Molecular and supramolecular room temperature phosphorescences from metal free carbonyl functionalized triazinic scaffold

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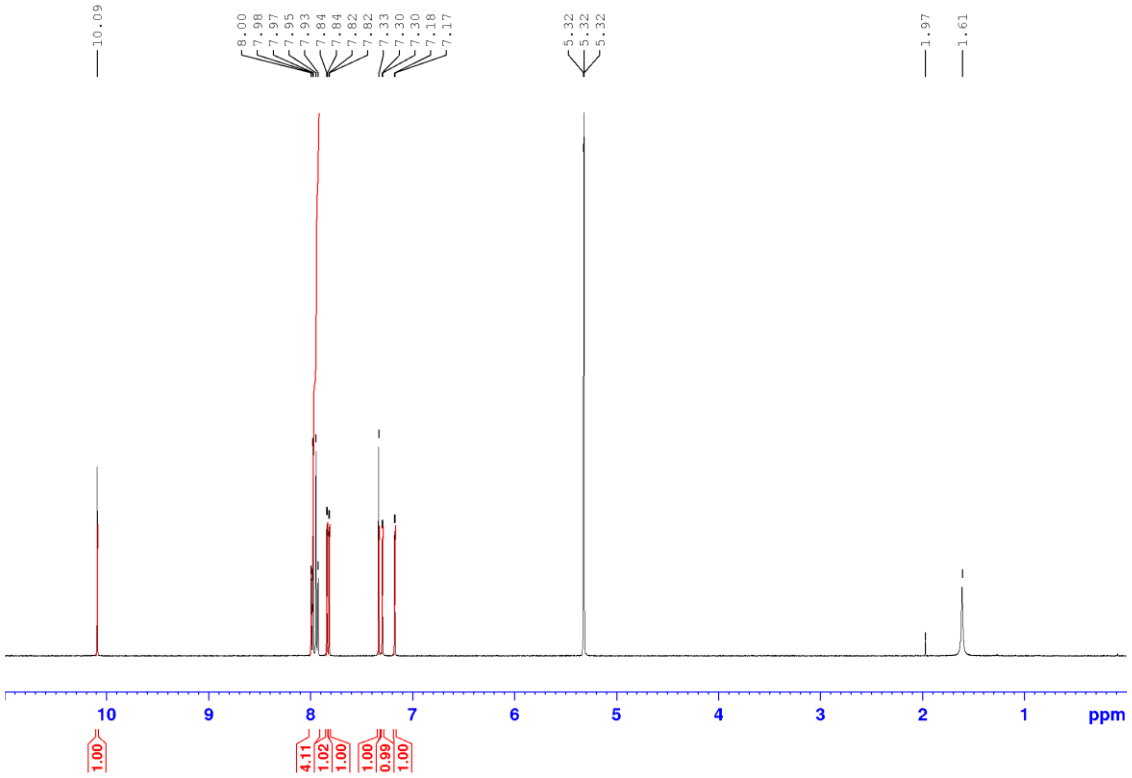


Figure S2. Expanded region of ^{1}H NMR spectrum of **TTPhCHO** (400 MHz, CD_2Cl_2, 298 K)

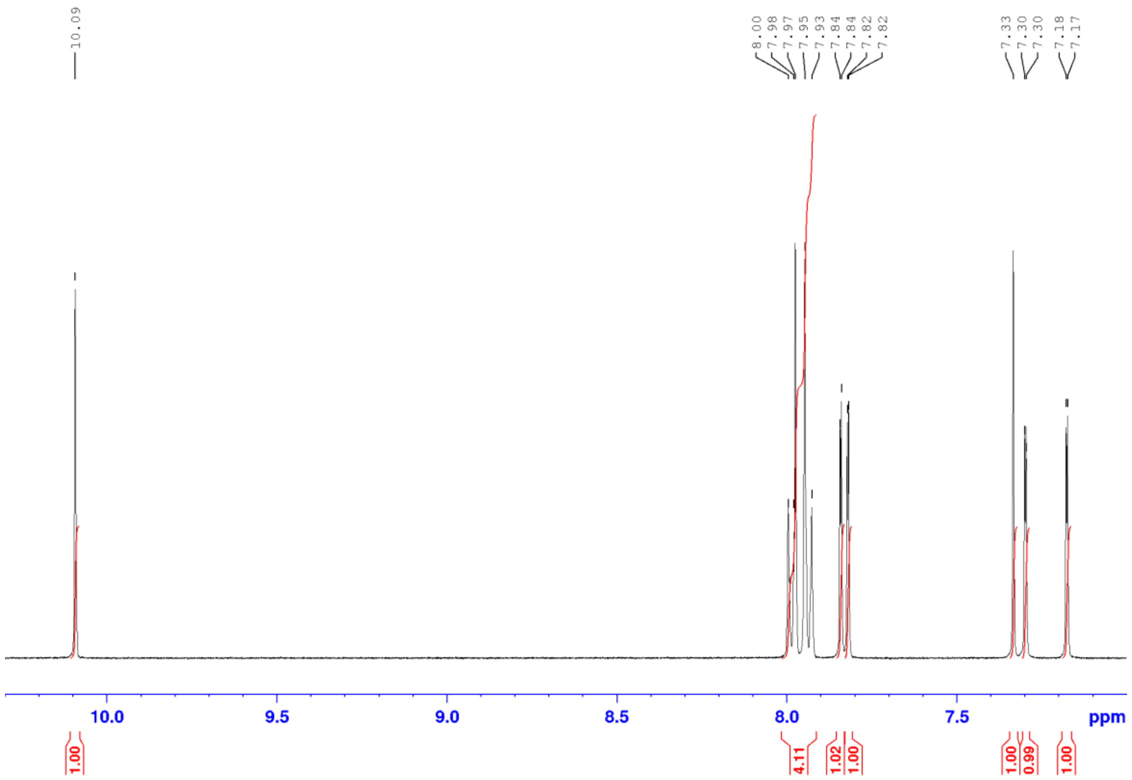


Figure S3. ^{13}C NMR spectrum of **TTPhCHO** (100 MHz, CD_2Cl_2, 298 K)

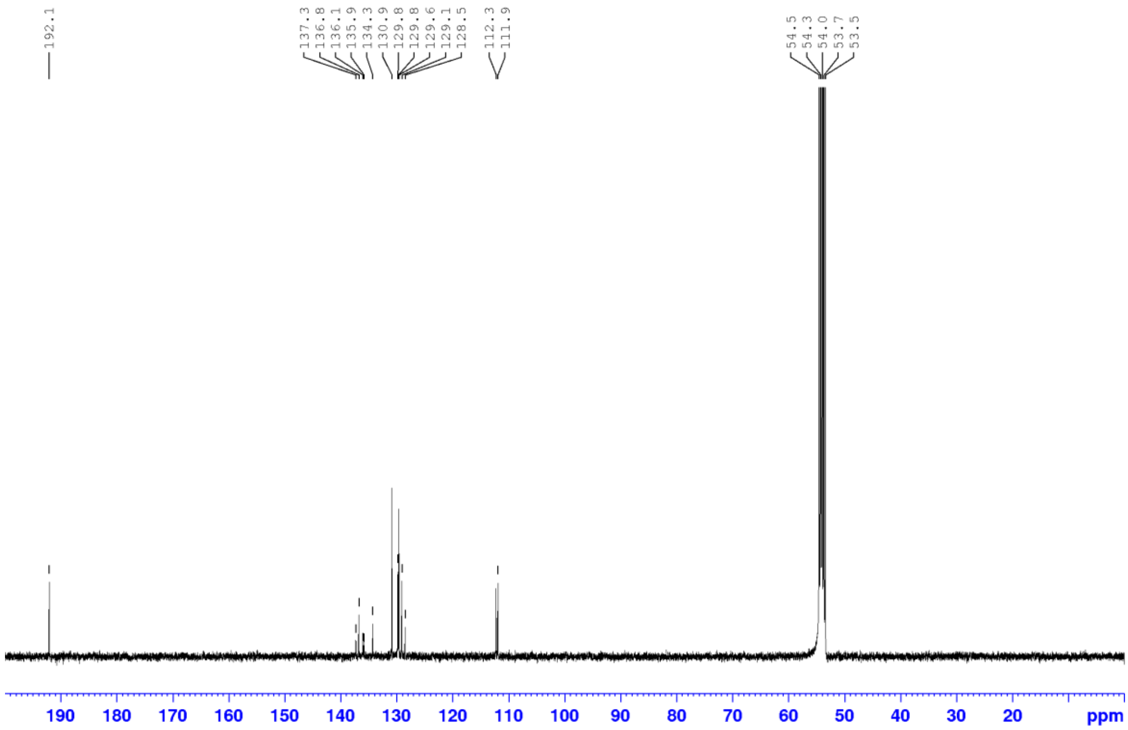


Figure S4. Expanded region of ^{13}C NMR spectrum of **TTPhCHO** (100 MHz, CD_2Cl_2, 298 K)

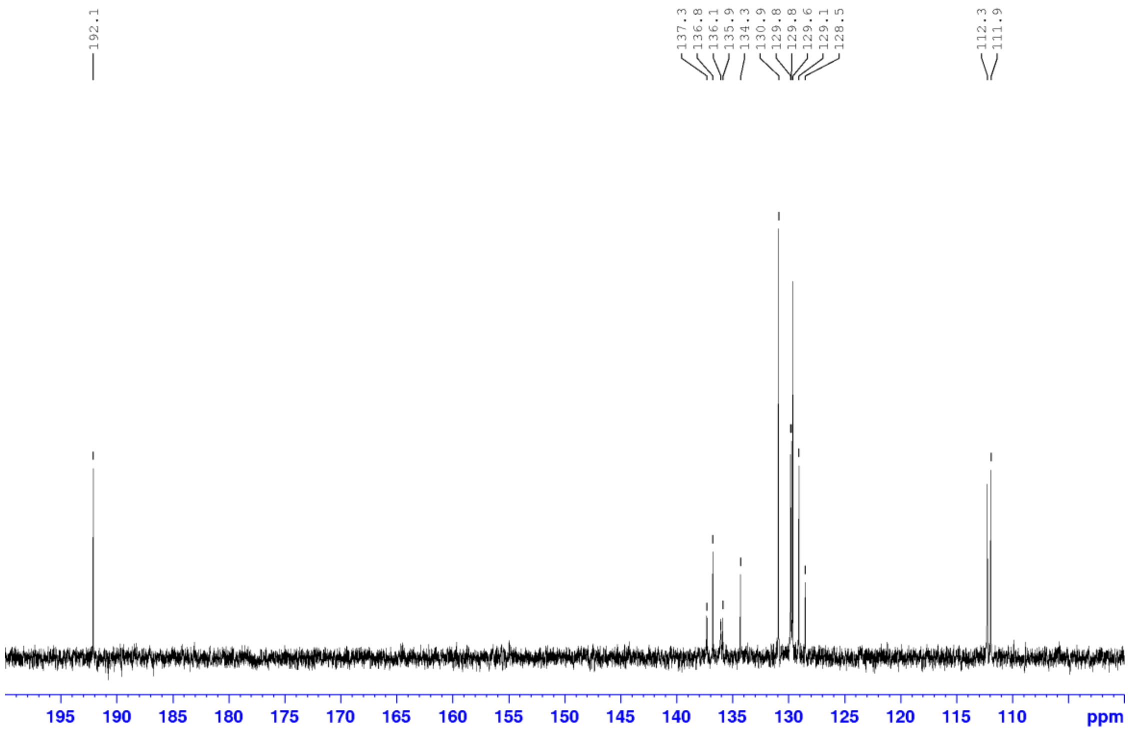


Figure S5. Expanded region of 2D ^{1}H-^{13}C HSQC NMR spectrum of **TTPhCHO** ($CDCl_3$, 298 K)

