Electronic Supplementary Material (ESI) for Materials Advances.

Correlating Structure and Photophysical Properties in Thiazolo[5,4-*d*]thiazole Crystal Derivatives for Use in Solid-State Photonic and Fluorescence-Based Optical Devices

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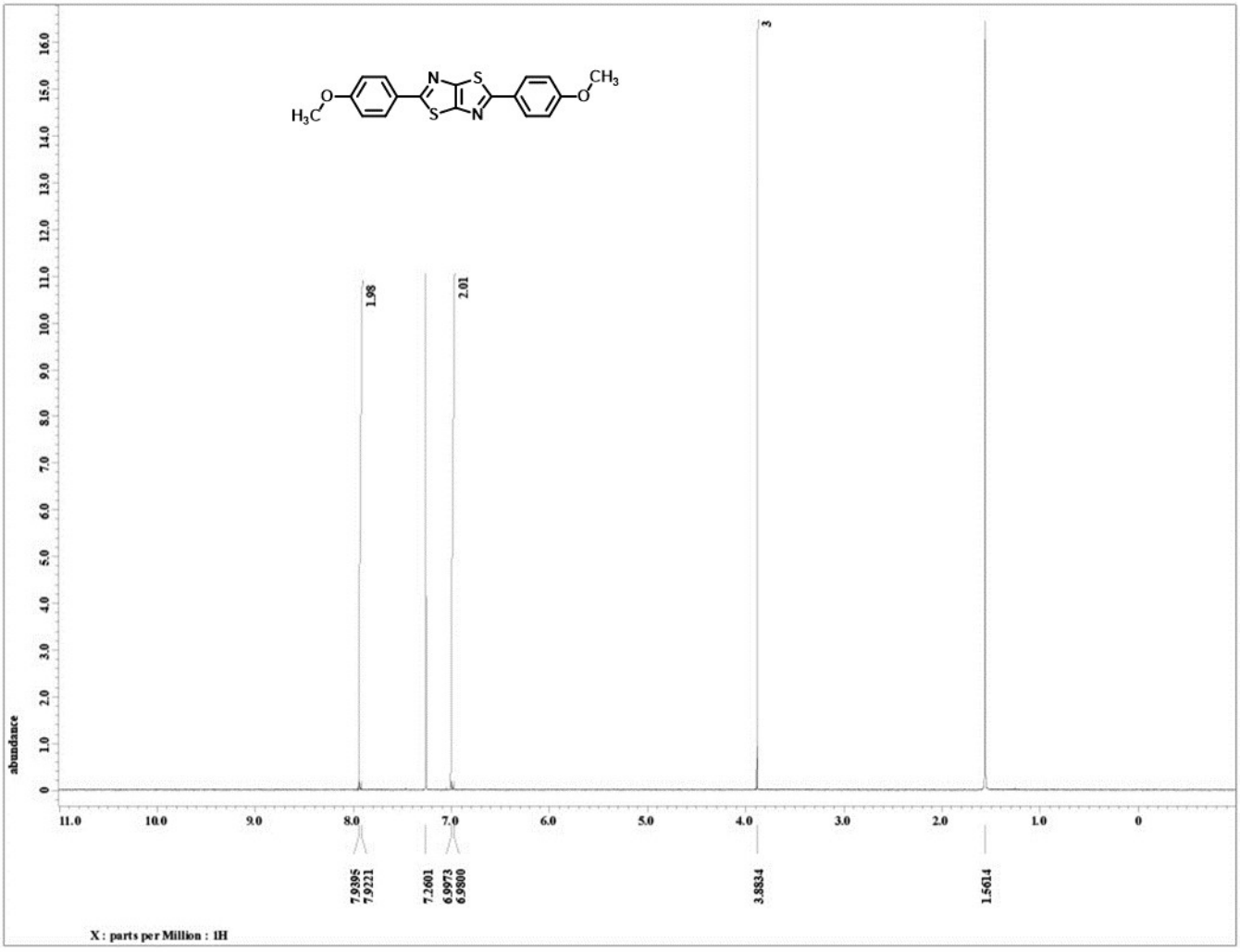
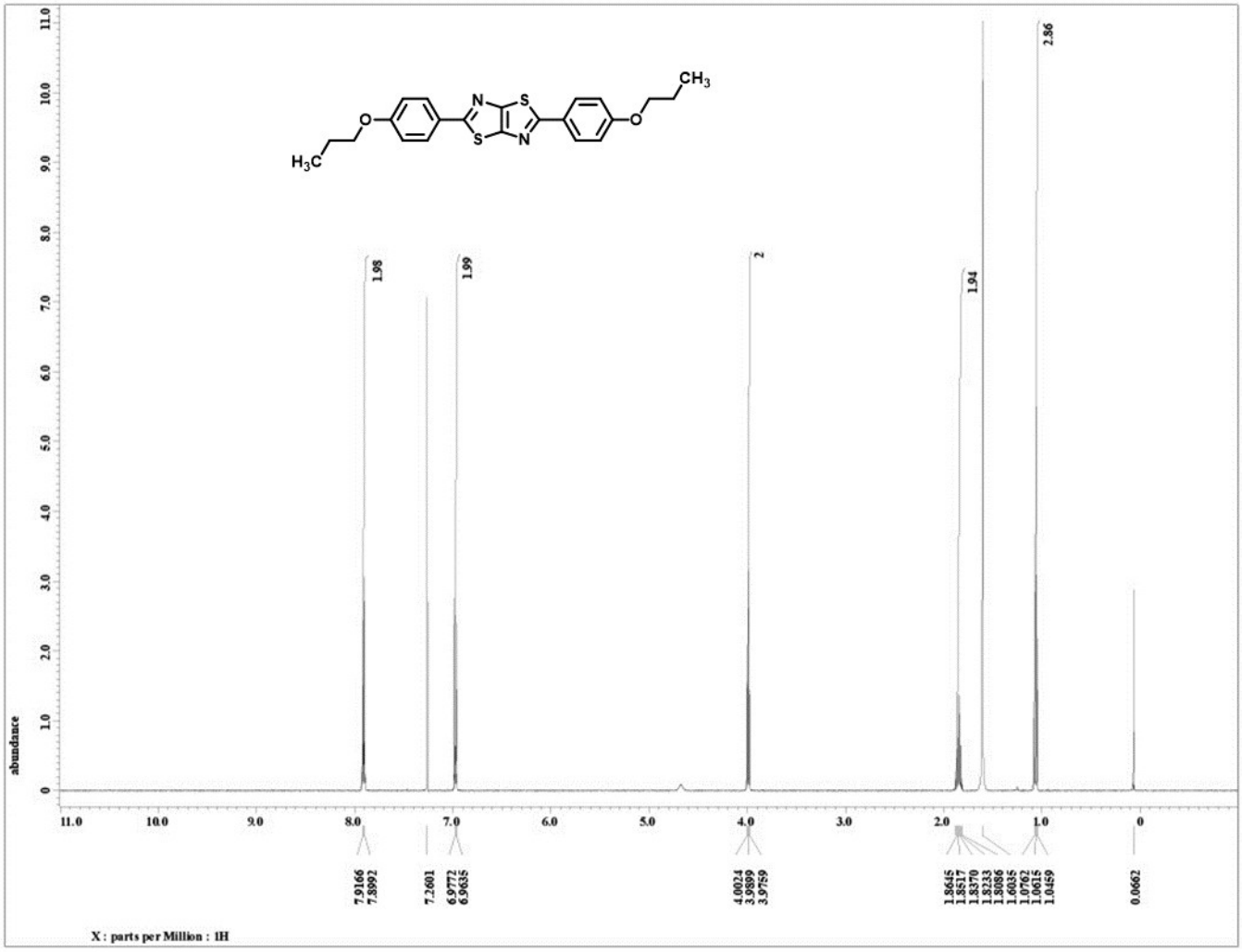
Section 1: Spectra Characterization

