Supplementary Information

Unravelling the intricated photophysical behavior of 3-(pyridin-2-yl)triimidazotriazine AIE and RTP polymorphs

Elena Lucenti,[a] Alessandra Forni,*[a] Andrea Previtali,‡[ab] Daniele Marinotto,‡[a] Daniele Malpicci,[b] Stefania Righetto,‡[b] Clelia Giannini,[b] Tersilla Virgili,[c] Piotr Kabacinski,[c] Lucia Ganzer,[c] Umberto Giovanella,[d] Chiara Botta,*[d] and Elena Cariati*[ab]

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1. Experimental details

1.1 General information

All reagents and model molecules were purchased from chemical suppliers and used without further purification unless otherwise stated. 3-bromotriimidazo[1,2-*a*:1',2'-*c*:1",2"-*e*][1,3,5]triazine (TT-Br) was prepared according to literature procedures [S1].

^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker AVANCE-400 instrument (400 MHz). Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak (DMSO, ^{1}H 2.50 ppm, ^{13}C 39.50 ppm) and to the NH_3 for ^{15}N resonances. Coupling constants (J) are given in hertz (Hz) and are quoted to the nearest 0.5 Hz. Peak multiplicities are described in the following way: s, singlet; d, doublet; t. triplet; m, multiplet. Mass spectra were recorded on a Thermo Fisher LCQ Fleet Ion Trap Mass Spectrometer equipped with UltiMate™ 3000 HPLC system.

UV-Visible spectra were collected by a Shimadzu UV3600 spectrophotometer. Photoluminescence quantum yields were measured using a C11347 Quantaurus–Absolute Photoluminescence Quantum Yield Spectrometer (Hamamatsu Photonics K.K), equipped with a 150 W Xenon lamp, an integrating sphere and a multichannel detector. Steady state emission and excitation spectra and photoluminescence lifetimes were obtained using both a FLS 980 (Edinburg Instrument Ltd) and a Nanolog (Horiba Scientific) spectrofluorimeter composed of a iH320 spectrograph equipped with a Synapse QExtra charge-coupled device. The steady state measurements were recorded by excitation with a monochromated 450 W Xenon arc lamp and the spectra are corrected for the instrument response. Phosphorescence spectra are obtained with a PPD-850 single photon detector module with time-gated separation by exciting with a pulsed Xe lamp. Photoluminescence lifetime measurements were performed using: Edinburgh Picosecond Pulsed Diode Laser EPL-375, EPLED-300, (Edinburg Instrument Ltd) and microsecond flash Xe-lamp (60W, 0.1÷100 Hz) with data acquisition devices time correlated single-photon counting (TCSPC) and multi-channel scaling (MCS) methods, respectively. Nanolog TCSPC measurements are performed using DeltaTime series DD-300 DeltaDiode and a DD-405L DeltaDiode Laser, with a PPD-850 single photon detector module and are analysed with the instrument software DAS6. Average lifetimes are obtained as $\tau_{av} = \sum \frac{A_i \tau_i^2}{A_i \tau_i}$ from bi-exponential or three-exponential fits. Low temperature measurements are performed by immersion of the sample in a LN_2 quartz dewar or with a variable temperature liquid nitrogen cryostat Oxford DN1704. Microscopy fluorescence images were collected with a Nikon Eclipse TE2000-U inverted confocal microscope by exciting with a 100 W Hg lamp with a 330–380 nm band-pass excitation filter

OLED devices were fabricated with the architecture Indium tin oxide (ITO)/poly-(3,4-ethylenedioxythiophene)-poly-(styrenesulfonic acid) (PEDOT:PSS, 35 nm)/polyvinylcarbazole (PVK) 67wt.%:2-(4-tert-Butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) 23wt.%:**TT-Py** 10wt.%/2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBI)/Barium(4nm)/Aluminum(100nm). The active layer film (80 nm) was deposited from 15 mg/ml CH_2Cl_2 solution by spin-coating at 3000 rpm in glove box. TPBI (20nm) was thermally evaporated in high vacuum. The device active area is 0.054mm^2. Photons emitted in forward direction through the glass substrate were collected by a calibrated photodiode. Current density-Luminance-voltage curves are recorded by Keithley 2602 apparatus.

1.2 Single crystal X-ray crystallographic studies

X-ray data of the three polymorphs of **TT-Py** were collected on a Bruker Apex II diffractometer using MoKα radiation. The structures were solved using direct methods and refined using a full-matrix least squares procedure based on F^2 using all data [S2]. Hydrogen atoms were placed at geometrically estimated positions. Details relating to the crystals and the structural refinements are presented in Table S1. The structure of **TT-Py-H** includes disordered cocrystallized water molecules. They are characterized by high mobility with three preferential sites in the asymmetric unit (denoted as O1W, O2W and O3W) for a total occupation factor 1.70. They are not self-consistent (owing to too short O1W...O1W', O2W...O2W' and O3W...O3W' distances) but form several possible water chains connecting different oxygen atoms along the a-direction, with intermolecular distances compatible with the formation of O-H...O hydrogen bonds between them. This indicates the presence of different and alternating chains of water molecules in the crystal structure, all of them connecting laterally organic molecules through C-H...O and O-H...N hydrogen bonds. Owing to the large disorder of the water molecules it is not possible to include the water hydrogen atoms in the refinement. Full details of crystal data and structure refinement, in CIF format, are available as Supplementary Information. CCDC reference numbers: 1998787 (**TT-Py-A**), 1998788 (**TT-Py-X**) and 1998789 (**TT-Py-H**).