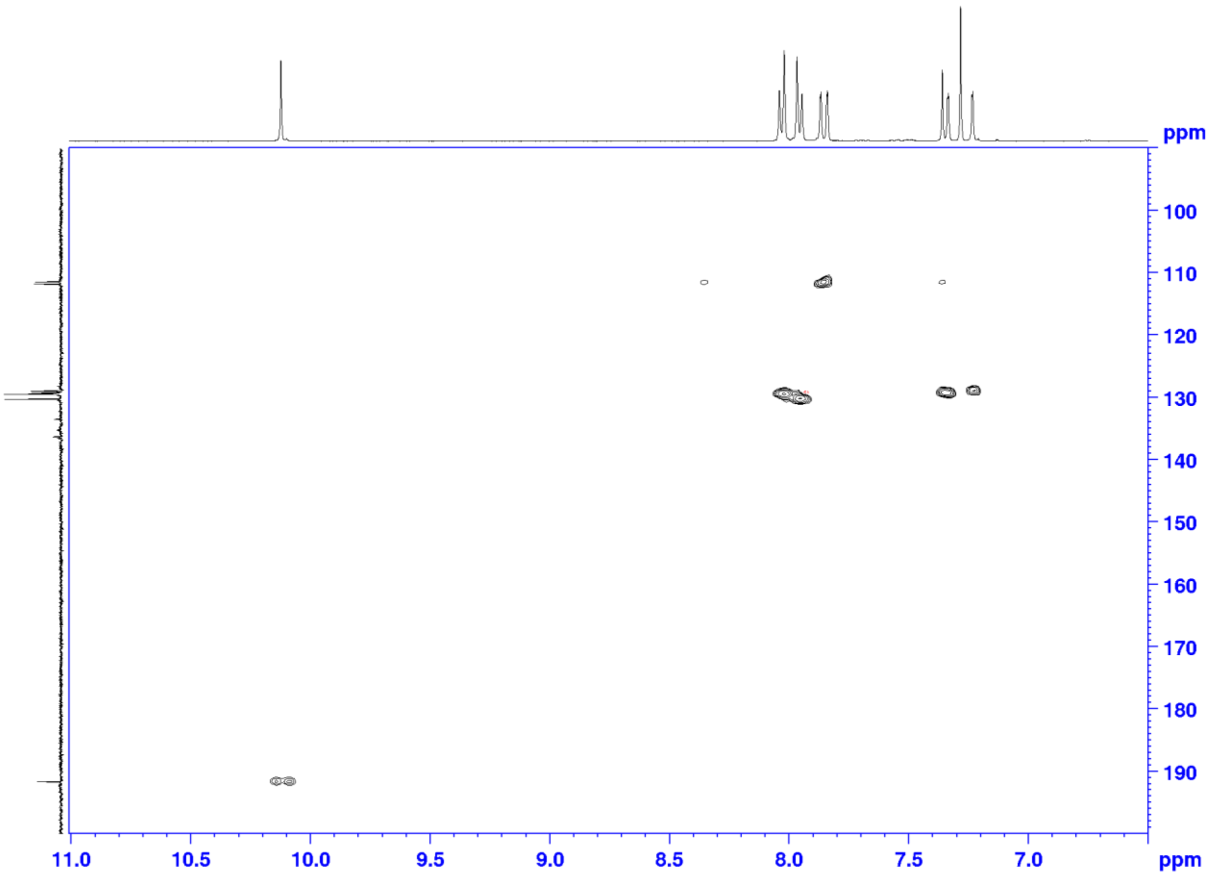


Figure S6. ^{1}H NMR spectrum of **TTPh(CHO)$_3$** (400 MHz, DMSO-d$_6$, 298 K)

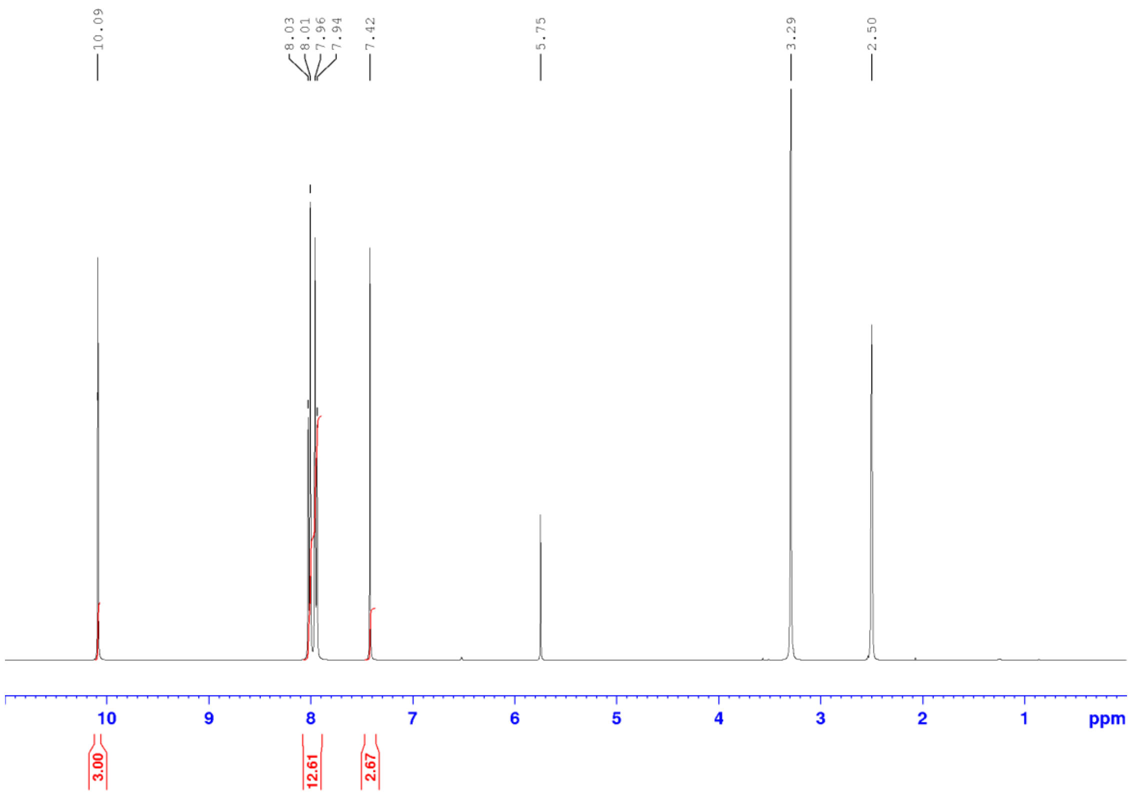


Figure S7. Expanded region of ^{1}H NMR spectrum of **TTPh(CHO)$_3$** (400 MHz, DMSO-d$_6$, 298 K)

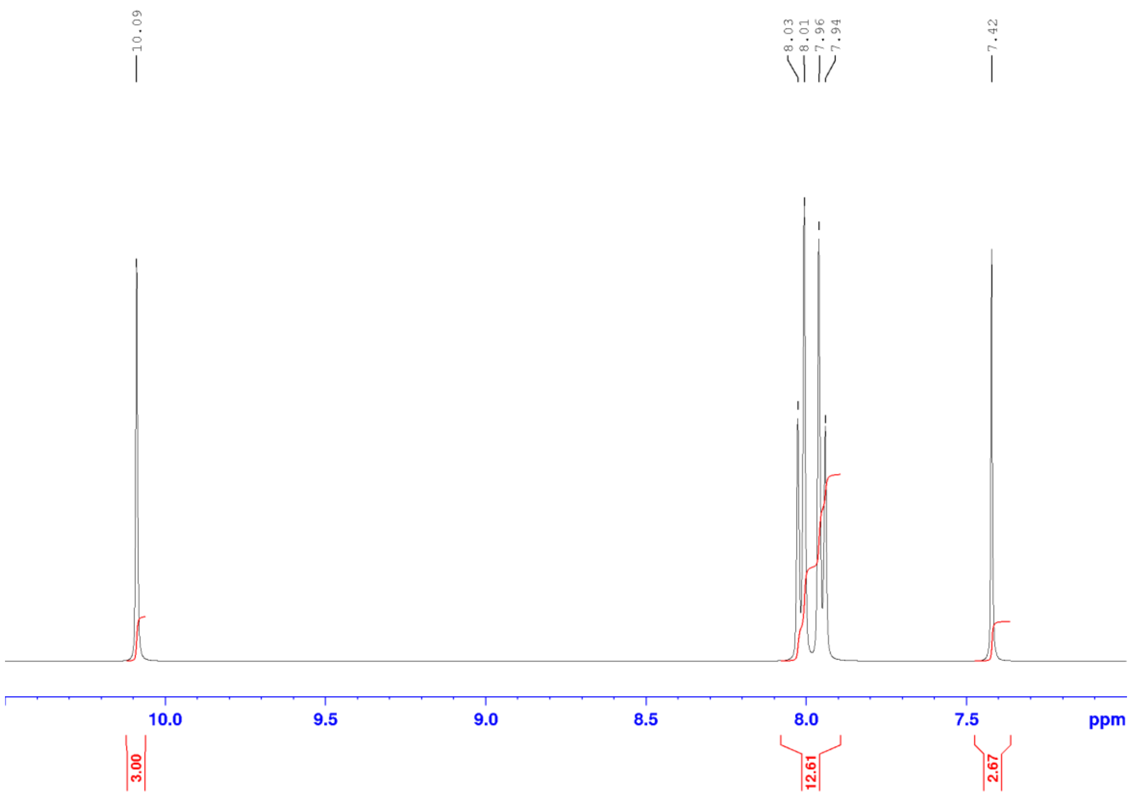


Figure S8. ^{13}C NMR spectrum of **TT(PhCHO)$_3$** (400 MHz, DMSO-d$_6$, 298 K)

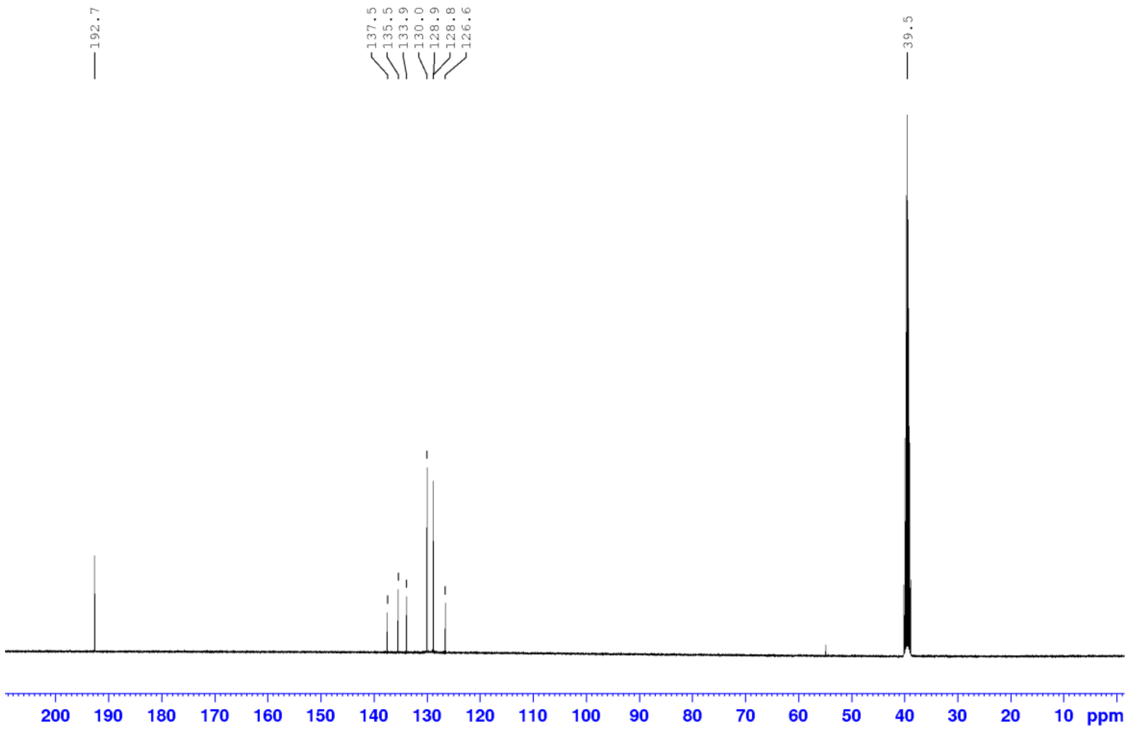


Figure S9. Expanded region of ^{13}C NMR spectrum of **TT(PhCHO)$_3$** (400 MHz, DMSO-d$_6$, 298 K)