Section 1.1: *[1]H-NMR Spectra*

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1.99
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1.94
2.86
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7.8992
7.2601
6.9772
6.9635
4.0024
3.9989
3.9759
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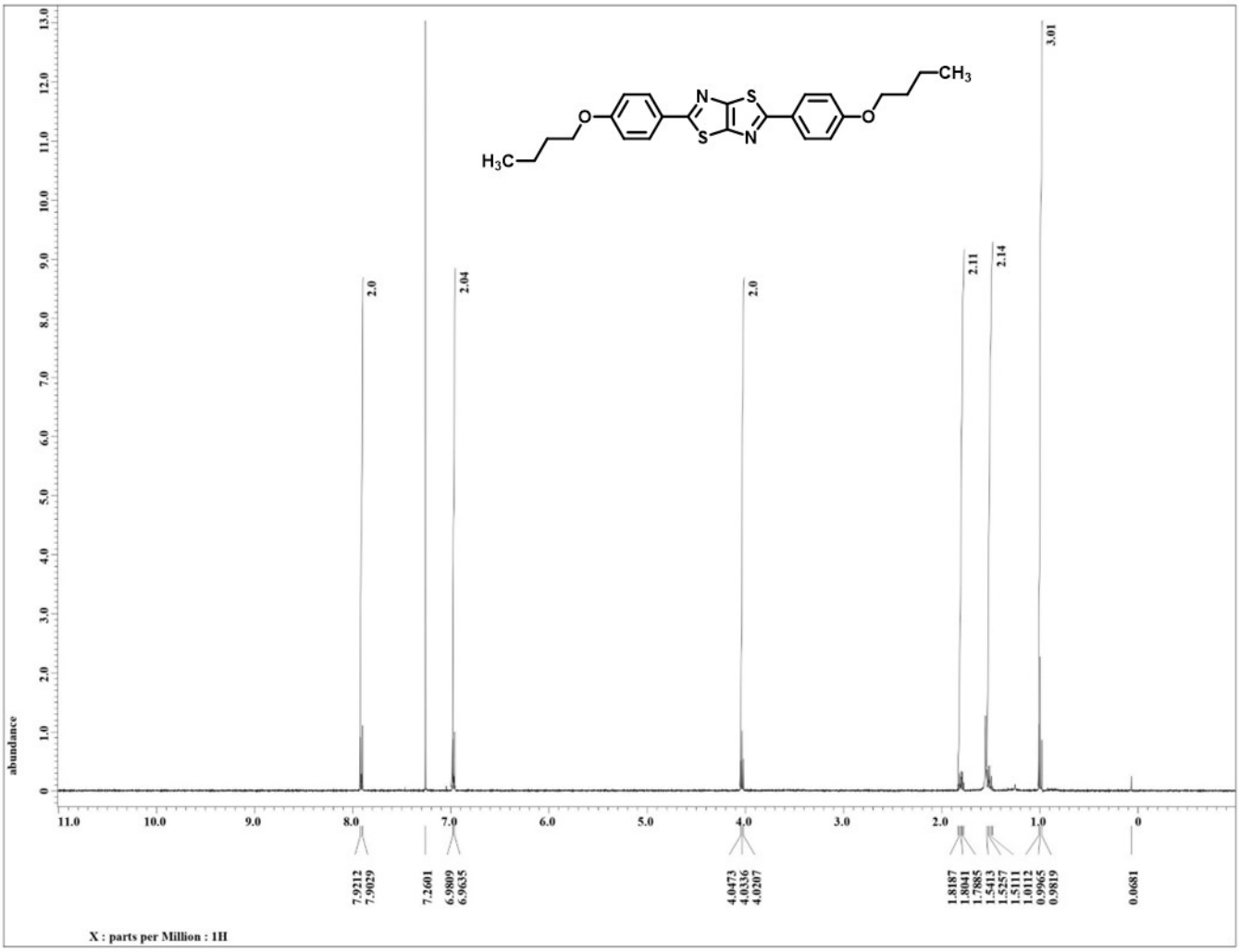
0.0662