1.3 Computational details

DFT and TDDFT calculations on monomeric **TT-Py** were performed with Gaussian 16 program (Revision A.03) [S3] using the 6-311++G(d,p) basis set. The geometries of **TT-Py** and its dimers have been optimized starting from the experimental structures as derived from X-ray studies. Based on previous theoretical results as obtained on the parent cyclic triimidazole and its mono-iodo and mono-, di- and tribromoderivatives, the ωB97X [S4] functional was used owing to its ability in correctly treating at the same time not only ground and excited states properties, but also intermolecular interactions. In fact, the PBE0 and CAM-B3LYP functionals were previously found to accurately reproduce the absorption spectrum of the isolated monomers but failed to provide stable π-π stacked dimers. On the other side, the B97D functional, while providing stable π-π dimers, was found to be instable for TDDFT calculations.

1.4 Ultrafast photophysical characterization

***Exc 290 nm**:* Ultrafast pump-probe measurements were carried out on a pump-probe setup fed by a Ti:sapphire laser (780-nm central wavelength, 100-fs pulses, 1-kHz repetition rate; Libra, Coherent). A fraction of the fundamental wavelength (FW) pulse was used to seed a home-built visible non-collinear optical parametric amplifier (NOPA). The broadband output centered at 580 nm was up-converted by second-harmonic generation in a 20-μm-thick BBO crystal, providing sub-20-fs pump pulses in the UV range (290 nm). The fluence used was of ~ 0.7 mJ/cm^2 on the sample. The probe pulses were obtained by focusing a ~1μJ fraction of the FW onto a 3-mm-thick calcium fluoride plate. Through white-light continuum generation we obtained a broadband probe pulse in the range between 320 and 650 nm. The transmitted probe beam was dispersed in a spectrometer (SP2300 Acton, Princeton Instruments) and detected using a linear image sensor driven and read out by a custom-built board (Stresing Entwicklungsbüro, Berlin, Germany).

Exc 390 nm: A Ti:sapphire regenerative amplifier (780-nm central wavelength, 100-fs pulses, 2-kHz repetition rate; Libra, Coherent). As excitation pulses, the second harmonic of the FW has been used (λ = 390 nm). The excitation density was kept ~ 9 mJ/cm^2 on the sample. White light generated with

a 2 mm-thick sapphire plate was used as a probe in the visible-near infrared range from 450 to 750 nm. For a spectrally-resolved detection of the probe light, spectrographs and CCD arrays were used. The chirp in the white light pulse was taken into account during the analysis and evaluation of the two-dimensional (wavelength and time) ΔT/T maps before extraction of the spectral and temporal data using homemade software. Overall, a temporal resolution of at least 100 fs was achieved for all excitation wavelengths.

1.5 Synthesis of 3-(pyridin-2-yl)triimidazo[1,2-a:1',2'-c:1'',2''-e][1,3,5]triazine (TT-Py)

TT-Py is obtained by Stille coupling between 3-bromotriimidazo[1,2-*a*:1',2'-*c*:1'',2''-*e*][1,3,5]triazine **(TT-Br)** and 2-(tributylstannyl)pyridine (Scheme 1). The reaction is performed in a closed cylindrical Pyrex flask (diameter 30 mm, length 300 mm) fitted with a central neck bearing a side neck equipped with a Rotaflo stopcock (previously described for the reductive carbonylation of silica-supported metal chlorides) [S5]. **TT-Br** (500 mg, 1.80 mmol), LiCl (685 mg, 16.16 mmol) and $Pd(PPh_3)_2Cl_2$ (38 mg, 0.054 mmol) are transferred inside the cylindrical flask, to this mixture 2-(tributylstannyl)pyridine (assay 85%, 1 mL, 2.70 mmol) and anhydrous toluene (15 mL) are added and three freeze-pump-thaw cycles are performed. The mixture is heated at 393 K under static nitrogen for 20 hours. After cooling to room temperature, the reaction mixture is added with NaOH 1M (20 mL) and stirred for 15 minutes. The biphasic solution is diluted with AcOEt (60 mL) and H_2O (40 mL) and separated. The aqueous phase is extracted with an additional 3×10 mL of AcOEt, and the combined organic phases are dried over Na_2SO_4, filtered. and evaporated to dryness. The crude product is purified by column chromatography on silica gel (CH_2Cl_2:MeOH = 95:5; R_f = 0.38) to give **TT-Py** (370 mg, yield 75%). Single crystals of the three different polymorphs are obtained as laminae (**TT-Py-A**), needles (**TT-Py-H**) and rectangular blocks (**TT-Py-X**) by slow evaporation of CH_2Cl_2/CH_3OH, CH_3CN/H_2O and CH_3CN solutions, respectively.
NMR data (9.4 T, DMSO-d_6, 298 K, δ, ppm): ^{1}H NMR 8.65 (ddd, *J* = 4.8, 1.7, 0.9 H, 1H), 8.10 (dt, *J* = 8.0, 0.9 Hz, 1H), 8.0 (d, *J* = 1.7 Hz, 1H), 7.98 (d, *J* = 1.6 Hz, 1H), 7.9 (tt, *J* = 5.6, 2.8 Hz, 1H), 7.54 (s, 1H), 7.41 (m, 1H), 7.31 (d, *J* = 1.7 Hz, 1H), 7.22 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR: 149.1 (CH), 147.4, 136.8, 135.9 (CH), 135.6, 129.4 (CH), 128.6 (CH), 127.9, 127.8 (CH), 124.8 (CH), 122.9 (CH), 111.8 (CH), 111.4 (CH); ^{15}N NMR: 308.4, 224.5, 218.8, 218.3, 154.3, 153.1, 149.8 (Fig. S1-S5).
MS (ESI-positive ion mode): m/z 276.2 $[M+H]^+$ (Fig. S6).