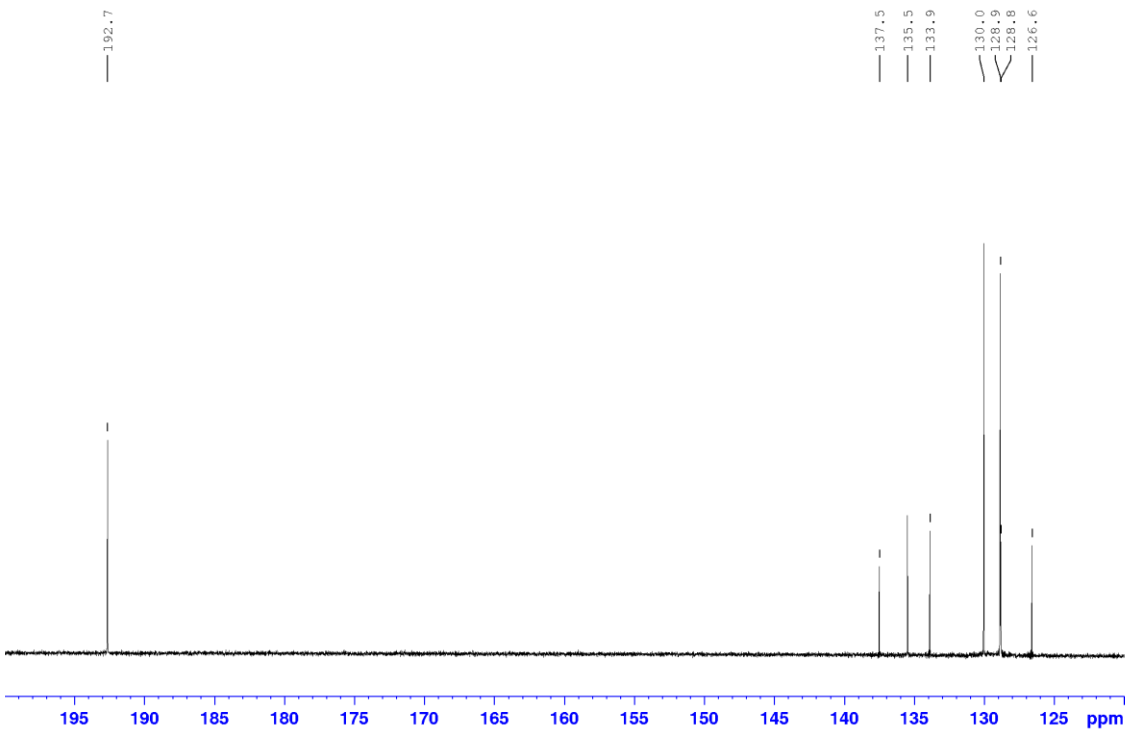
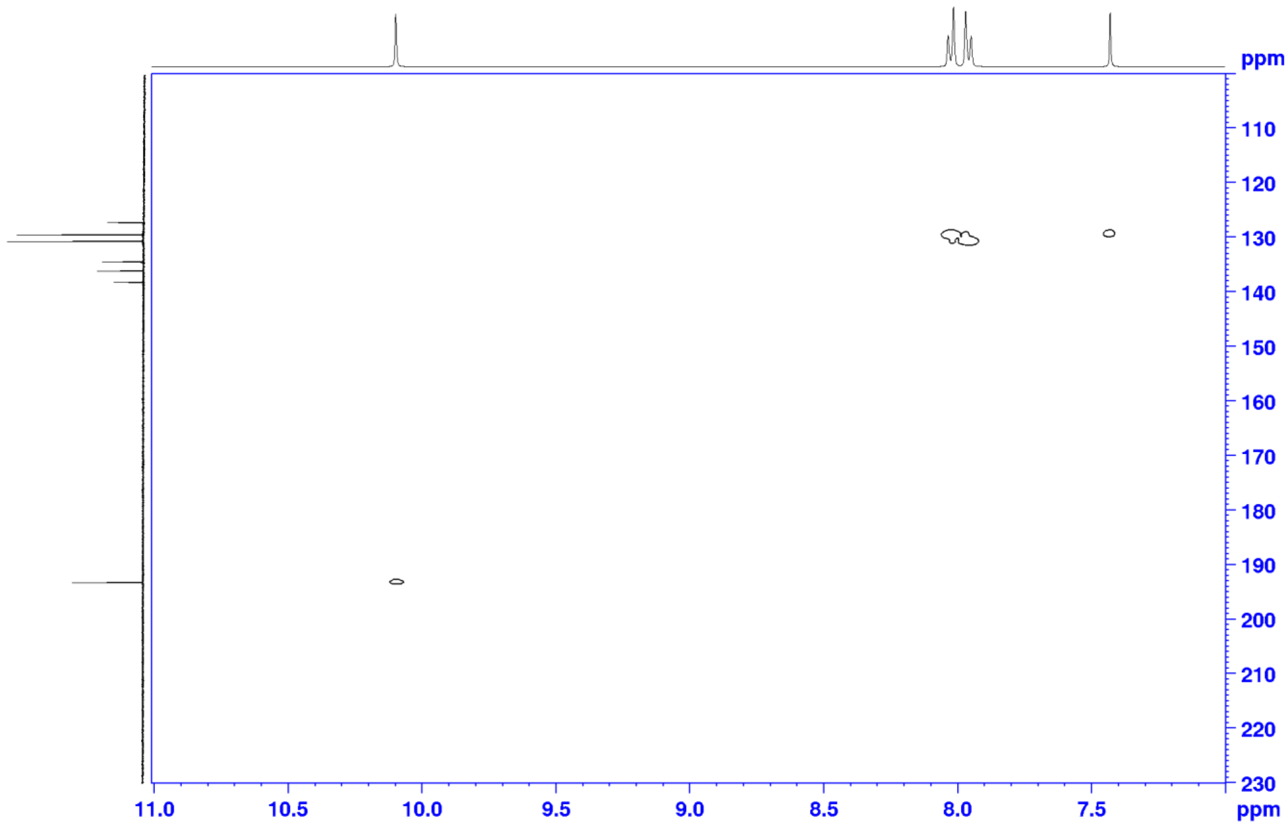


Figure S10. Expanded region of 2D ^{1}H-^{13}C HSQC NMR spectrum of **TT(PhCHO)$_3$** (DMSO-d_6, 298 K)



2. Photophysical Data

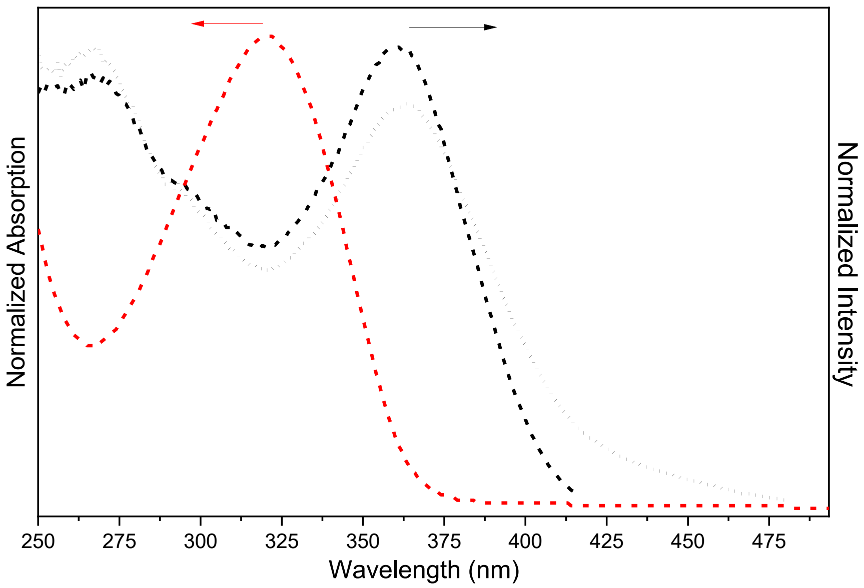


Figure S11. Red: absorption spectra of **TTPhCHO** in DCM (10^{-5} M). Black: excitation spectra in PMMA, 0.5 w%; λ_{em} = 433 nm (dashed) and λ_{em} = 500 nm (dotted).

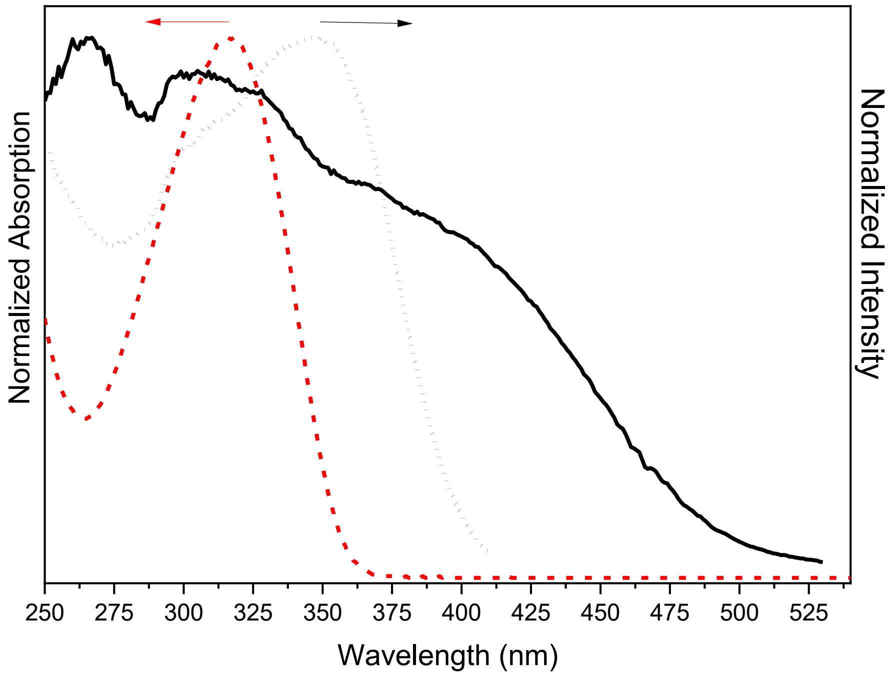


Figure S12. Red: absorption spectra of **TT(PhCHO)₃** in DCM (10^{-5} M) (dashed). Black: excitation spectra in PMMA 0.5 w%; continuous λ_{em} = 550 nm, dotted λ_{em} = 425 nm.

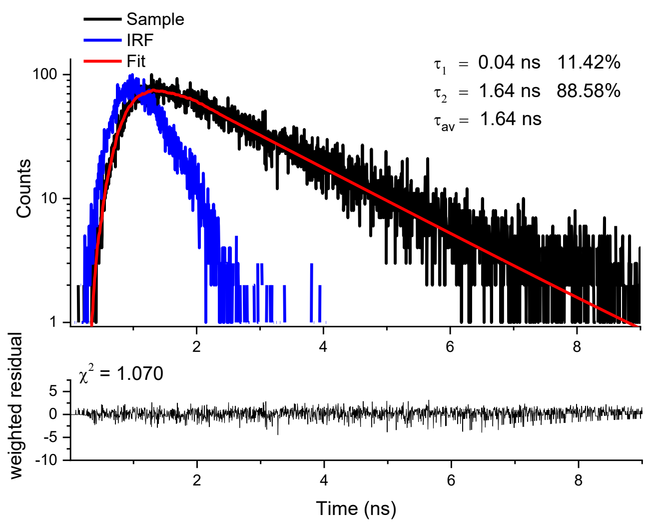


Figure S13. Lifetime measurement (λ_{exc} = 300 nm, λ_{em} = 378 nm) of **TTPhCHO** in DCM (10^{-5} M) at 298 K.

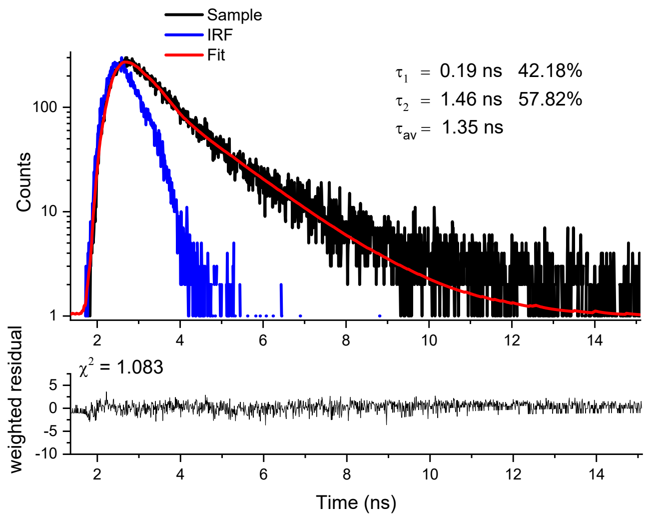


Figure S14. Lifetime measurement (λ_{exc} = 300 nm, λ_{em} = 378 nm) of **TTPhCHO** in PMMA (0.5 w%) at 298 K.

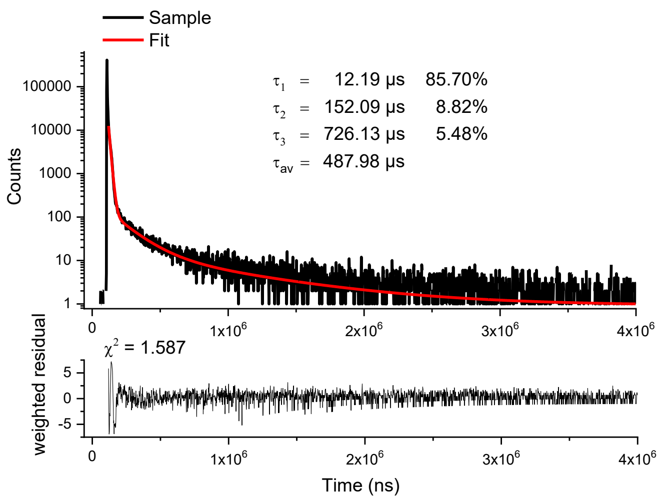


Figure S15. Lifetime measurement (λ_{exc} = 300 nm, λ_{em} = 434 nm) of **TTPhCHO** in PMMA (0.5 w%) at 298 K.

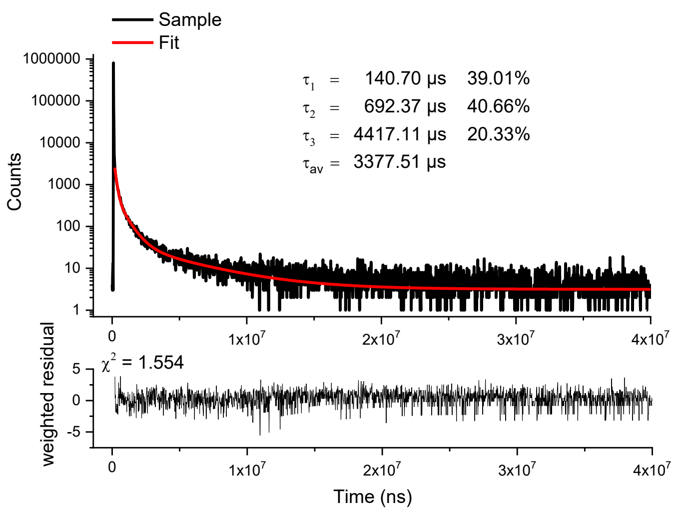


Figure S16. Lifetime measurement (λ_{exc} = 300 nm, λ_{em} = 500 nm) of **TTPhCHO** in PMMA (0.5 w%) at 298 K.