abundance
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2.0
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2.14
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7.2601
6.9809
6.9635
4.0473
4.0336
4.0207
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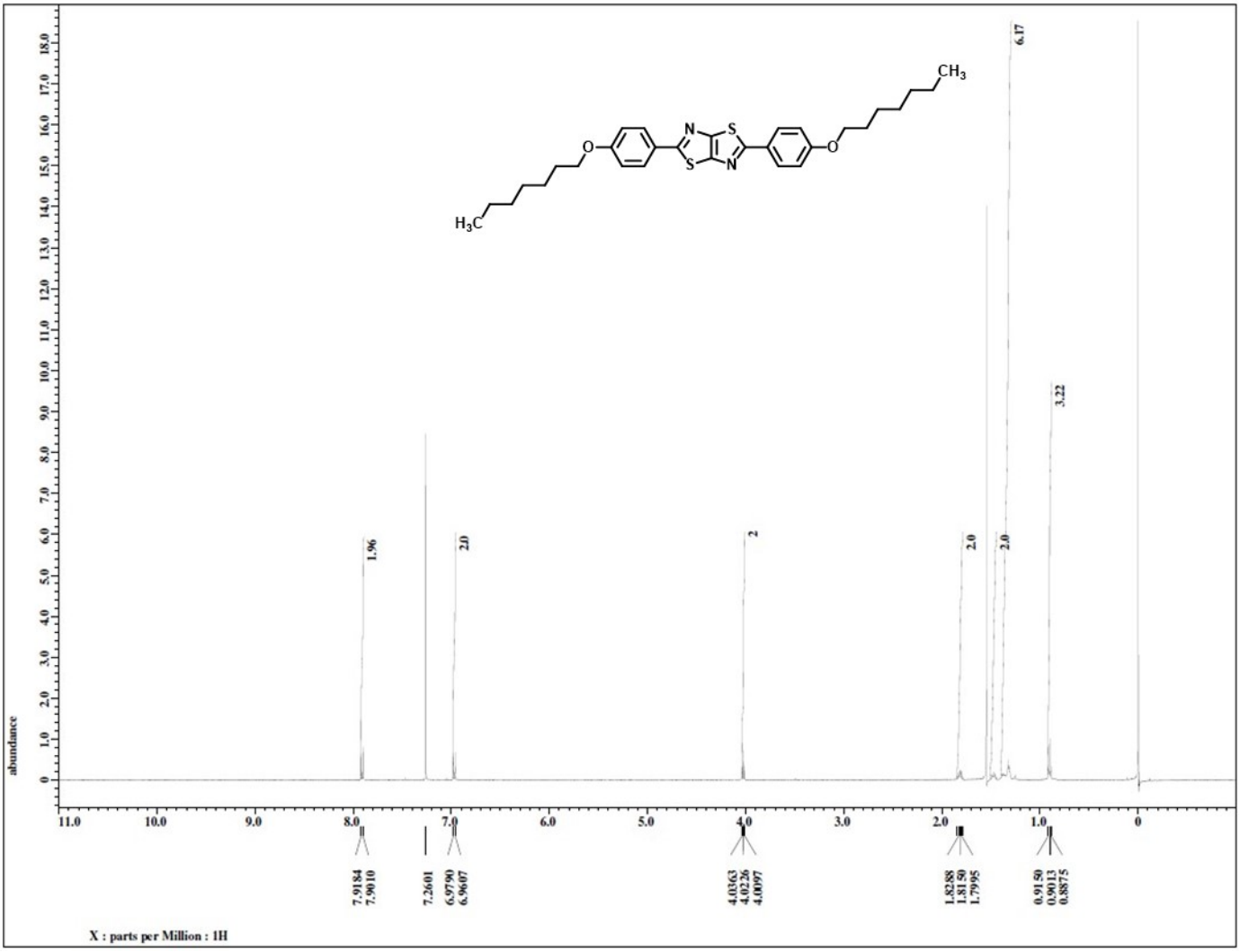
abundance
X : parts per Million : 1H
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2.0
2
2.0
2.0
6.17
3.22
7.9184
7.9010
7.2601
6.9790
6.9607
4.0363
4.0226
4.0097
1.8288
1.8150
1.7995
0.9150
0.9013
0.8875