Films of **TT-Py** dispersed in polymethylmethacrylate (PMMA) were prepared by spincoating (2000 rpm, 60 s) a dichloromethane solution (**TT-Py**/PMMA = 5 or 10 wt%; PMMA = 10 wt% with respect to the solvent) on a quartz substrate.

2. NMR and Mass Spectra of TT-Py

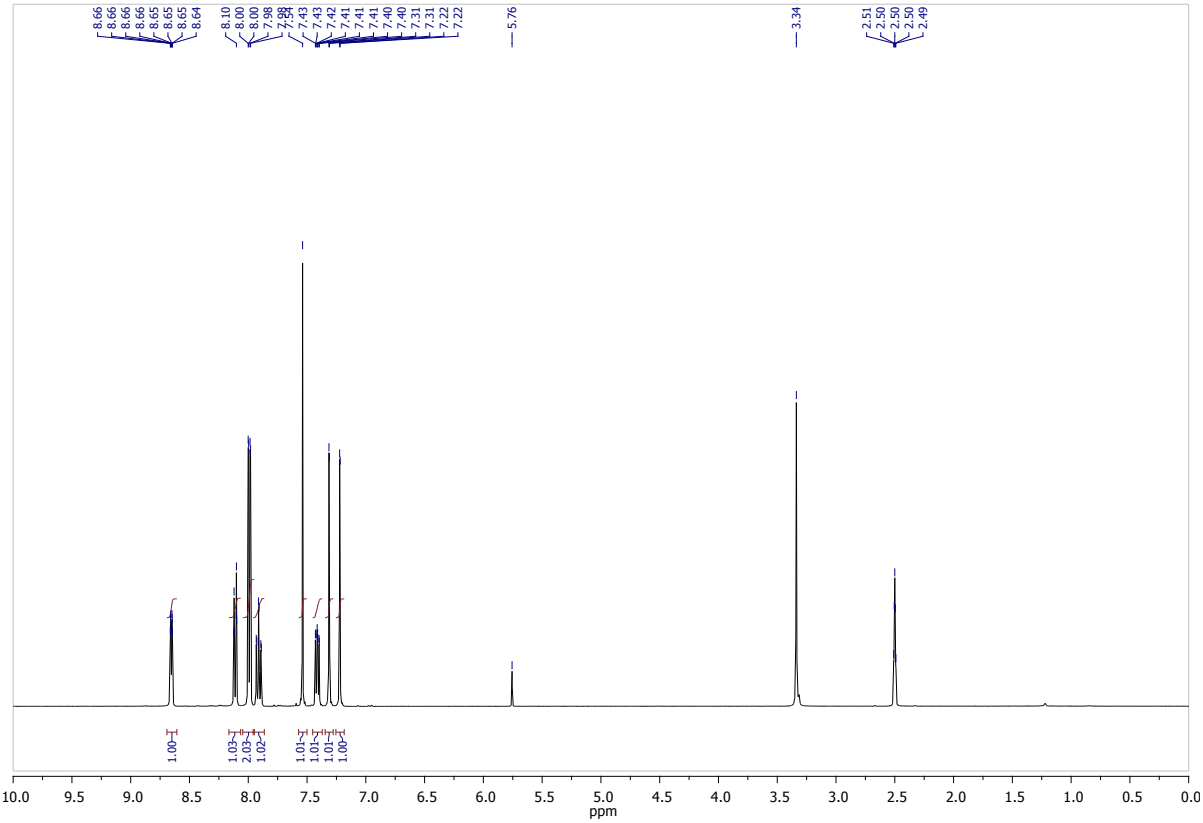


Figure S1. ^{1}H NMR spectrum of **TT-Py** (400 MHz, DMSO-d_6, 298 K)