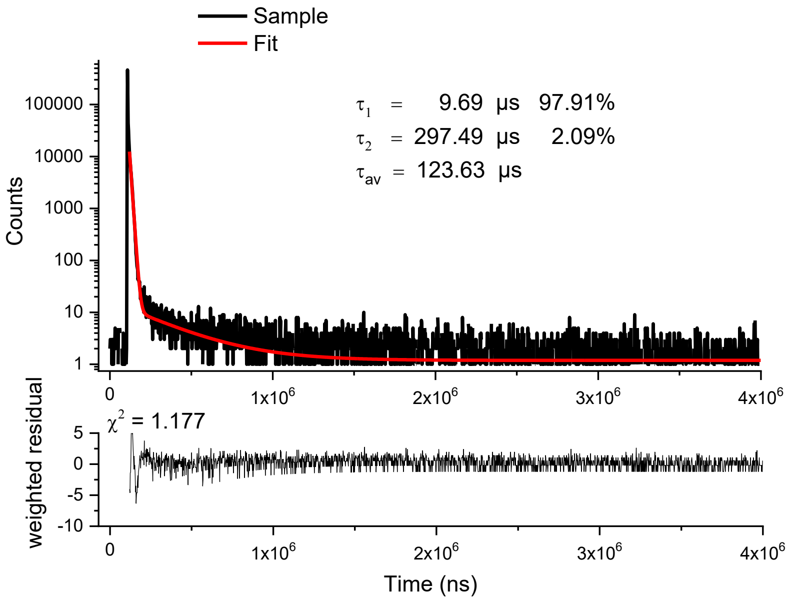


Figure S17. Lifetime measurement (λ_{exc} = 374 nm, λ_{em} = 431 nm) of **TTPhCHO** crystals at 298 K.

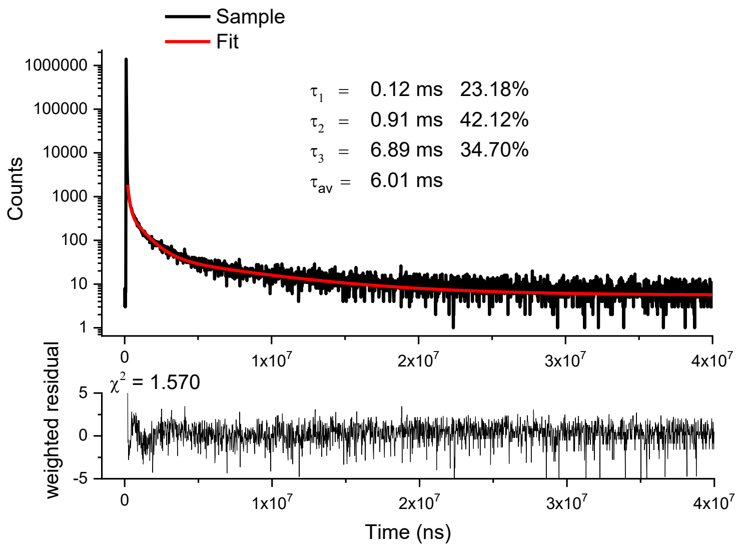
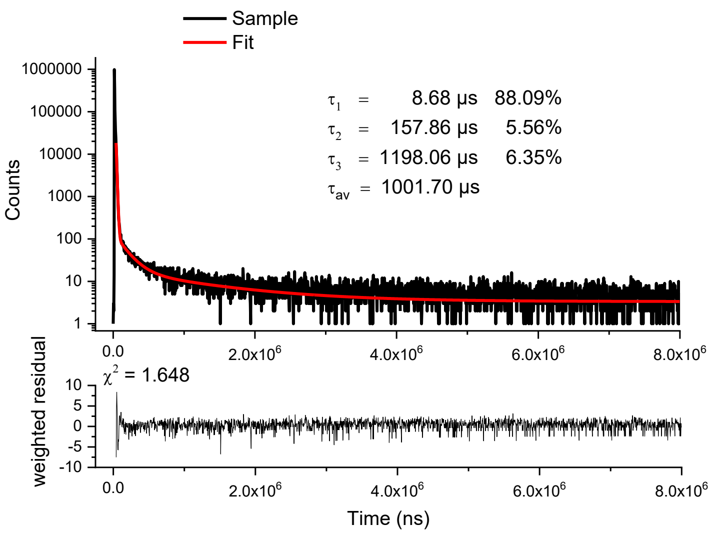


Figure S18. Lifetime measurement (λ_{exc} = 374 nm, λ_{em} = 525 nm) of **TTPhCHO** crystals at 298 K.



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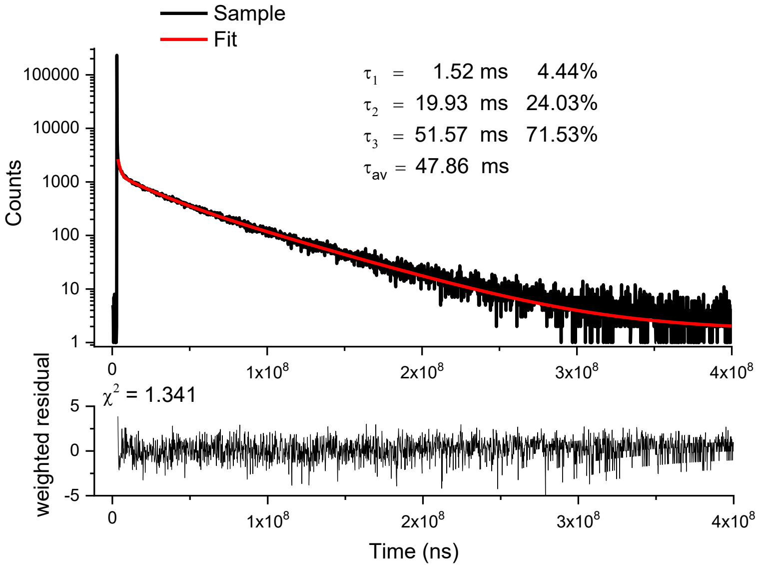

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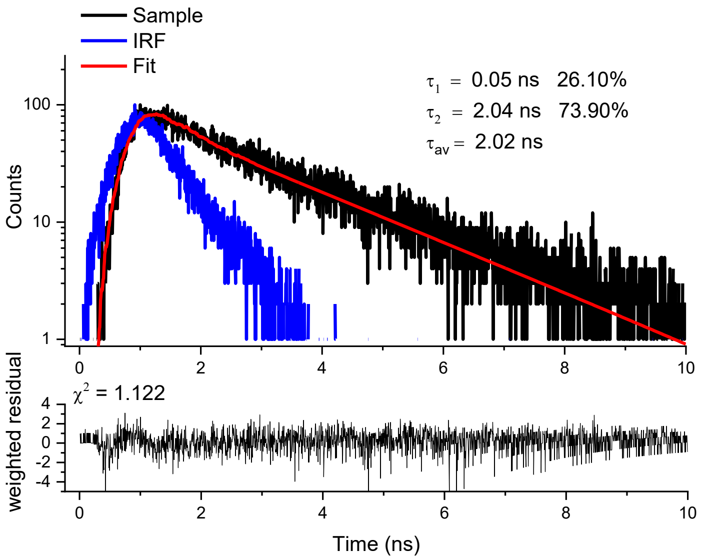


Figure S21. Lifetime measurement (λ_{exc} = 300 nm, λ_{em} = 377 nm) of **TT(PhCHO)$_3$** in DCM (10^{-5} M) at 298 K.

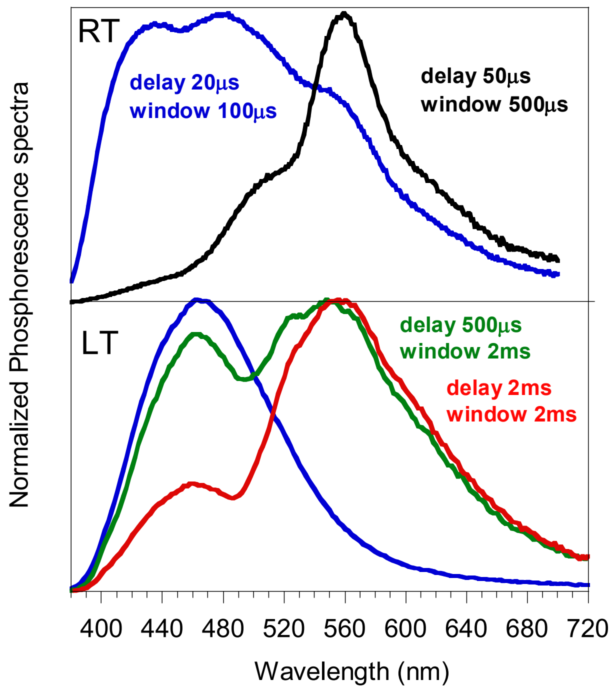


Figure S22. Normalized Phosphorescence spectra of **TTPhCHO** powders at Room Temperature (top panel) and at 87 K (bottom panel) measured for different delays and integration windows (λ_{exc} = 300 nm).

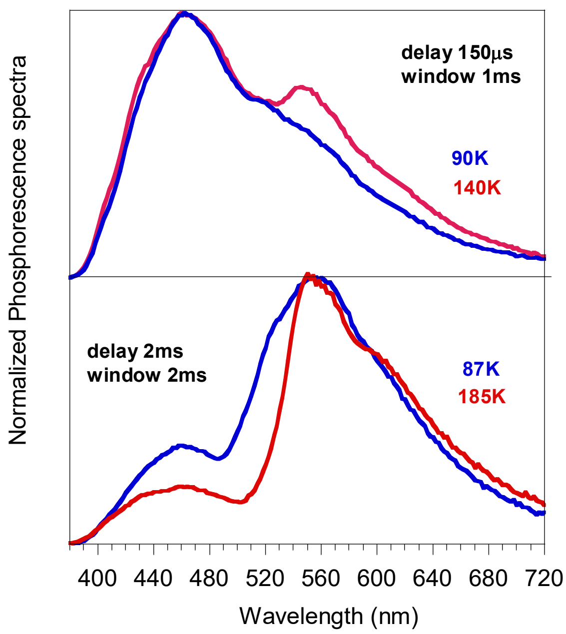


Figure S23. Normalized Phosphorescence spectra of **TTPhCHO** powders measured at different temperatures, different delays and integration windows (λ_{exc} = 300 nm).

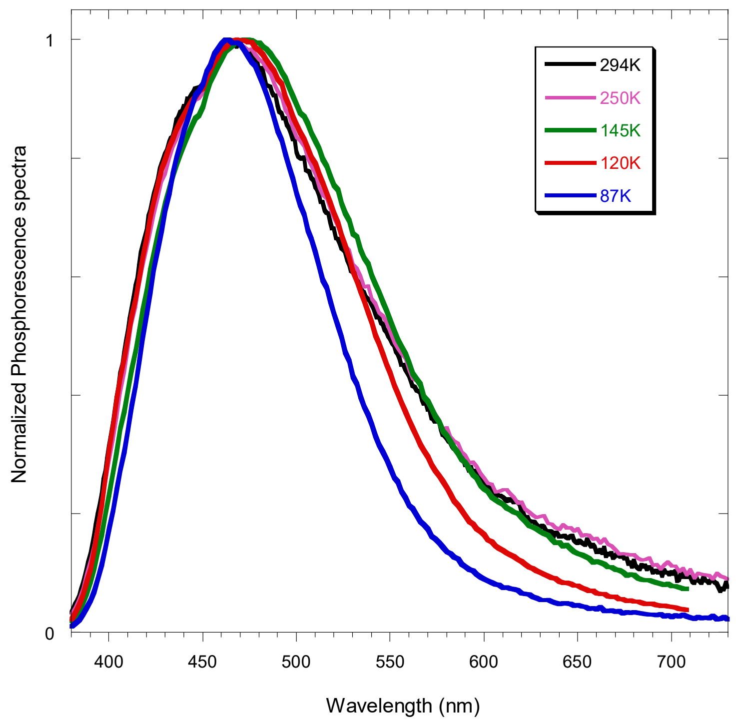


Figure S24. Normalized Phosphorescence spectra. Temperature dependence of **TTPhCHO** powders recorded at 2 0µs delay and 100 µs window (294 K, black; 250 K, pink; 145 K, green, 120 K, red; 87 K blue; λ_{exc} = 300 nm).

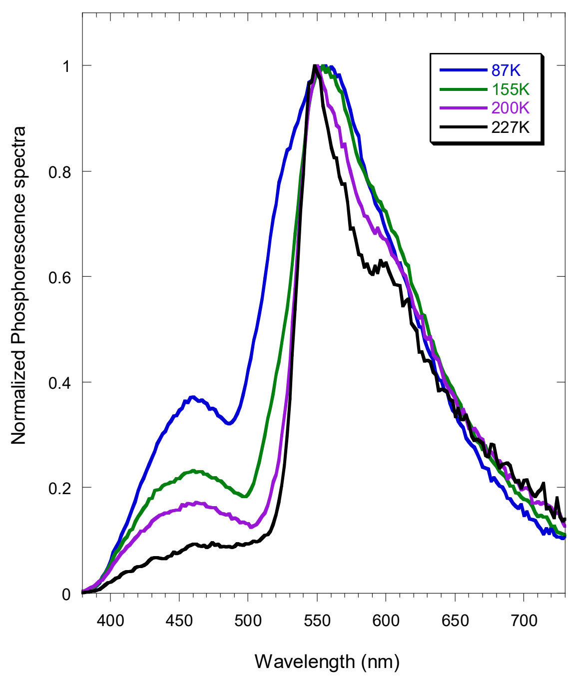


Figure S25. Normalized Phosphorescence spectra. Temperature dependence of **TTPhCHO** powders recorded at 2 ms delay and 2 ms window (λ_{exc} = 300 nm).