Section 1.2: *MALDI-TOF-MS*

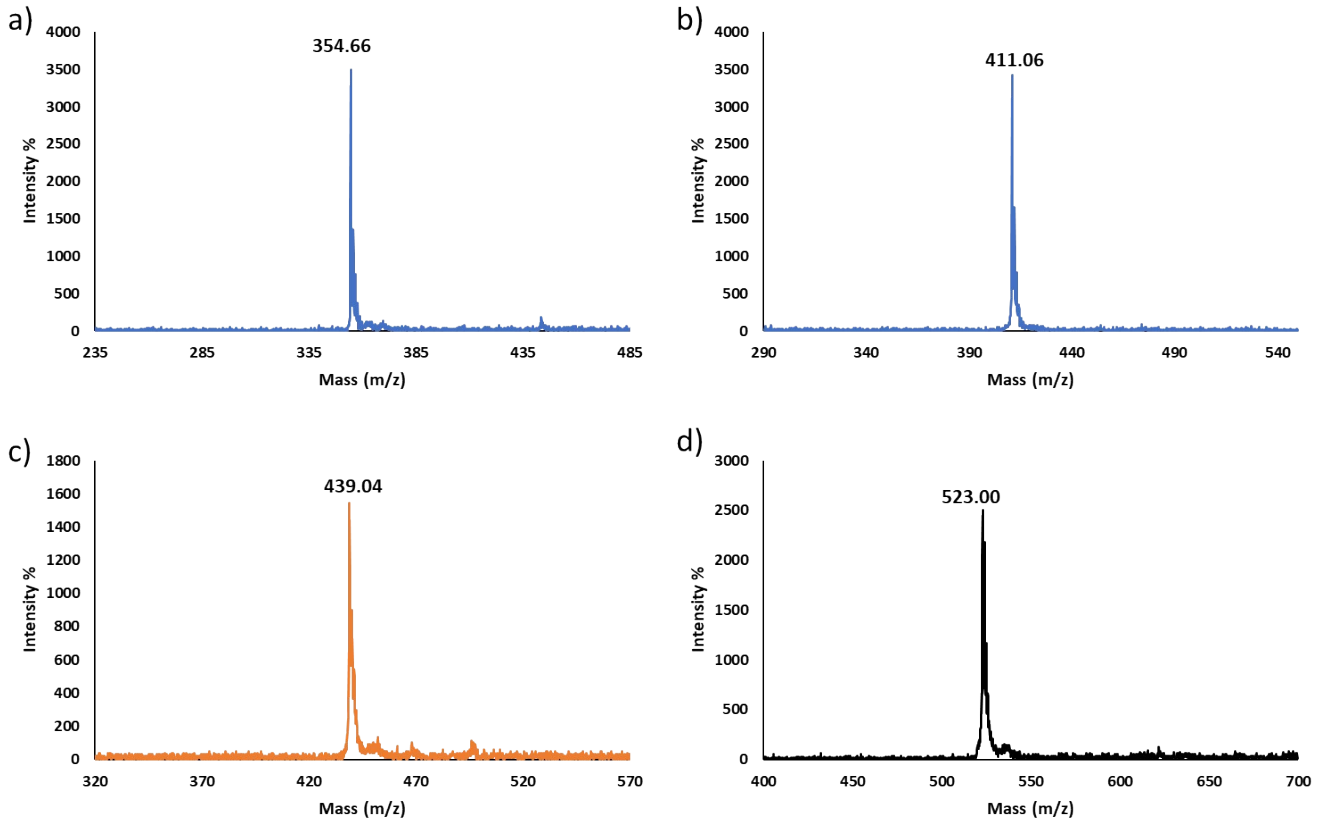

Figure S1: Maldi-TOF-MS Spectra of a) $(MeOPh)_2TTz$, b) $(PrOPh)_2TTz$, c) $(BuOPh)_2TTz$, and d) $(HepOPh)_2TTz$

Section 2: X-Ray Characterization

Section 2.1: *Single Crystal Structure Data and Refinement*

Table S1: Summary of crystallographic data of dialkoxyphenyl TTzs

Identification code	$(PrOPh)_2TTz$	$(BuOPh)_2TTz$	$(HepOPh)_2TTz$
CSD Deposition Number	2257069	2257068	2257067
Empirical formula	$C_{22}H_{22}N_2O_2S_2$	$C_{24}H_{26}N_2O_2S_2$	$C_{30}H_{38}N_2O_2S_2$
Formula weight	410.564	438.618	522.781
Temperature/K	100.00(10)	100.00(10)	100.00(10)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
a/Å	16.2976(4)	5.4441(5)	31.0223(11)
b/Å	7.46099(19)	7.4759(7)	7.1900(3)
c/Å	7.9920(2)	14.1023(13)	6.0107(2)
α/°	90	84.330(8)	90
β/°	96.418(2)	82.922(8)	91.400(3)
γ/°	90	70.044(8)	90
Volume/Å^3	965.71(4)	534.39(9)	1340.29(9)
Z	2	1	2
ρ_{calc}g/cm^3	1.412	1.363	1.295
μ/mm^{-1}	2.669	2.446	2.032
F(000)	434.6	233.3	562.9
Crystal size/mm^3	0.378 × 0.364 × 0.197	0.565 × 0.511 × 0.036	0.165 × 0.141 × 0.035
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.92 to 133.34	12.62 to 133.6	8.56 to 133.84
Index ranges	$-19 \le h \le 19$, $-7 \le k \le 8$, $-9 \le l \le 8$	$-6 \le h \le 5$, $-8 \le k \le 6$, $-16 \le l \le 16$	$-36 \le h \le 36$, $-8 \le k \le 7$, $-6 \le l \le 7$
Reflections collected	8742	4008	12196
Independent reflections	1698 [R_{int} = 0.0335, R_{sigma} = 0.0206]	1873 [R_{int} = 0.0374, R_{sigma} = 0.0367]	2371 [R_{int} = 0.0772, R_{sigma} = 0.0466]
Data/restraints/parameters	1698/0/141	1873/0/137	2371/0/176
Goodness-of-fit on F^2	1.075	1.075	1.103
Final R indexes [I>=2σ (I)]	R_1 = 0.0300, wR_2 = 0.0733	R_1 = 0.0366, wR_2 = 0.0945	R_1 = 0.0744, wR_2 = 0.2012
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0780	R_1 = 0.0431, wR_2 = 0.1008	R_1 = 0.0971, wR_2 = 0.2214
Largest diff. peak/hole / e Å^{-3}	0.22/-0.28	0.40/-0.28	0.82/-0.43

Section 2.2: ***Correlation between Volume of Unit Cell and Alkyl Chain Length***

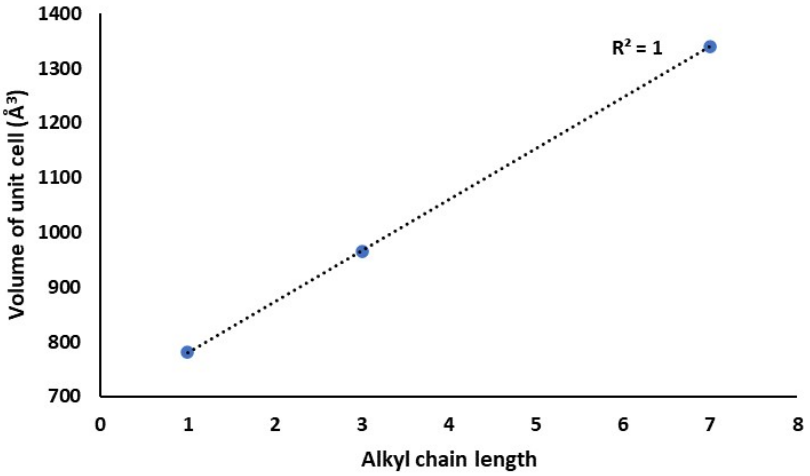

Figure S2: Crystals packed in monoclinic crystal system showed a perfect correlation between volume of unit cell and alkyl chain length.