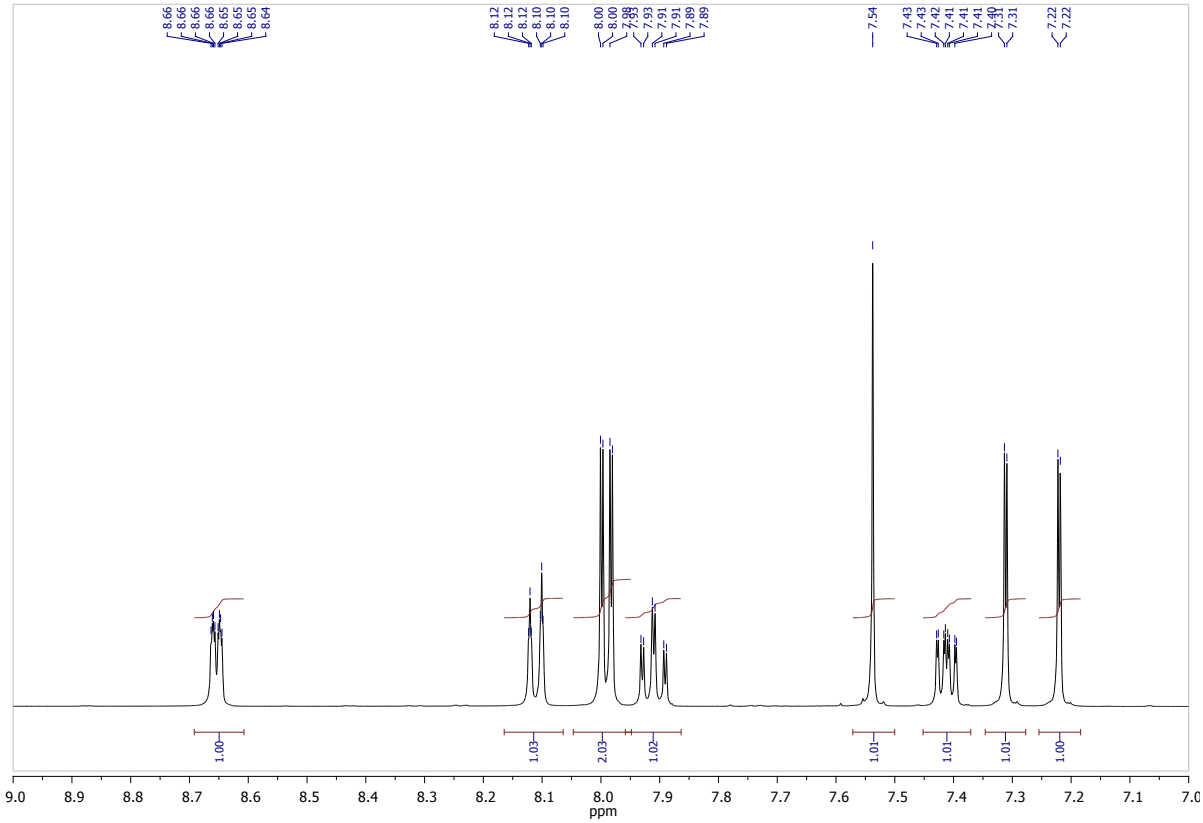


Figure S2. Expanded region of ^{1}H NMR spectrum of **TT-Py** (400 MHz, DMSO-d_6, 298 K)

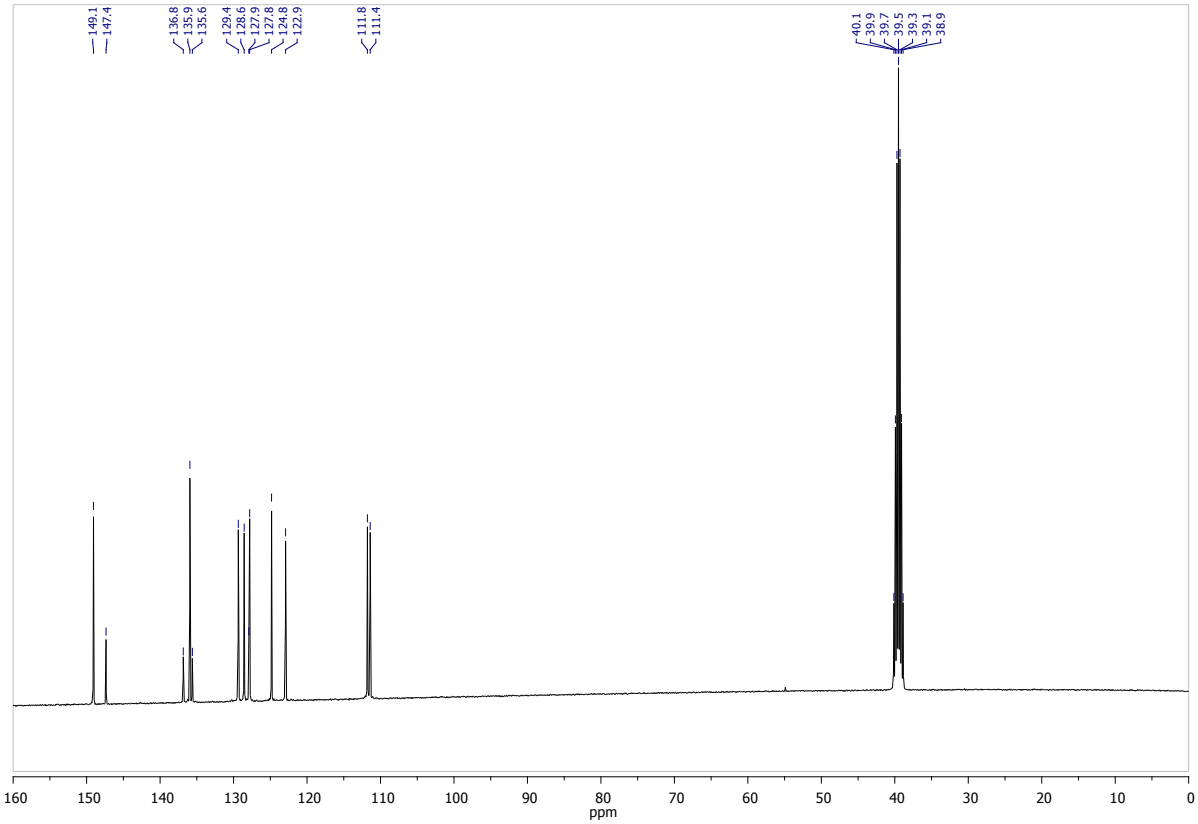


Figure S3. ^{13}C NMR spectrum of **TT-Py** (400 MHz, DMSO-d_6, 298 K)