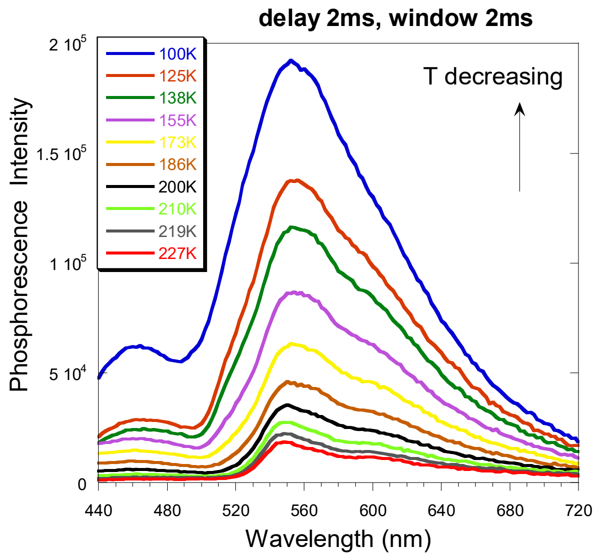


Figure S26. Temperature dependence of Phosphorescence spectra of **TTPhCHO** powders recorded at 2 ms delay and 2 ms window (λ_{exc} = 300 nm).

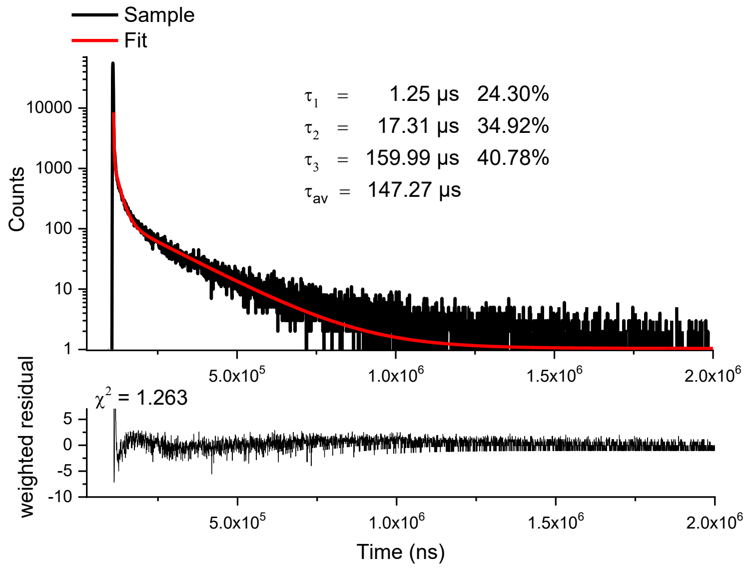


Figure S27. Lifetime measurement (λ_{exc} = 250 nm, λ_{em} = 425 nm) of **TT(PhCHO)$_3$** in PMMA (0.5 w%) at 298 K.

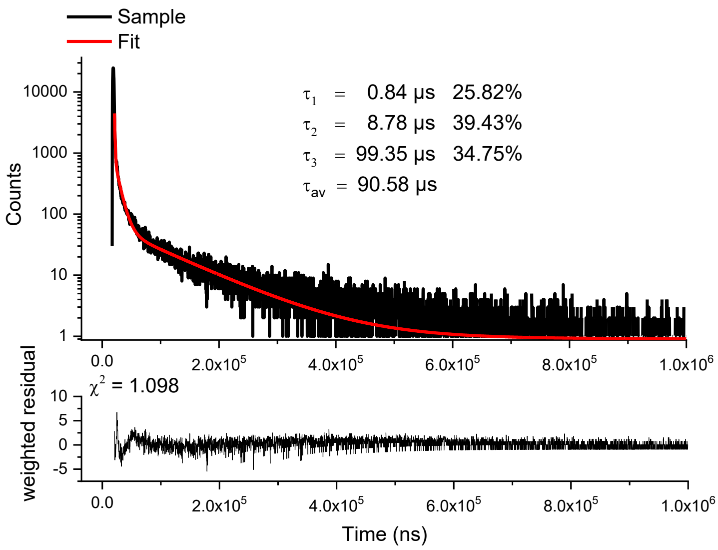


Figure S28. Lifetime measurement (λ_{exc} = 250 nm, λ_{em} = 550 nm) of **TT(PhCHO)$_3$** in PMMA (0.5 w%) at 298 K.

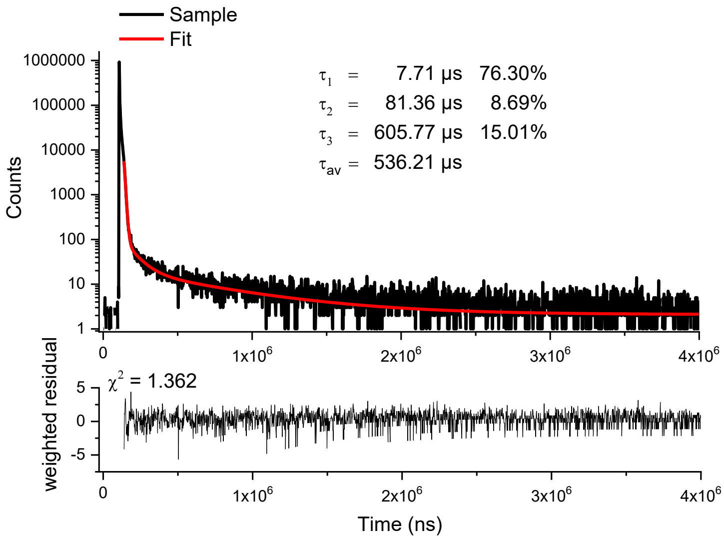


Figure S29. Lifetime measurement (λ_{exc} = 384 nm, λ_{em} = 409 nm) of **TT(PhCHO)$_3$** crystals at 298 K.

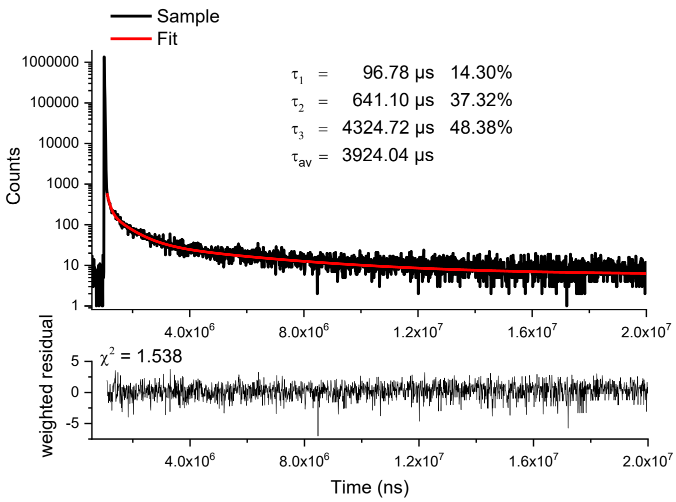


Figure S30. Lifetime measurement (λ_{exc} = 384 nm, λ_{em} = 515 nm) of **TT(PhCHO)$_3$** crystals at 298 K.

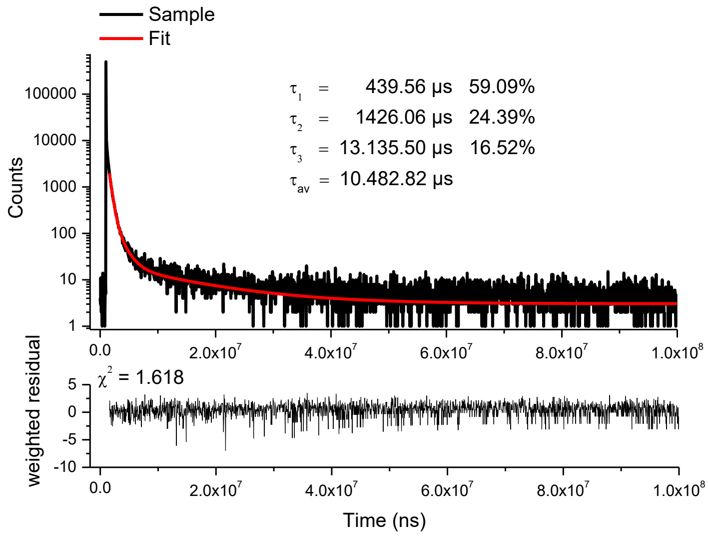


Figure S31. Lifetime measurement (λ_{exc} = 384 nm, λ_{em} = 575 nm) of **TT(PhCHO)$_3$** crystals at 298 K.

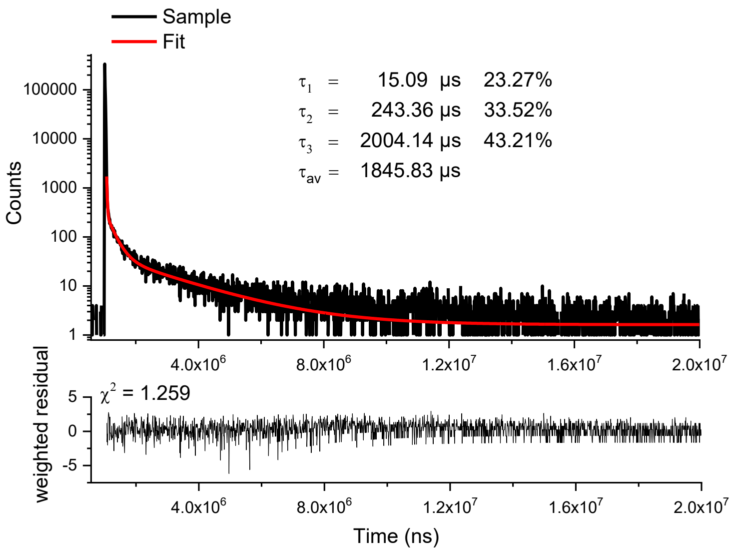


Figure S32. Lifetime measurement (λ_{exc} = 384 nm, λ_{em} = 419 nm) of **TT(PhCHO)$_3$** crystals at 77 K.

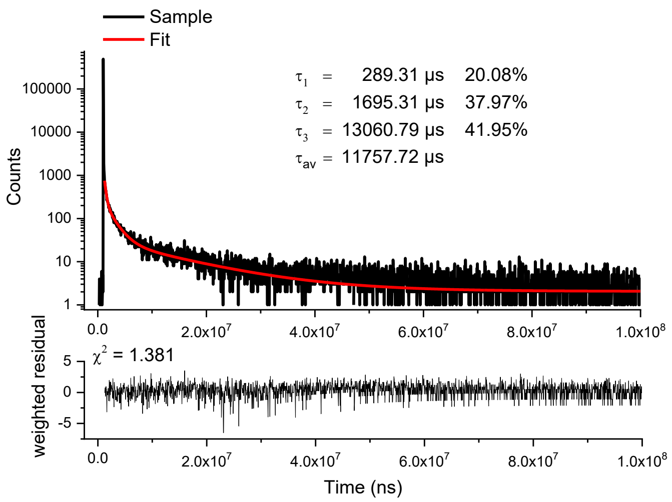


Figure S33. Lifetime measurement (λ_{exc} = 384 nm, λ_{em} = 505 nm) of **TT(PhCHO)$_3$** crystals at 77 K.

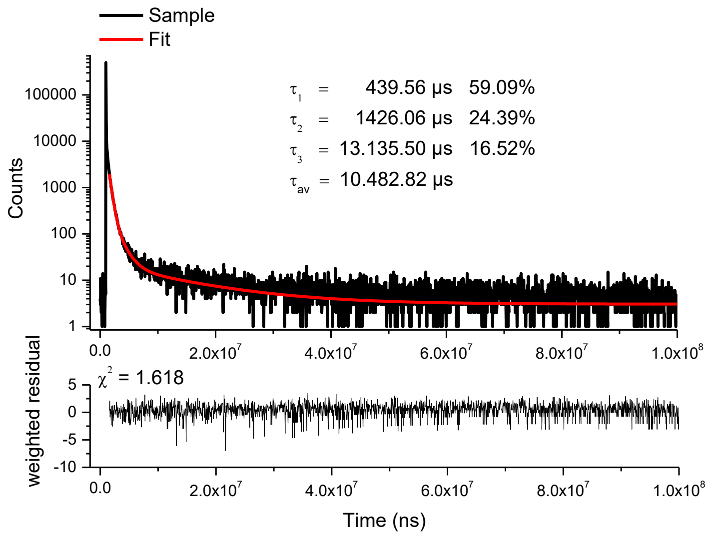


Figure S34. Lifetime measurement (λ_{exc} = 384 nm, λ_{em} = 560 nm) of **TT(PhCHO)$_3$** crystals at 77 K.