Section 2.3: Pictorial representation of interaction energies in TTz crystals

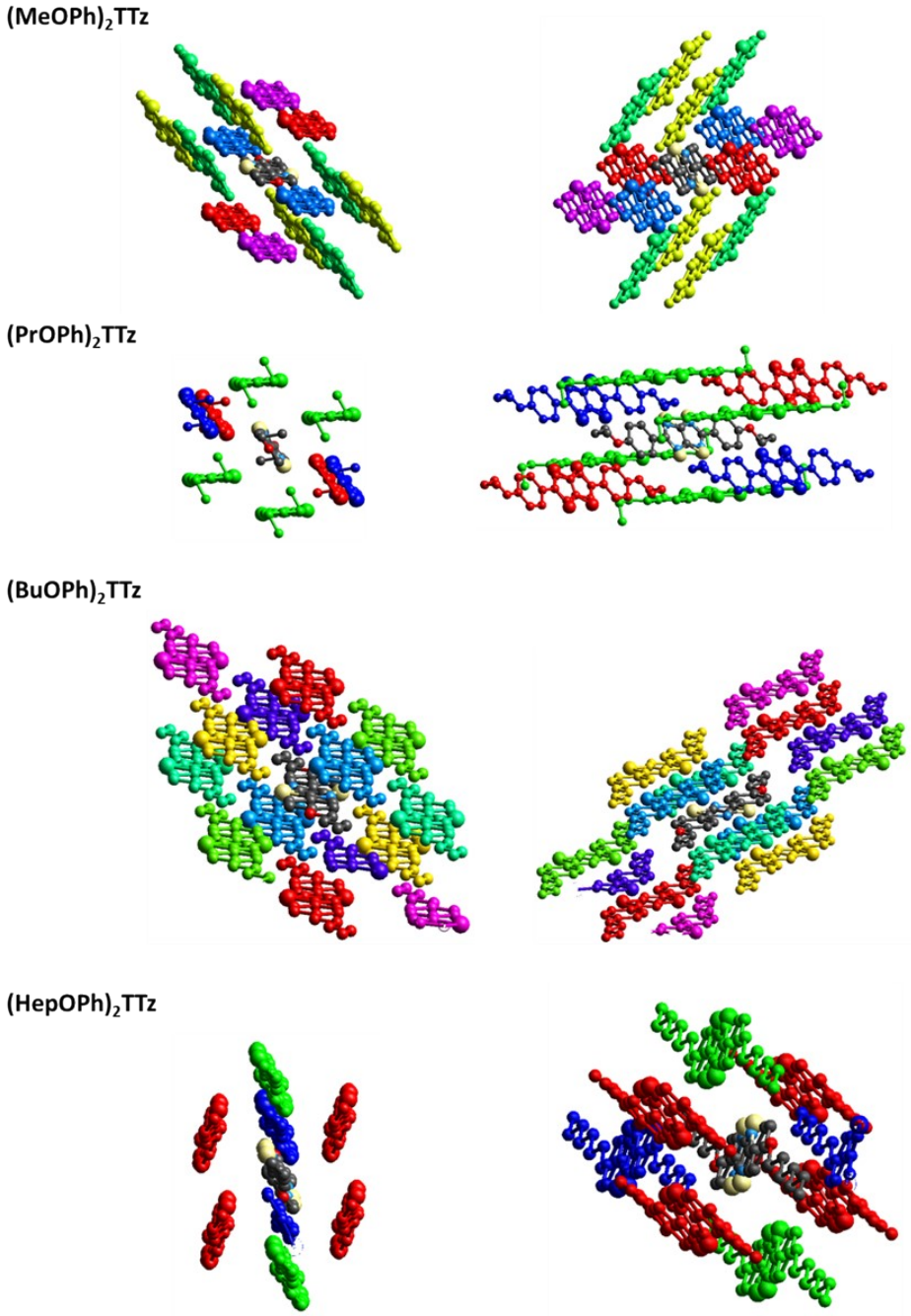

Figure S3: Color-coded pictorial representation of interaction energy in TTz crystals with respect to one central reference molecule.

Section 2.4: Intermolecular interaction energies in TTz crystals

Table S2: Details of intermolecular interaction energies in TTz crystals

	Pair label (*cf* Fig 3)	Orientation	Color	N	R (Å)	E_{ele} (kJ/mol)	E_{pol} (kJ/mol)	E_{dis} (kJ/mol)	E_{rep} (kJ/mol)	E_{tot} (kJ/mol)
$(MeOPh)_2TTz$	a)	Cofacial	Red	2	3.98	-6.98	-2.44	-80.74	36.34	-53.70
	b)	Orthogonal	Green	4	10.67	-11.73	-1.48	-25.69	14.28	-24.60
	c)	Parallel	Blue	2	19.04	-7.82	-1.18	-8.80	0.00	-17.90
	d)	Orthogonal	Yellow	4	11.47	-5.60	-0.89	-16.03	6.30	-16.20
		Cofacial	Purple	2	18.52	3.28	-0.37	-5.75	0.00	-2.80
$(PrOPh)_2TTz$	e)	Orthogonal	Green	4	5.47	-54.65	-7.03	-101.65	93.75	-69.70
	f)	Cofacial	Blue	2	7.99	-28.12	-5.25	-58.62	75.52	-16.60
	g)	Cofacial	Red	2	18.94	-0.11	-0.07	-8.97	0.00	-9.20
$(BuOPh)_2TTz$	h)	Cofacial	Red	2	15.29	-11.20	-1.41	-58.53	0.00	-71.10
		Cofacial	Blue	2	14.1	1.16	-1.70	-68.29	0.00	-68.80
		Cofacial	Green	2	15.96	-29.81	-1.26	-27.35	0.00	-58.50
		Cofacial	Teal	2	14.48	-10.36	-2.00	-33.01	0.00	-45.40
		Cofacial	Yellow	2	5.44	-10.36	-5.25	-44.68	22.93	-37.40
		Cofacial	Purple	2	28.46	0.85	0.00	-4.88	0.00	-4.00
		Cofacial	Pink	2	28.8	0.11	0.00	-0.70	0.00	-0.60
$(HepOPh)_2TTz$	i)	Orthogonal	Red	4	4.69	-72.51	0.00	-137.88	99.37	-111.00
	j)	Cofacial	Green	2	6.01	-79.06	-7.62	-78.39	110.44	-54.70
		Cofacial	Blue	2	33.54	0.21	0.00	-7.06	0.00	-6.80

R = distance between molecular centroids

$E_{tot}=E_{ele} + E_{pol} + E_{dis} + E_{rep}$

Where,

E_{ele} = classical electrostatic energy of interaction between monomer charge distributions

E_{rep} = exchange–repulsion energy

E_{dis} = dispersion energy

E_{pol} = Polarization energy

Since k_BT = 2.5 kJ/mol and the error to which the sublimation enthalpy can be measured is approximately 5 kJ/mol for organic compounds, molecular pairs with $E_{tot} \sim$ 5 kJ/mol should be ignored.

Section 2.5: List of contacts from crystal packing data of $(C_nOPh)_2TTz$ crystals

Table S3: $(C_nOPh)_2TTz$ crystal packing data with emphasis on interchromophoric interactions. For atom labelling sequence *cf.* Figure S4.