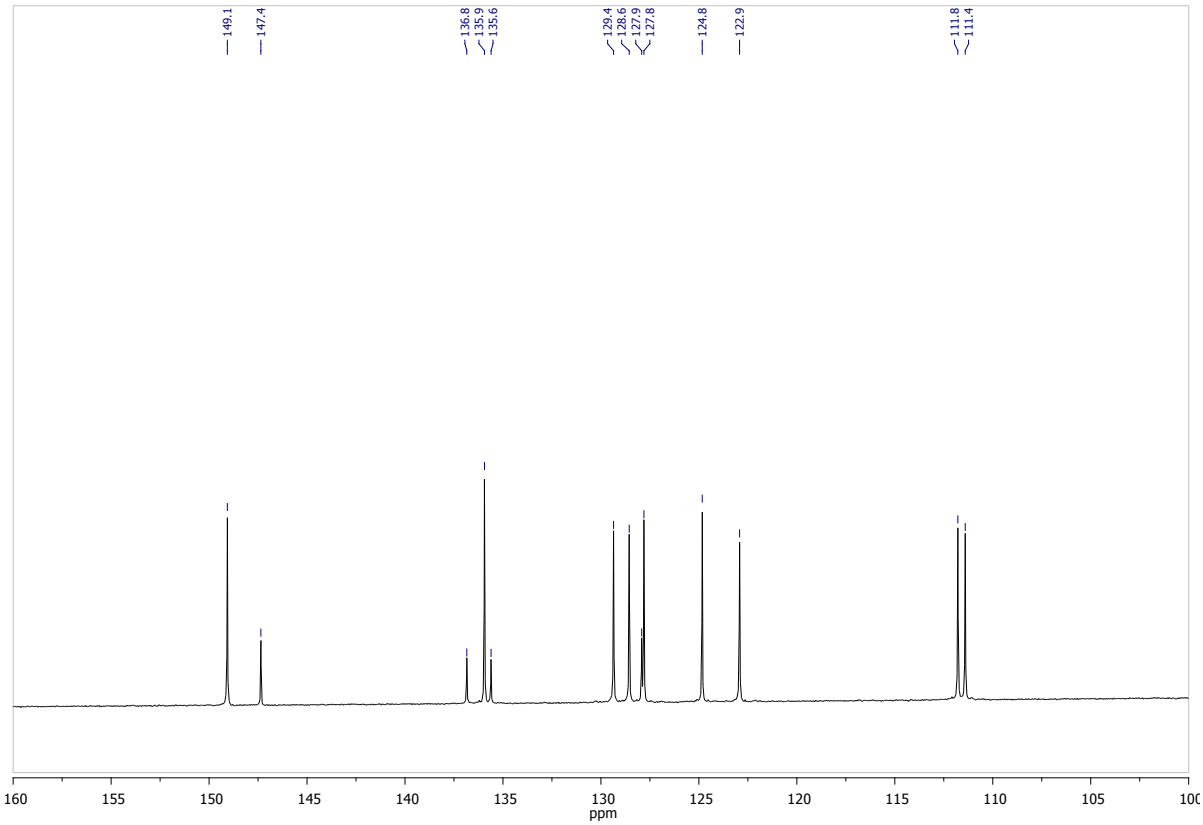


Figure S4. Expanded region of ^{13}C NMR spectrum of **TT-Py** (400 MHz, DMSO-d_6, 298 K)