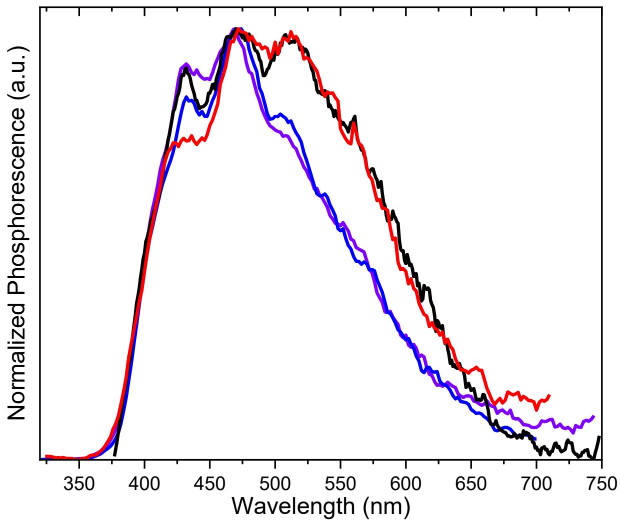


Figure S35. Phosphorescence spectra of PMMA films of **TTPhCHO** (0.5 w/w%) at 298K, λ_{exc} = 280 nm at different delays: delay 0.1 ms, window 0.2 ms, violet line; delay 0.2 ms, window 0.5 ms, blue line; delay 0.2 ms, window 2 ms, black line; delay 1 ms, window 5 ms, red line.

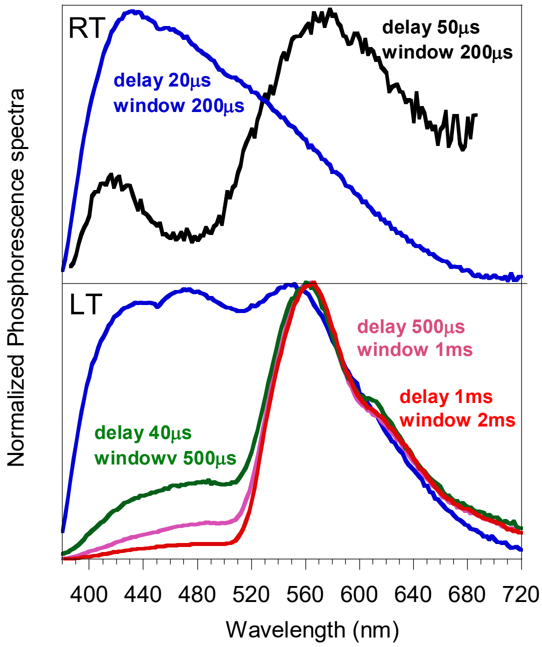


Figure S36. Normalized Phosphorescence spectra of **TT(PhCHO)₃** powders at Room Temperature (top panel) and at 87K (bottom panel) measured for different delays and integration windows (λ_{exc} = 340 nm).

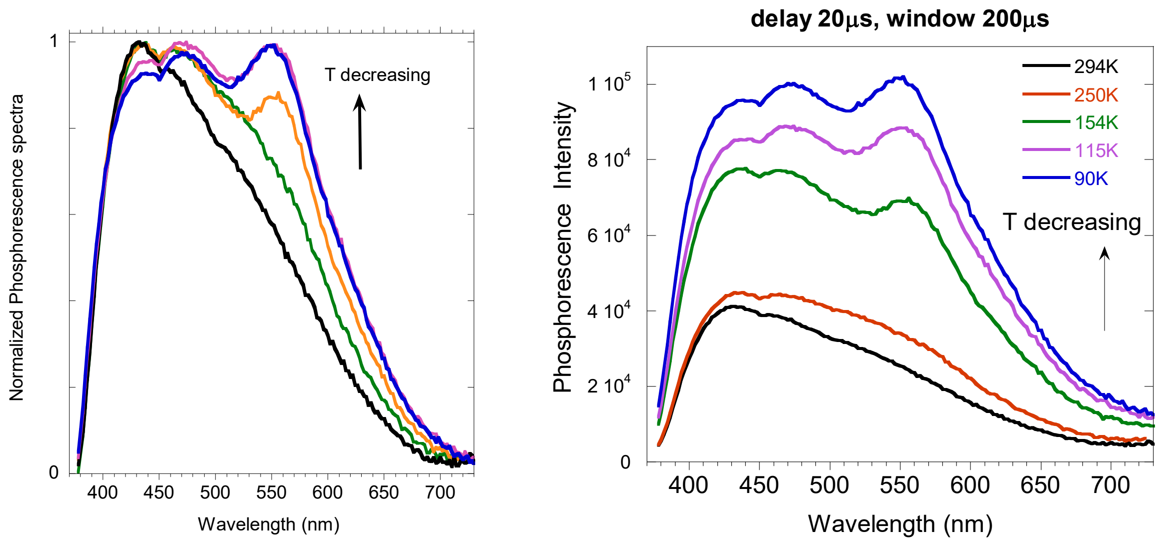


Figure S37. Normalized (left) and Non-Normalized (right) Phosphorescence spectra. Temperature dependence of **TT(PhCHO)₃** powders recorded at 20 μs delay and 200 μs window (294 K, black; 250 K, green; 154 K, orange, 115 K, pink; 87 K blue; λ_{exc} = 340 nm).

3. Crystallographic Data

Table S1. Crystal data and structure refinement parameters for **TTPhCHO** and **TT(PhCHO)$_3$.CH$_2$Cl$_2$**.

	TTPhCHO	**TT(PhCHO)$_3$.CH$_2$Cl$_2$**
Empirical formula moiety	$C_{16}H_{10}N_6O$	$C_{30}H_{18}N_6O_3 \cdot CH_2Cl_2$
Empirical formula sum	$C_{16}H_{10}N_6O$	$C_{31}H_{20}Cl_2N_6O_3$
FW (g mol^{-1})	302.30	595.43
Crystal system	monoclinic	monoclinic
Space group	P 2/n	C 2/c
a/Å	17.2524(4)	36.6472(7)
b/Å	3.87680(10)	7.55030(10)
c/Å	39.7649(12)	20.7484(4)
α/deg	90	90
β/deg	96.793(3)	105.117(2)
γ/deg	90	90
V/Å^3	2640.97(12)	5542.36(17)
Z	8	8
T/K	296(2)	293(2)
D_{calcd} g/cm^3	1.521	1.427
μ(CuKα)/mm^{-1}	0.844	2.487
F(000)	1248	2448
Crystal size/mm^3	0.10 x 0.01 x 0.01	0.27 x 0.05 x 0.02
Collected reflections	27341	56158
Independent reflections	5276	6014
Observed [$I > 2\sigma(I)$] reflections	3541	4306
R_{int}	0.0787	0.0691
R_σ	0.0682	0.0370
S	1.025	1.070
Data/restraints/parameters	5276/0/415	6014/51/451
R_1, wR_2 [$I > 2\sigma(I)$]	0.0520, 0.1229	0.0569, 0.1580
R_1, wR_2 (all data)	0.0862, 0.1398	0.0763, 0.1748
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.172, -0.235	0.352, -0.363

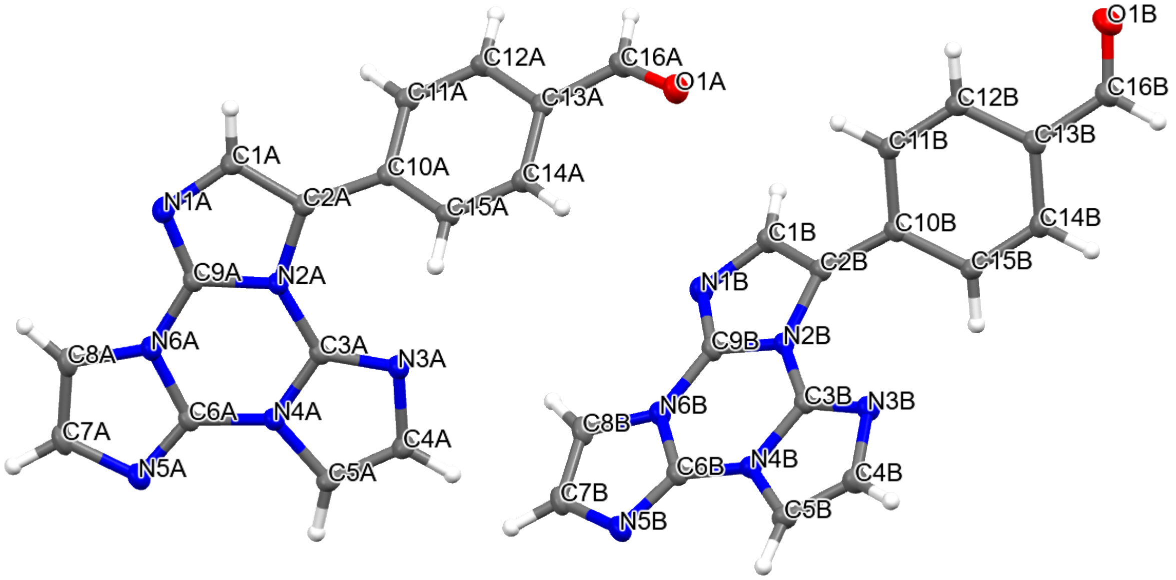


Figure S38. ORTEP plot of **TTPhCHO** with the atom numbering scheme. Ellipsoids are plotted at the 30% probability level.

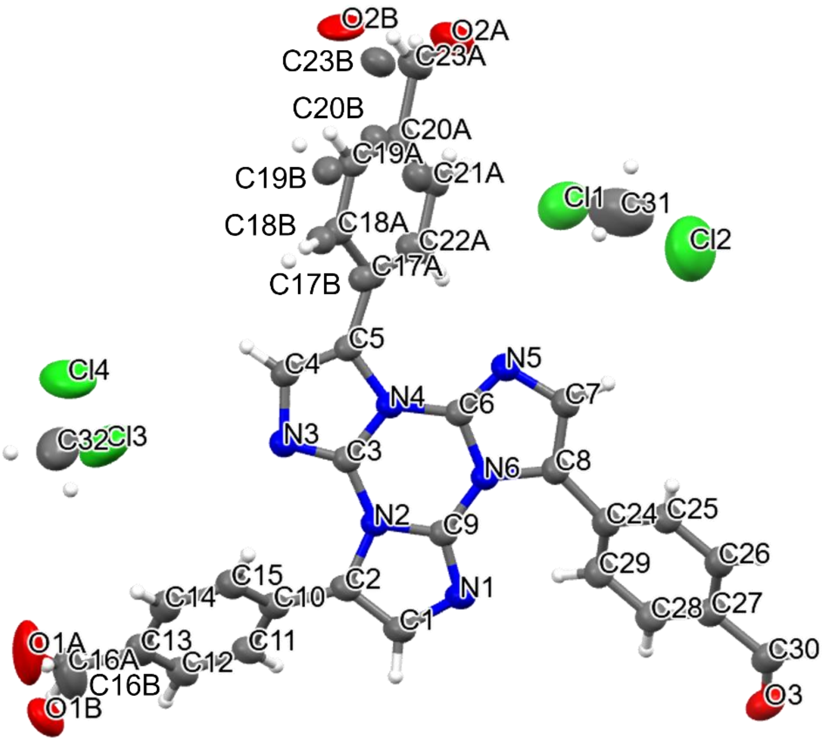


Figure S39. ORTEP plot of **TT(PhCHO)$_3$.CH$_2$Cl$_2$** with the atom numbering scheme. Ellipsoids are plotted at the 30% probability level.

4. Computational Results

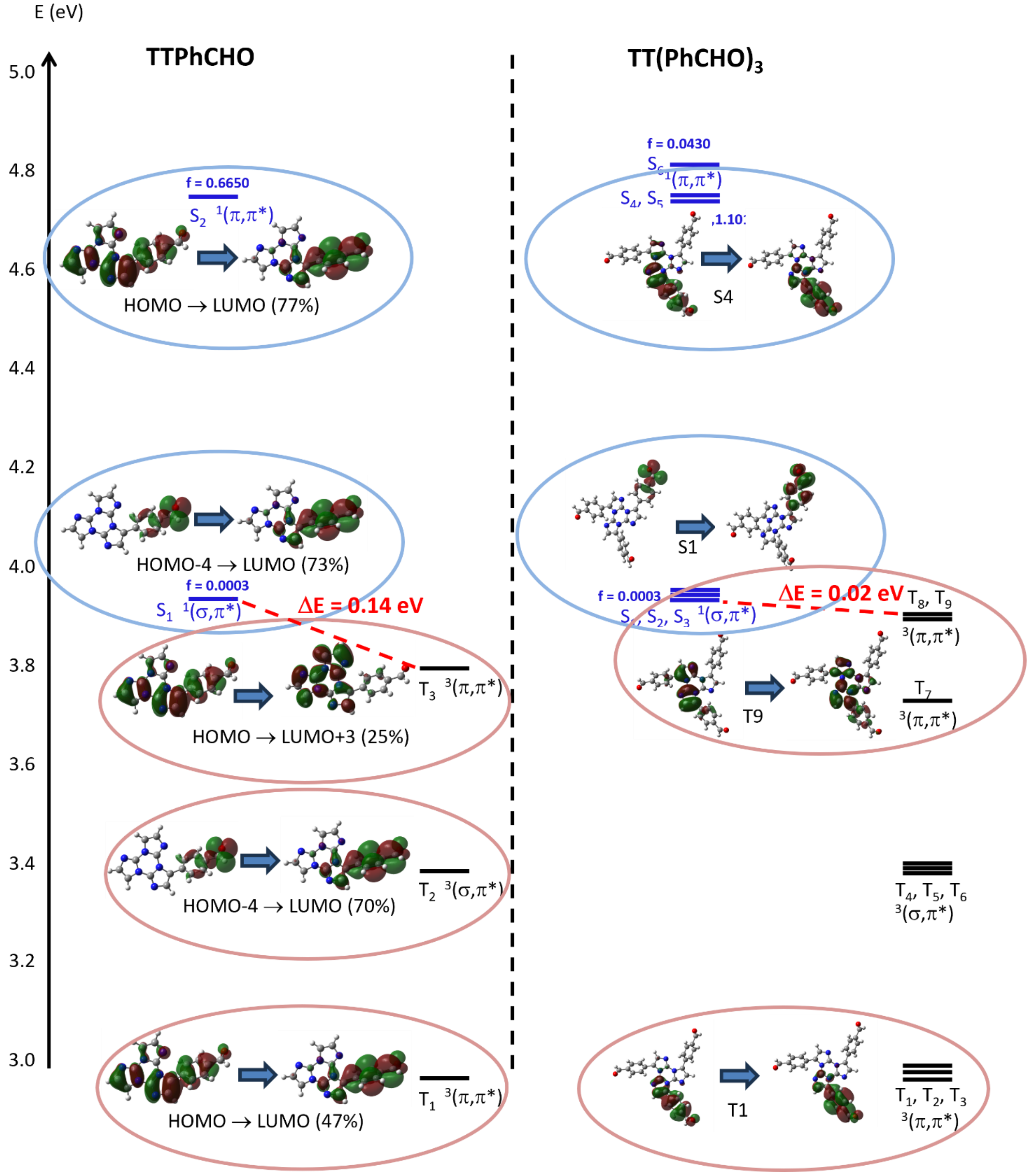


Figure S40. Electronic levels computed for **TTPhCHO** and **TT(PhCHO)₃** at molecular level with most important NTOs. In blue are reported the singlet levels with oscillator strength $f \geq 0.0001$ and the corresponding values of f (see detailed information in Tables S2 and S3).

