030(4)	0.017(4)	0.000(3)	-0.002(4)	-0.019(4)
C41	0.017(5)	0.032(5)	0.032(4)	-0.009(4)	0.006(4)	-0.010(4)
C42	0.044(7)	0.031(5)	0.019(4)	-0.007(3)	0.006(4)	-0.024(5)
C43	0.038(6)	0.042(5)	0.021(4)	0.010(4)	-0.007(4)	-0.022(5)
C44	0.026(5)	0.040(5)	0.021(4)	0.003(3)	-0.002(4)	-0.018(4)
C45	0.031(6)	0.020(4)	0.021(4)	-0.006(3)	0.004(4)	-0.014(4)
C46	0.029(6)	0.031(5)	0.034(5)	0.008(4)	-0.015(4)	-0.012(4)
C47	0.030(6)	0.024(4)	0.024(4)	0.000(3)	0.002(4)	-0.014(4)