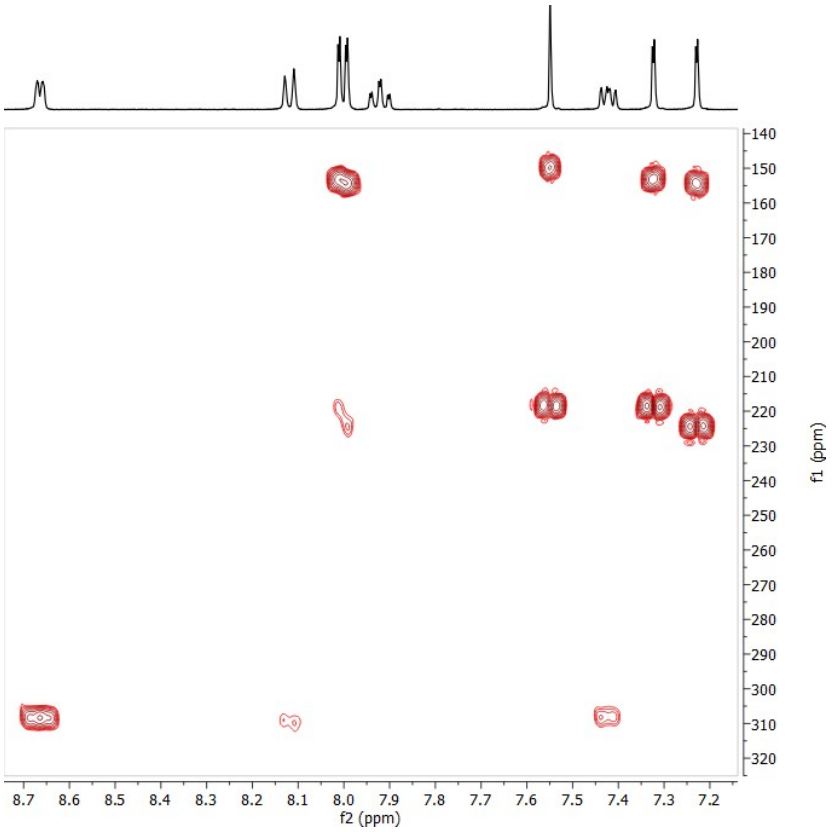


Figure S5. ^{15}N NMR spectrum of **TT-Py** (400 MHz, DMSO-d_6, 298 K)