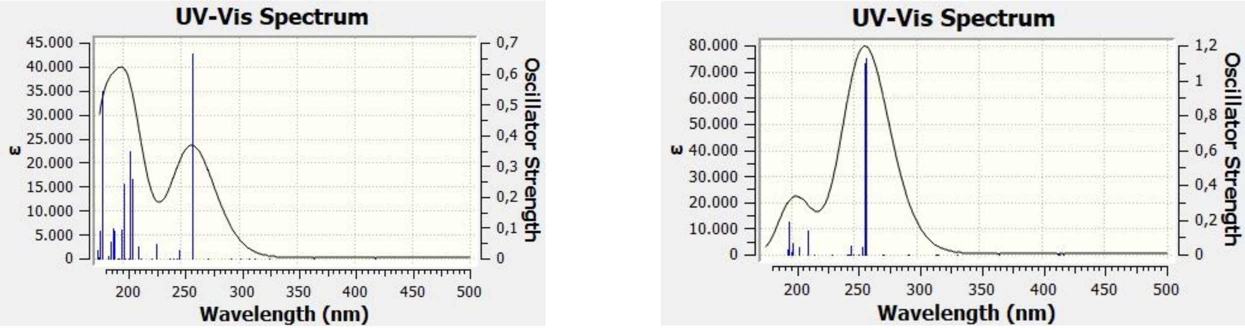


Figure S41. ωB97X/6-311++G(d,p) computed absorption spectrum of **TTPhCHO** (left) and **TT(PhCHO)$_3$** (right), resulting from convolution of the excitation energies (blue sticks) with 0.40 eV of half-bandwidth.

Table S2. ωB97X/6-311++G(d,p) excitation energies, oscillator strengths and composition of the first singlet states computed for **TTPhCHO**.

```
Excitation energies and oscillator strengths:

T1 Excited State   1:      Triplet-A      2.9661 eV  418.00 nm  f=0.0000  <S**2>=2.000
      73 -> 79        0.29736
      75 -> 82       -0.10629
      75 -> 84        0.20035
      76 -> 79        0.21746
      78 -> 79        0.48257

T2 Excited State   2:      Triplet-A      3.3955 eV  365.15 nm  f=0.0000  <S**2>=2.000
      74 -> 79        0.59075
      74 -> 82        0.18765
      74 -> 93        0.16405
      74 -> 94       -0.12630
      74 -> 99        0.12692

T3 Excited State   3:      Triplet-A      3.8008 eV  326.20 nm  f=0.0000  <S**2>=2.000
      73 -> 79        0.23218
      75 -> 84        0.12204
      76 -> 79        0.11471
      77 -> 81       -0.29903
      78 -> 79       -0.16964
      78 -> 82        0.35601
      78 -> 84        0.20135

S1 Excited State   4:      Singlet-A      3.9423 eV  314.50 nm  f=0.0003  <S**2>=0.000
      74 -> 79        0.60295
      74 -> 82        0.18658
      74 -> 93        0.15474
      74 -> 94       -0.11566
      74 -> 99        0.11958

T4 Excited State   5:      Triplet-A      4.0174 eV  308.62 nm  f=0.0000  <S**2>=2.000
      73 -> 79        0.16415
      76 -> 82        0.18705
      76 -> 84        0.12148
      77 -> 81        0.44659
      77 -> 82       -0.12148
      78 -> 79       -0.11455
      78 -> 81        0.11706
      78 -> 82        0.11477
      78 -> 93        0.11422

T5 Excited State   6:      Triplet-A      4.1061 eV  301.95 nm  f=0.0000  <S**2>=2.000
      76 -> 81        0.42362
      77 -> 79       -0.11849
      77 -> 81        0.12323
      77 -> 82        0.25271
      77 -> 84        0.18017
      77 -> 93       -0.15534
      78 -> 81       -0.17899

T6 Excited State   7:      Triplet-A      4.2272 eV  293.30 nm  f=0.0000  <S**2>=2.000
      75 -> 79        0.65229

T7 Excited State   8:      Triplet-A      4.5338 eV  273.46 nm  f=0.0000  <S**2>=2.000
```

```
      73 -> 79        -0.18893
      75 -> 80         0.20427
      75 -> 82        -0.21434
      75 -> 84         0.45309
      75 -> 86         0.11004
      76 -> 79        -0.11487
      78 -> 79        -0.17897
      78 -> 82        -0.16078

S2 Excited State   9:      Singlet-A      4.7603 eV  260.45 nm  f=0.6650  <S**2>=0.000
      73 -> 79         0.11684
      76 -> 79         0.18813
      78 -> 79         0.61944
      78 -> 82        -0.11083

T8 Excited State  10:      Triplet-A      4.9845 eV  248.74 nm  f=0.0000  <S**2>=2.000
      73 -> 79         0.10316
      73 -> 81        -0.13119
      73 -> 82         0.16496
      77 -> 82         0.16711
      78 -> 81         0.39028
      78 -> 82        -0.10897
      78 -> 84        -0.20072
      78 -> 93         0.14922
      78 ->100        -0.11452
```

Table S3. ωB97X/6-311++G(d,p) excitation energies, oscillator strengths and composition of the first singlet states computed for **TT(PhCHO)$_3$**.

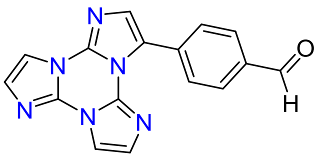
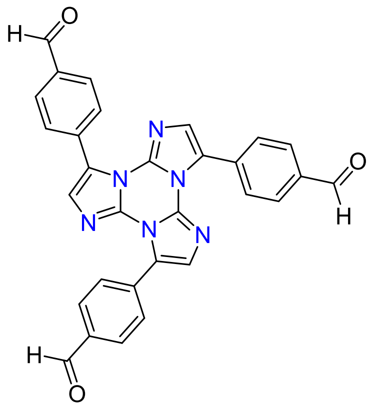
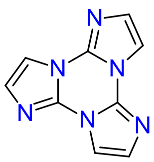
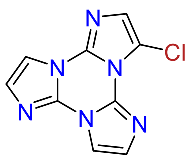
```
Excitation energies and oscillator strengths:

T1 = (T1)' Excited State   1:      Triplet-A      2.9710 eV  417.31 nm  f=0.0000  <S**2>=2.000
     121 ->135         0.14934
     122 ->133         0.15003
     123 ->134        -0.20905
     128 ->143        -0.10427
     130 ->133         0.10503
     130 ->135         0.27383
     131 ->133        -0.23591
     132 ->134         0.33850

T2 = (T1)' Excited State   2:      Triplet-A      2.9937 eV  414.16 nm  f=0.0000  <S**2>=2.000
     121 ->134         0.15938
     122 ->134         0.12932
     123 ->133        -0.15305
     123 ->135        -0.19967
     130 ->134         0.31057
     131 ->134        -0.18755
     132 ->133         0.22219
     132 ->135         0.23464

T3 = (T1)' Excited State   3:      Triplet-A      3.0029 eV  412.88 nm  f=0.0000  <S**2>=2.000
     121 ->133         0.10256
     122 ->133        -0.18649
     122 ->135         0.24208
     123 ->134        -0.10175
     127 ->142         0.11845
     130 ->133         0.30136
     131 ->133         0.23558
     131 ->135        -0.26184
     132 ->134         0.13814

T4 = (T2)' Excited State   4:      Triplet-A      3.3880 eV  365.95 nm  f=0.0000  <S**2>=2.000
     125 ->133        -0.24200
     125 ->134         0.42286
     125 ->135        -0.32248
     125 ->137        -0.13755
     125 ->138        -0.12592
     125 ->159        -0.10574

T5 = (T2)' Excited State   5:      Triplet-A      3.3886 eV  365.88 nm  f=0.0000  <S**2>=2.000
     124 ->133         0.44207
     124 ->135        -0.39217
     124 ->138         0.18634
     124 ->156        -0.12179
     124 ->158         0.11377
```