	Pair label (*cf* Fig 3)	Orientation	Color	Interaction	Distance, (Å)	Angle, (degrees)	Frequency of Interaction	Number of molecules	Total
$(MeOPh)_2TTz$	a)	Cofacial	Red	C_9-H—O_1	2.935	149.48	2	2	4
				π-$\pi_{phenyl\ centroid}$	3.985		2	2	4
	b)	Orthogonal	Green	C_5-H—S_1	3.519	120.35	1	4	4
				C_5-H—N_1	2.964	178.48	1	4	4
				C_9—S_1	3.468	173.66	1	4	4
	c)		Yellow	C_9-H—N_1	2.912	161.62	1	4	4
				C_7-H—S_1	3.851	169.5	1	4	4
	d)	Parallel	Blue	C_9-H—O_1	2.537	144.74	2	2	4
$(PrOPh)_2TTz$	e)	Orthogonal	Green	C_8-H—S_1	3.839		1	4	4
				C_{10}-H—O_1	3.249	127.93	1	4	4
				C_{11}-H—O_1	3.44	122.36	1	4	4
				C_{10}-H—O_1	3.922	135.47	1	4	4
				C_2—S_1	3.38		1	4	4
				S—S	3.488		1	4	4
				C_7-H—C_3	2.88	136.06	1	4	4
				S_1—C_3	3.327		1	4	4
				C_4—S_1	3.379		1	4	4
	f)	Cofacial	Blue	C_7-H—N_1	3.35	126.41	2	2	4
				C_9-H—N_1	2.986	72.88	2	2	4
				C_8—S_1	3.456		2	2	4
	g)	Cofacial	Red	C_{11}-H—O_1	3.799	142.93	2	2	4
$(BuOPh)_2TTz$	h)	Cofacial	Red	C_{12}-H—S_1	3.266	123.54	2	14	28
				C_9-H—O_1	3.321	124.83	2	14	28
				C_{12}-H—N_1	3.255	170.66	2	14	28
				C_{10}-H—$\pi_{phenyl\ centroid}$	2.856	138.1	2	14	28
				C_{11}-H—$\pi_{phenyl\ centroid}$	3.591		2	14	28
				C_{12}-H—$TTz_{centroid}$	3.601	142.8	2	14	28

$(HepOPh)_2TTz$	i)	Orthogonal	Red	C_{10}-H—O_1	3.11	141.73	1	4	4
				C_5-H—O_1	3.893	147.75	1	4	4
				C_{11}-H—O_1	3.519	131.74	1	4	4
				C_9-H—O_1	3.016	144.94	1	4	4
				C_4-H—S_1	3.599	123.69	1	4	4
				C_7-H—C_6	2.826	124.37	1	4	4
				S_1—C_2	3.311		1	4	4
				S_1—C_1	3.392		1	4	4
				C_4-H—C_3	2.895	124.17	1	4	4
				C_4-H—C_2	2.892	144.2	1	4	4
	j)	Cofacial	Green	C_{11}-H—O1	3.062	170.29	2	2	4
				C_7-H—H-C_9	2.345	157.81	2	2	4
				S—S	3.118		1	2	2

Section 2.6: Atom labelling sequence

The atom labelling sequence of $(HepOPh)_2TTz$ is shown in Figure S3. Truncated labelling sequence can be used for other TTz derivatives.

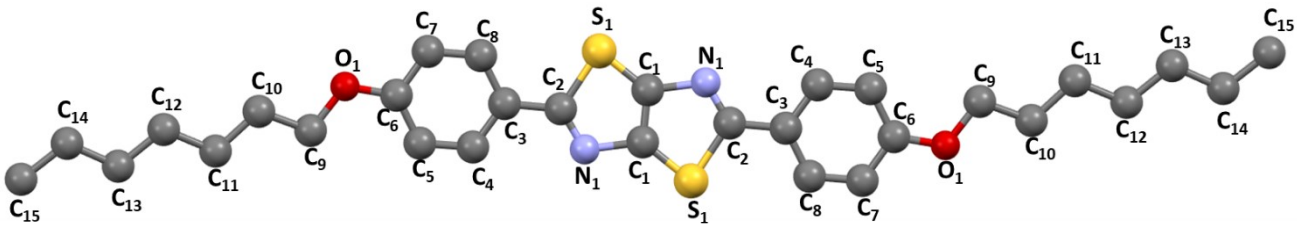

Figure S4. $(HepOPh)_2TTz$ with labelled non-hydrogen atoms

Section 2.7: Distribution of intermolecular contacts to Hirshfeld surface area

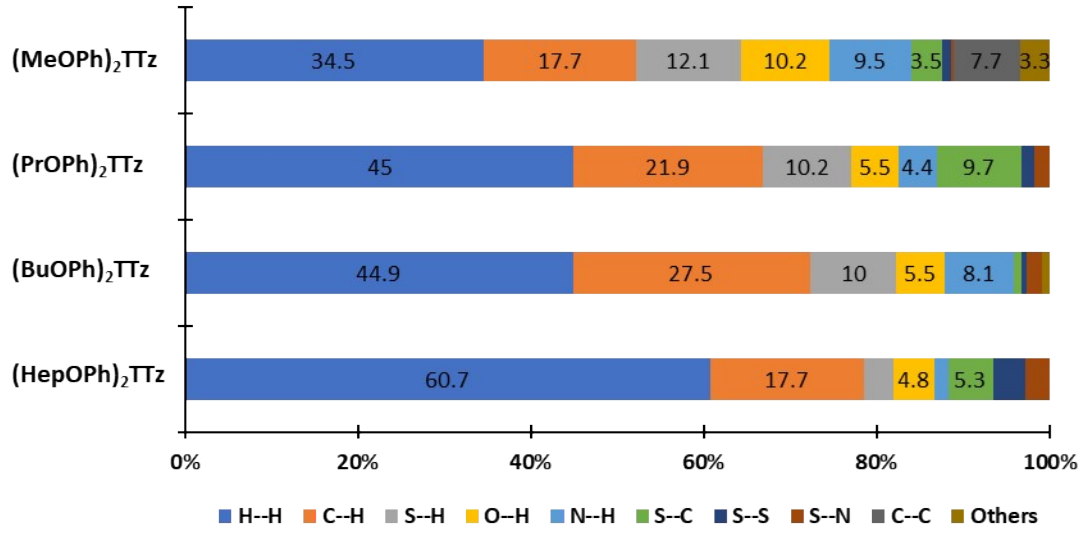

Figure S5: Relative contribution of the intermolecular contacts to the Hirshfeld surface area for (CnOPh)2TTz crystals.