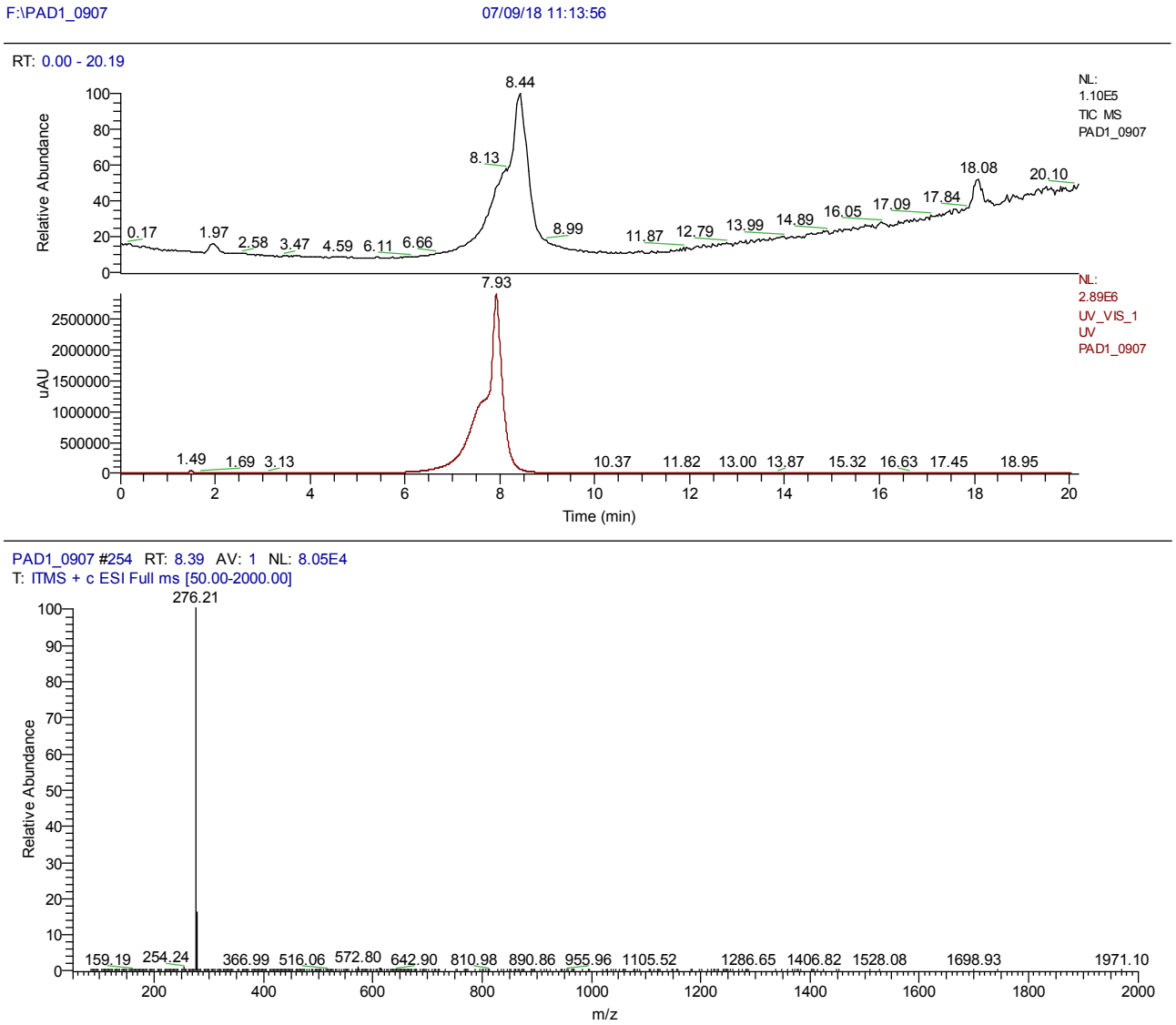


Figure S6. HPLC-MS spectra of **TT-Py**

3. Photophysical Data and Spectra of TT-Py

3.1 Electronic absorption, Steady State and Time resolved emission Spectra

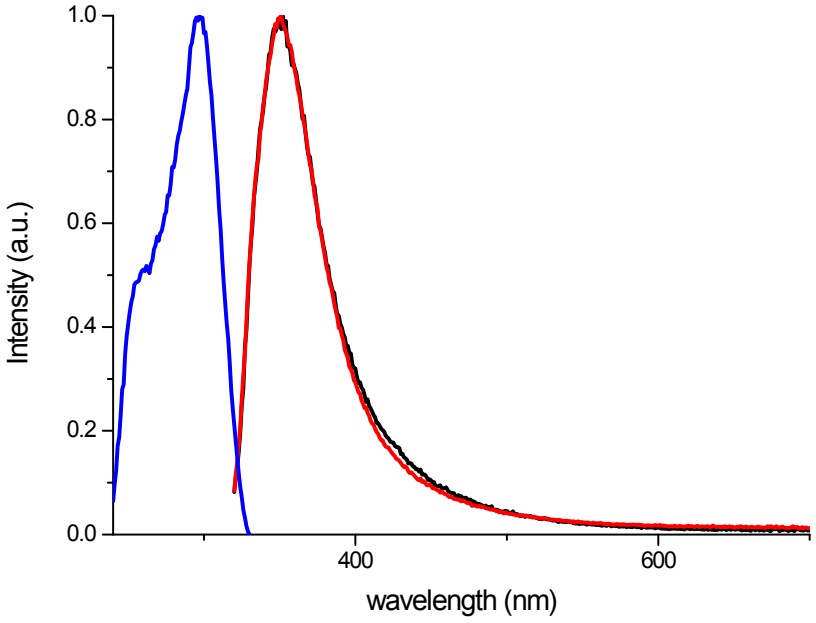


Figure S7. Emission spectra of **TT-Py** in CH_2Cl_2 solution (10^{-5} M) at 298 K: λ_{exc}=300nm (black line), λ_{exc}=340nm (red line) and excitation spectra λ_{em}=350nm (blue line).

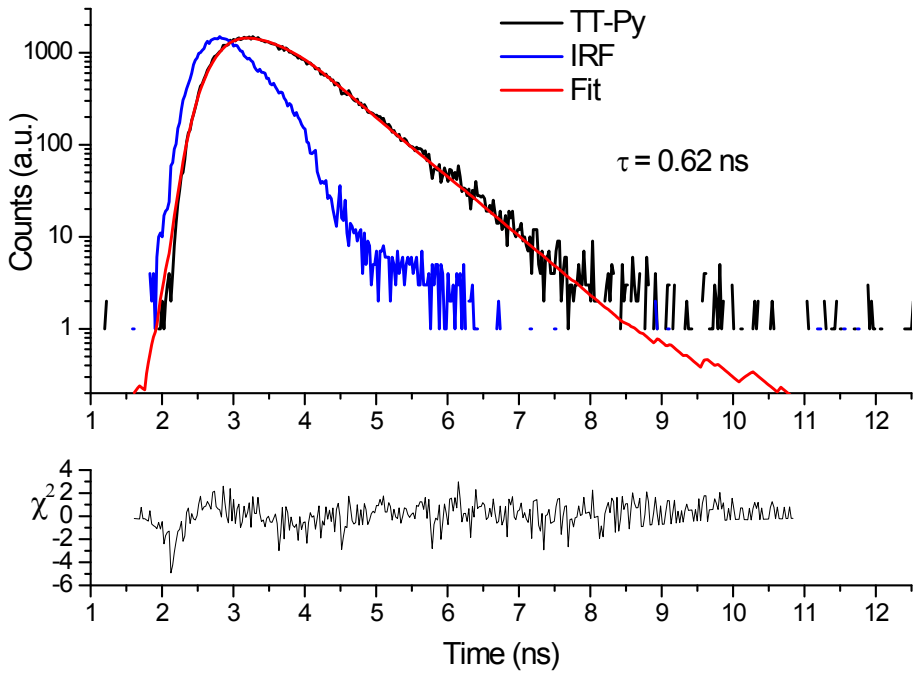


Figure S8. Lifetime measurement (λ_{exc}=300nm, λ_{em}=351nm) of **TT Py** in CH_2Cl_2 solution (10^{-5} M) at 298 K.

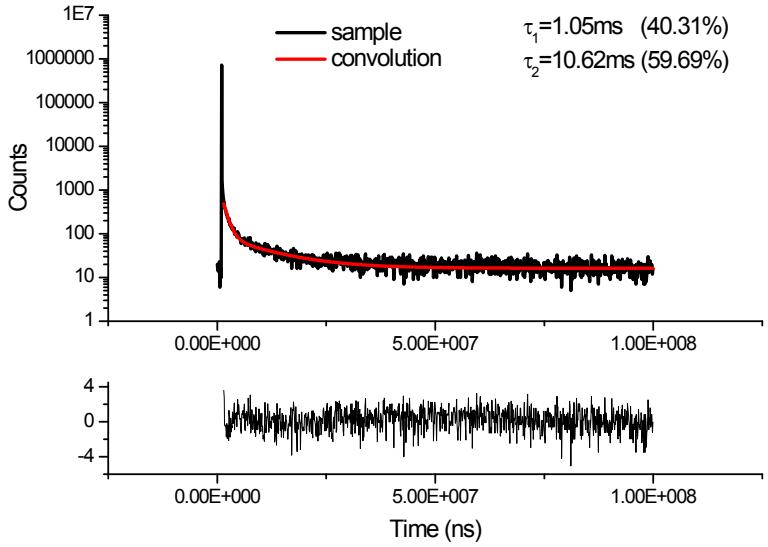


Figure S9. Lifetime measurement (λ_{exc}=300nm, λ_{em}=350nm) of **TT-Py** in CH_2Cl_2 solution (10^{-5} M) at 298 K. τ_{av} = 10.02 ms