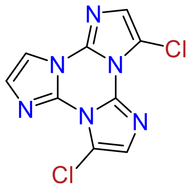
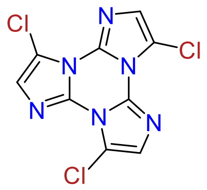
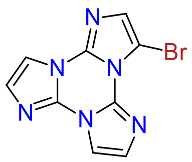
```
T6 = (T2)' Excited State   6:      Triplet-A      3.3902 eV  365.72 nm  f=0.0000  <S**2>=2.000
     126 ->133         0.28365
     126 ->134         0.38536
     126 ->135         0.33435
     126 ->137        -0.17935
     126 ->155        -0.12987

T7 = (T3)' Excited State   7:      Triplet-A      3.7314 eV  332.27 nm  f=0.0000  <S**2>=2.000
     121 ->135        -0.11620
     122 ->133        -0.18841
     123 ->134         0.20060
     131 ->133        -0.16069
     131 ->138         0.28972
     131 ->142        -0.14460
     132 ->134         0.15523
     132 ->137         0.27133
     132 ->143        -0.15634

T8 = (T3)' Excited State   8:      Triplet-A      3.9122 eV  316.91 nm  f=0.0000  <S**2>=2.000
     121 ->134         0.15565
     122 ->135        -0.10705
     123 ->133        -0.12411
     130 ->137        -0.14493
     130 ->138        -0.15747
     130 ->143         0.11284
     131 ->134         0.14102
     131 ->137         0.18998
     132 ->133        -0.13323
     132 ->138         0.19457

T9 = (T3)' Excited State   9:      Triplet-A      3.9153 eV  316.66 nm  f=0.0000  <S**2>=2.000
     121 ->133        -0.12564
     121 ->134        -0.10622
     122 ->133         0.12458
     123 ->134         0.11659
     123 ->135         0.10434
     130 ->137         0.14513
     130 ->138        -0.14654
     131 ->133         0.13912
     131 ->138        -0.20462
     132 ->134         0.13775
     132 ->137         0.19630

S1 = (S1)' Excited State  10:      Singlet-A      3.9357 eV  315.02 nm  f=0.0003  <S**2>=0.000
     125 ->133        -0.24737
     125 ->134         0.43216
     125 ->135        -0.32826
     125 ->137        -0.13642
     125 ->138        -0.12522

S2 = (S1)' Excited State  11:      Singlet-A      3.9365 eV  314.96 nm  f=0.0003  <S**2>=0.000
     124 ->133         0.45198
     124 ->135        -0.39921
     124 ->138         0.18455
     124 ->156        -0.11406
     124 ->158         0.10569

S3 = (S1)' Excited State  12:      Singlet-A      3.9378 eV  314.86 nm  f=0.0003  <S**2>=0.000
     126 ->133         0.28994
     126 ->134         0.39384
     126 ->135         0.34027
     126 ->137        -0.17851
     126 ->155        -0.12204

T10= (T4)' Excited State  13:      Triplet-A      4.2216 eV  293.69 nm  f=0.0000  <S**2>=2.000
     127 ->134         0.21779
     127 ->135        -0.23805
     129 ->133        -0.27044
     129 ->134         0.41742
     129 ->135        -0.25782

T11= (T4)' Excited State  14:      Triplet-A      4.2249 eV  293.46 nm  f=0.0000  <S**2>=2.000
     127 ->133         0.38443
     127 ->135        -0.27955
     128 ->133        -0.27558
     128 ->135         0.20872
     129 ->133        -0.14927
```

```
     129 ->135         0.22960

T12= (T4)' Excited State  15:      Triplet-A      4.2352 eV  292.75 nm  f=0.0000  <S**2>=2.000
     127 ->133         0.15630
     127 ->134         0.20525
     127 ->135         0.13301
     128 ->133         0.25955
     128 ->134         0.37430
     128 ->135         0.31933
     129 ->133        -0.11426
     129 ->134        -0.10098
     129 ->135        -0.10743

T13= (T5)' Excited State  16:      Triplet-A      4.5318 eV  273.59 nm  f=0.0000  <S**2>=2.000
     122 ->133         0.11095
     123 ->134        -0.12969
     127 ->139         0.11675
     127 ->140        -0.14817
     127 ->141         0.22465
     128 ->136         0.12412
     128 ->137         0.17759
     128 ->141         0.12884
     128 ->143         0.21543
     128 ->145         0.12048
     129 ->138        -0.12270
     129 ->142        -0.17829
     129 ->143        -0.15154
     130 ->135         0.15874
     132 ->134         0.10461
     132 ->137        -0.10689

T14= (T5)' Excited State  17:      Triplet-A      4.5366 eV  273.29 nm  f=0.0000  <S**2>=2.000
     123 ->135         0.10688
     127 ->137        -0.13572
     127 ->140        -0.12066
     127 ->143        -0.21962
     128 ->137        -0.11827
     128 ->139        -0.12397
     128 ->141        -0.23797
     128 ->143        -0.14911
     129 ->136         0.12842
     129 ->141         0.10954
     129 ->142        -0.17536
     129 ->144        -0.11686
     129 ->145         0.10545
     130 ->134        -0.11850
     130 ->137         0.10414
     132 ->135        -0.11394

T15= (T5)' Excited State  18:      Triplet-A      4.5376 eV  273.24 nm  f=0.0000  <S**2>=2.000
     122 ->135         0.12351
     127 ->136         0.13465
     127 ->138        -0.12158
     127 ->142        -0.25368
     127 ->145         0.13616
     128 ->141         0.11631
     128 ->142         0.12090
     129 ->140        -0.19678
     129 ->141         0.15616
     129 ->143        -0.21178
     130 ->133         0.12263
     131 ->135        -0.11839

S4 = (S2)' Excited State  19:      Singlet-A      4.7708 eV  259.88 nm  f=1.1257  <S**2>=0.000
     123 ->135        -0.10825
     130 ->133         0.12987
     130 ->134         0.36865
     131 ->134        -0.25197
     132 ->133         0.32184
     132 ->135         0.27641

S5 = (S2)' Excited State  20:      Singlet-A      4.7843 eV  259.15 nm  f=1.1018  <S**2>=0.000
     122 ->135         0.12957
     130 ->133         0.37096
     130 ->134        -0.14158
     131 ->133         0.18349
     131 ->135        -0.29459
     132 ->134         0.34226
```

```
S6 = (S2)' Excited State  21:      Singlet-A      4.8264 eV  256.89 nm  f=0.0430  <S**2>=0.000
     130 ->135        -0.26827
     131 ->133         0.43697
     131 ->138        -0.13472
     132 ->134        -0.33694
     132 ->137        -0.10968

T16= (T6)' Excited State  22:      Triplet-A      4.8965 eV  253.21 nm  f=0.0000  <S**2>=2.000
     121 ->135         0.11107
     130 ->155        -0.10441
     131 ->134         0.21691
     131 ->137         0.25420
     131 ->143        -0.11475
     132 ->133         0.22723
     132 ->138        -0.28462
     132 ->142         0.11199
     132 ->169        -0.10043

T17= (T6)' Excited State  23:      Triplet-A      4.9588 eV  250.03 nm  f=0.0000  <S**2>=2.000
     121 ->133        -0.11043
     121 ->137        -0.11004
     121 ->138         0.11630
     123 ->135        -0.10449
     130 ->133         0.15986
     130 ->138        -0.23206
     131 ->133        -0.10410
     131 ->137        -0.12592
     132 ->134        -0.10020
     132 ->135        -0.16604
     132 ->138        -0.13075
     132 ->153        -0.11465
     132 ->155        -0.13987

T18= (T6)' Excited State  24:      Triplet-A      4.9617 eV  249.88 nm  f=0.0000  <S**2>=2.000
     121 ->134        -0.10187
     122 ->135        -0.10767
     130 ->134         0.15870
     130 ->137         0.22354
     130 ->143        -0.10499
     131 ->134         0.12304
     131 ->135        -0.16249
     131 ->138         0.12078
     131 ->153        -0.12423
     131 ->155        -0.11966
     131 ->168        -0.10528
     132 ->137        -0.10246
```

Table S4. RT photophysical parameters of selected **TTs**

		Φ (%)	Origin	λ_{em} (nm)	τ_{av}	Reference
 **TTPhCHO**	DCM	0.8	S_1-S_0	374	1.64 ns	This work
	PMMA	0.7	S_1-S_0	360	1.35 ns	
			T_1-S_0	434	488 μs	
			T^{IEC}-S_0	470		
			T^{H}-S_0	530	3.38 ms	
	cryst	7	T_1-S_0	430	123.6 μs	
			T^{IEC}-S_0	480		
			T^{H}-S_0	560	6.01 ms	
 **TT(PhCHO)3**	DCM	0.6	S_1-S_0	374	2.02 ns	This work
	PMMA	1.3	T_1-S_0	434	147.3 μs	
			T^{H}-S_0	555	90.6 μs	
	cryst	0.8	T_1-S_0	410	536.2 μs	
			T^{IEC}-S_0	515	3.92 ms	
			T^{H}-S_0	575		
 **TT**	DCM	2	S_1-S_0	400	7.09 ns	1
	pwd	18	S_1-S_0	425	9.89 ns	
			T^{H}-S_0	520	0.555 s	
	cryst	30	S_1-S_0	400	7.67 ns	
			T^{H}-S_0	525	0.970 s	
 **1Cl**	cryst	24	S_n-S_0	333, 348	0.77 ns	2
			S_1-S_0	350	1.02 ns	
			T_1-S_0	405, 428	269.74 μs	
			T^{H}-S_0	510	25.99 ms	

<table>
<tr><th colspan="2"></th><th>Φ (%)</th><th>Origin</th><th>λ_{em} (nm)</th><th>τ_{av}</th><th>Reference</th></tr>
<tr><td rowspan="4">
2Cl</td><td rowspan="4">cryst</td><td rowspan="4">12</td><td>S_n-S_0</td><td>329</td><td>n.d.</td><td rowspan="4">2</td></tr>
<tr><td>S_1-S_0</td><td>397</td><td>1.41 ns</td></tr>
<tr><td>T_1-S_0</td><td>434</td><td>1.33 ms</td></tr>
<tr><td>T^H-S_0</td><td>481, 512, 552</td><td>49.13 ms</td></tr>
<tr><td rowspan="5">
3Cl</td><td rowspan="5">cryst</td><td rowspan="5">9</td><td>S_n-S_0</td><td>327, 341, 349</td><td>n.d.</td><td rowspan="5">2</td></tr>
<tr><td>S_1-S_0</td><td>373</td><td>0.65 ns</td></tr>
<tr><td>T_1-S_0</td><td>416, 438</td><td>13.66 ms</td></tr>
<tr><td>T^H-S_0</td><td>492, 523</td><td>142.45 ms</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td rowspan="4">
1Br</td><td>DCM</td><td>3</td><td>S_n-S_0</td><td>328, 342, 358</td><td>0.68 ns</td><td rowspan="4">3, 4</td></tr>
<tr><td rowspan="3">pwd</td><td rowspan="3"><0.1</td><td>S_n-S_0</td><td>326, 345, 365, 382</td><td>0.89 ns</td></tr>
<tr><td>S_1-S_0</td><td>426, 530</td><td>5.52 ns</td></tr>
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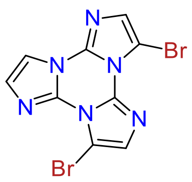
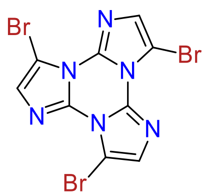
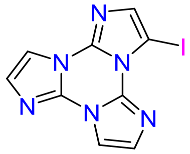
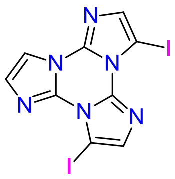
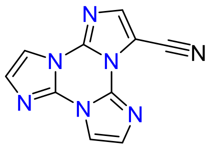
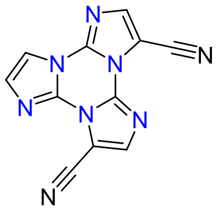
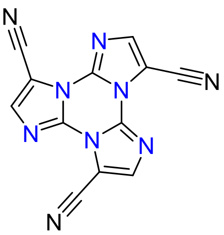
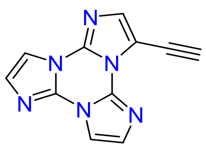
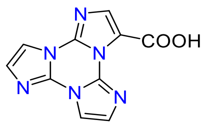
<tr><td rowspan="4">
2Br</td><td>DCM</td><td><0.1</td><td>S_n-S_0</td><td>380</td><td>5.22 ns</td><td rowspan="4">3, 4</td></tr>
<tr><td rowspan="3">pwd</td><td rowspan="3">14</td><td>S_n-S_0</td><td>395, 419, 443</td><td>0.91 ns</td></tr>
<tr><td>T^{Br}-S_0</td><td>470</td><td>1.07 ms</td></tr>
<tr><td>T^H-S_0</td><td>553, 600, 646</td><td>28.85 ms</td></tr>
<tr><td rowspan="6">
3Br</td><td>DCM</td><td><0.1</td><td>S_n-S_0</td><td>370</td><td>10.91 ns</td><td rowspan="6">3</td></tr>
<tr><td rowspan="5">pwd</td><td rowspan="5"><0.1</td><td>S_n-S_0</td><td>394, 418, 444</td><td>1.02 ns</td></tr>
<tr><td>S_1-S_0</td><td>415, 437</td><td>n.d.</td></tr>
<tr><td>T^H-S_0</td><td>555, 605, 656</td><td>18.42 ms</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td rowspan="3"></td><td>DCM</td><td></td><td></td><td></td><td></td><td rowspan="3">5</td></tr>
<tr><td rowspan="2">cryst</td><td rowspan="2"><0.1</td><td>S_1-S_0</td><td>476</td><td>1.37 ns</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

		Φ (%)	Origin	λ_{em} (nm)	τ_{av}	Reference
 1I			T^H-S_0	517, 563, 612	63.69 ms	
			T_1-S_0	630	0.53 μs	
 2I	cryst	7	S_1-S_0	443	1.23 ns	5
			T^H-S_0	625	9.47 ms	
			T_1-S_0	680	3.47 ms	
 TT-1CN	DMSO	21	S_1-S_0	396	3.39 ns	
	cryst	6.2	S_1-S_0	354	2.34 ns	
			T_1-S_0	375, 391, 411, 437	2.03 ms	
			T^H-S_0	453, 483, 506, 543	11.67 ms	
 TT-2CN	DMSO	3.5	S_1-S_0	388	1.37 ns	6
	cryst	30.1	S_1-S_0	354	2.19 ns	
			T_1-S_0	425	3.31 ms	
			T^H-S_0	545	68.32 ms	
 TT-3CN	DMSO	<1.0	S_1-S_0	350	2.26 ns	
	cryst	12.3	S_1-S_0	327, 340, 357, 374	1.94 ns	
			T_1-S_0	379, 399	3.80 ms	
			T^{IEC}-S_0	473	12.12 ms	
 TT-CCH	DCM	2	S_1-S_0	363	n.d.	7
	PMMA	3	S_1-S_0	342	0.99 ns	
			S^H-S_0	383	1.46 ns	
			T_1-S_0	439	0.16 ms	
			T^H-S_0	522	6.9 ms	
	cryst	16	S_1-S_0	314, 326, 338	n.d.	
			S^H-S_0	354, 367, 377	1.05 ns	
			T_1-S_0	396, 420	0.25 ms	
			T^H-S_0	545	4.66 ms	

		Φ (%)	Origin	λ_{em} (nm)	τ_{av}	Reference
 **TT-COOH**	DMSO	3.8	S_2-S_0	327, 343	n.d.	8
			S_1-S_0	404	3.55 ns	
	cryst	26	S_2-S_0	342	2.32 ns	
			S_1-S_0	386, 408, 432	2.75 ns	
			T_2-S_0	445	3.64 ms	
			T_1-S_0	487	5.58 ms	
			T^H-S_0	549, 590, 642	117 ms	

T^{IEC}: triplet associated with intermolecular electronic coupling mechanism, T^{Br}: triplet located on Br halogen bond; T^H: triplet from π-π aggregate

5. References

1. E. Lucenti, A. Forni, C. Botta, L. Carlucci, C. Giannini, D. Marinotto, A. Previtali, S. Righetto and E. Cariati, H-Aggregates Granting Crystallization-Induced Emissive Behavior and Ultralong Phosphorescence from a Pure Organic Molecule, *J. Phys. Chem. Lett.*, 2017, **8**, 1894-1898.
2. C. Giannini, A. Forni, D. Malpicci, E. Lucenti, D. Marinotto, A. Previtali, L. Carlucci and E. Cariati, Room temperature phosphorescence from organic materials: Unravelling the emissive behaviour of chloro-substituted derivatives of cyclic triimidazole, *Eur. J. Org. Chem.*, 2021, **2021**, 2041-2049.
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