Section 2.8: Shape index of the Hirshfeld surfaces

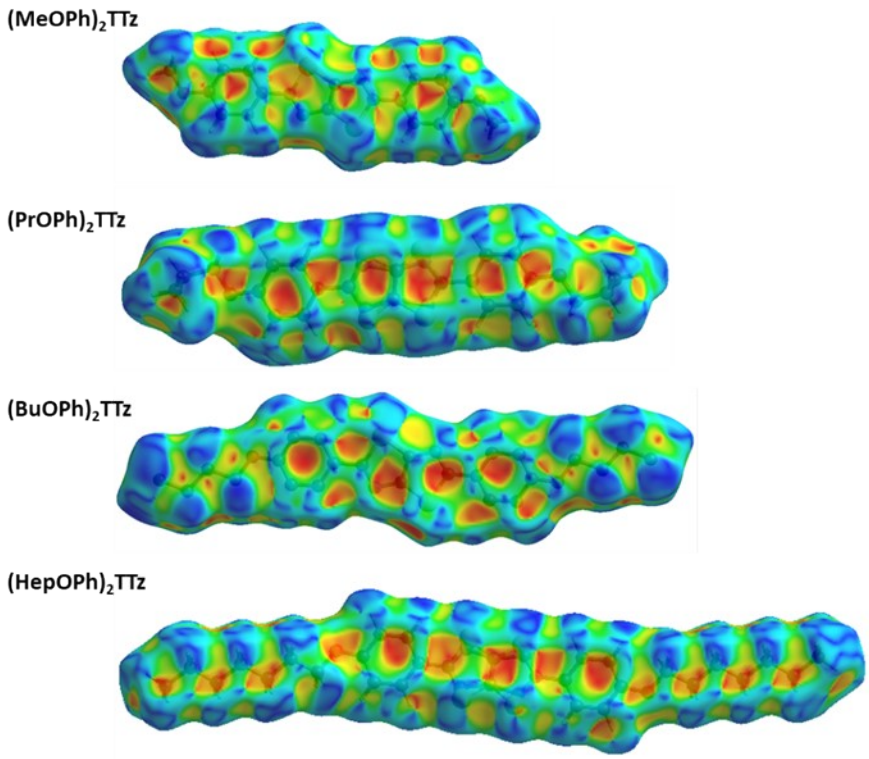

Figure S6. Shape index of the Hirshfeld surfaces of the $(C_nOPh)_2TTz$ crystals. π- π orbital overlap is represented by adjacent red and blue triangles on the Hirshfeld surface. The absence of adjacent red and blue triangles is indicative of lack of π- π orbital overlap.[1]

Section 2.9: *Powder X-Ray Diffractograms of TTz Crystals*

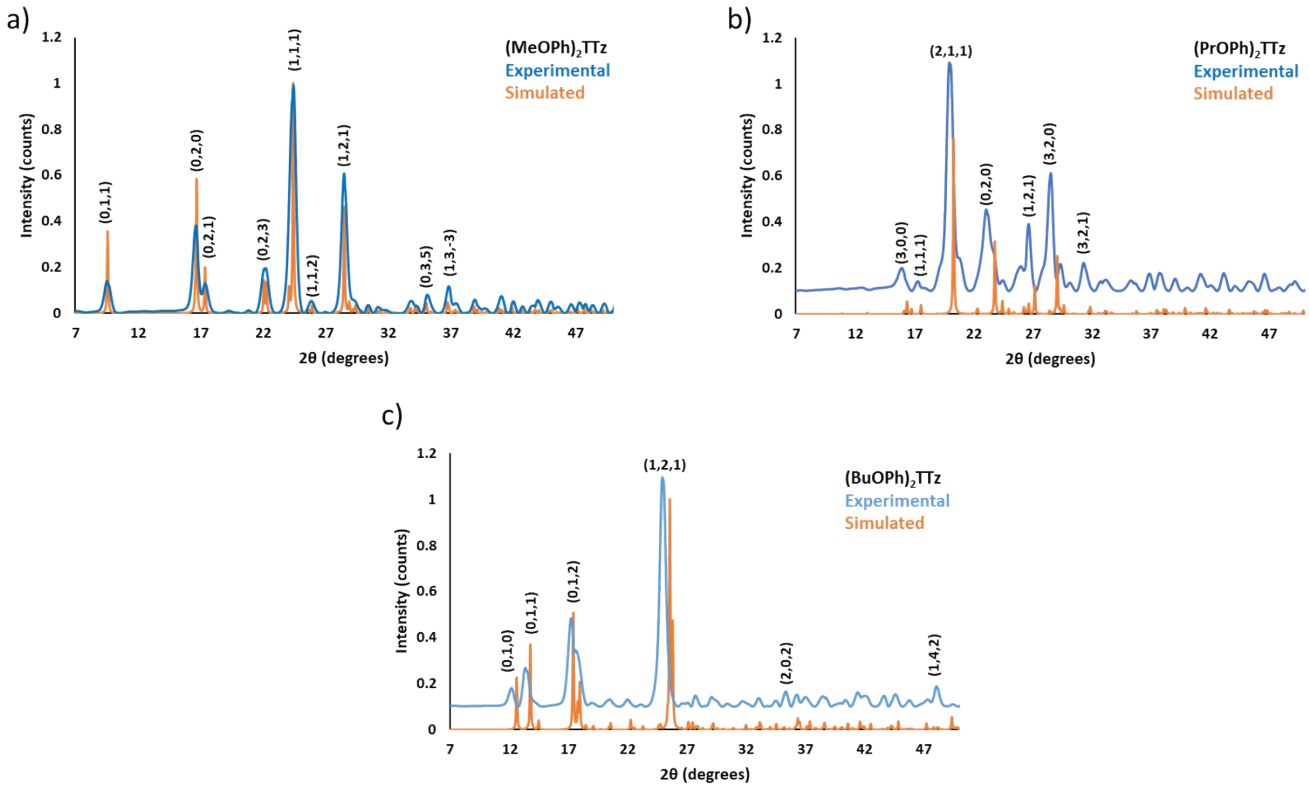

Figure S7: Comparison of experimental and simulated powder XRD patterns of a) $(MeOPh)_2TTz$, b) $(PrOPh)_2TTz$, c) $(BuOPh)_2TTz$.

Section 3: Photophysical Characterization

Section 3.1: DFT Simulated Raman Spectra

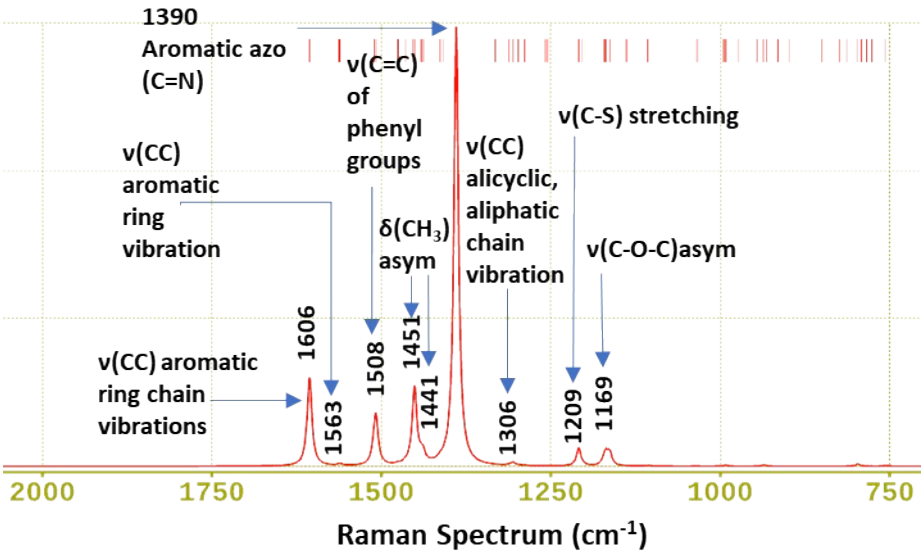

Figure S8: DFT Simulated Raman Spectra with peak assignments.

Section 3.2: Lattice-Phonon Raman Spectra of TTz Crystals

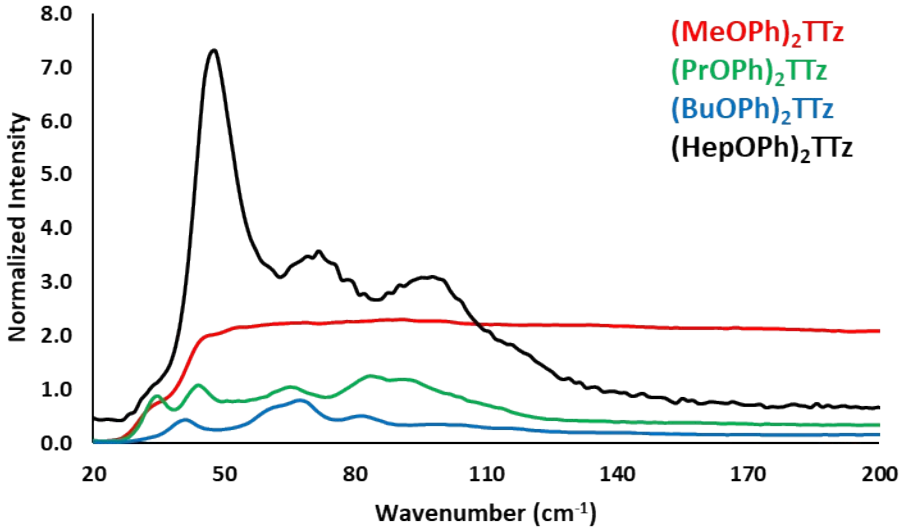

Figure S9: Lattice-Phonon Raman Spectra of TTz Crystals.

Section 3.3: *Time Dependent Photostability Measurement of TTz Crystals*

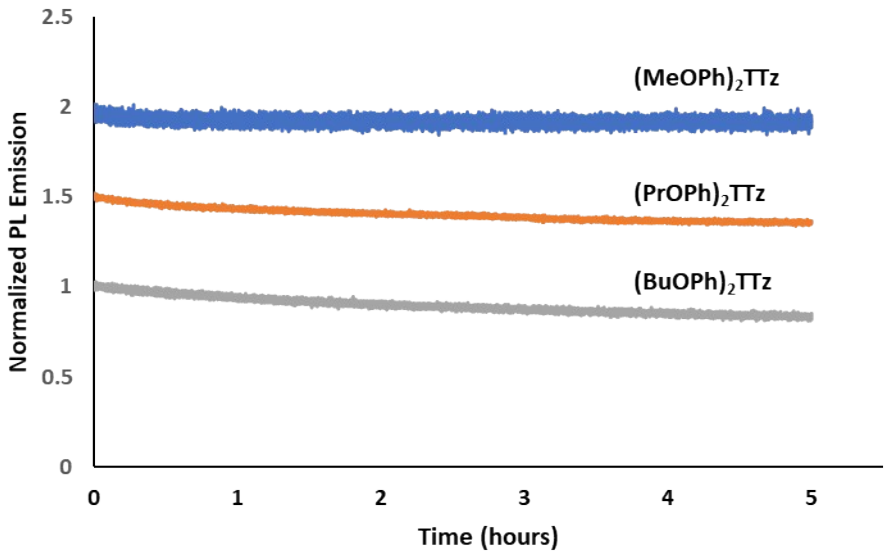

Figure S10: Time dependent photostability measurement of TTz Crystals under constant illumination by 400 nm in ambient conditions.

Material	**Decrease in PL Intensity after 5 hours of illumination**
$(MeOPh)_2TTz$	8 %
$(PrOPh)_2TTz$	14 %
$(BuOPh)_2TTz$	15 %

Section 4: References

(1) Shikhaliyev, N. Q.; Çelikesir, S. T.; Akkurt, M.; Bagirova, K. N.; Suleymanova, G. T.; Toze, F. A. Crystal structure and Hirshfeld surface analysis of (E)-1-(4-chlorophenyl)-2-[2, 2-dichloro-1-(4-fluorophenyl) ethenyl] diazene. *Acta Crystallographica Section E: Crystallographic Communications* **2019**, *75* (4), 465-469.