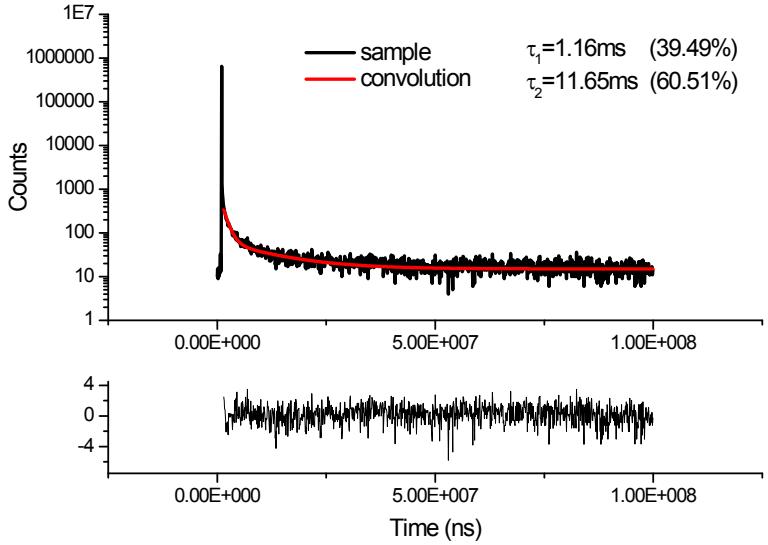


Figure S10. Lifetime measurement (λ_{exc}=300nm, λ_{em}=408nm) of **TT-Py** in CH_2Cl_2 solution (10^{-5} M) at 298 K. τ_{av} = 11.01ms

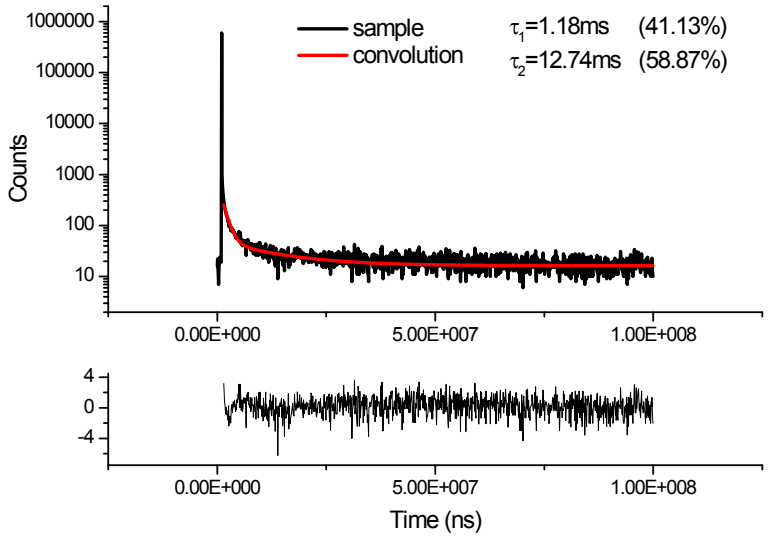


Figure S11. Lifetime measurement (λ_{exc}=300nm, λ_{em}=500nm) of **TT-Py** in CH_2Cl_2 solution (10^{-5} M) at 298 K. τ_{av} = 12.04ms

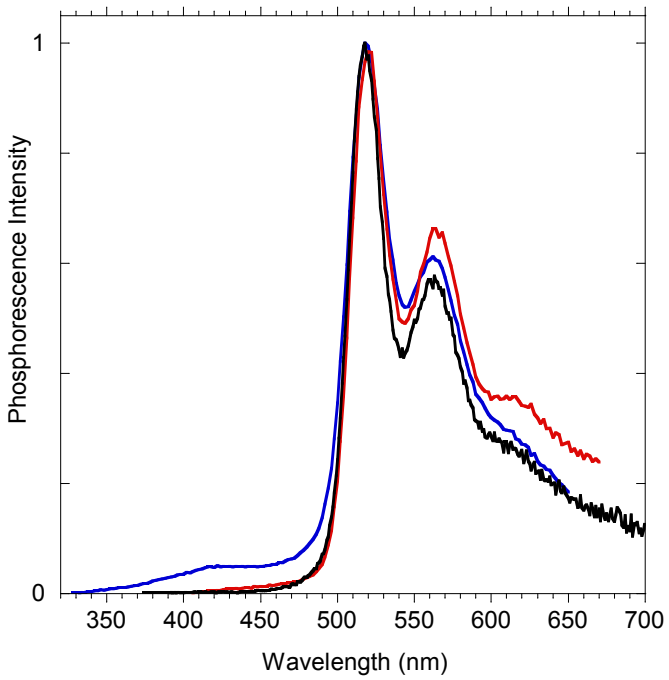


Figure S12. Time evolution of phosphorescence spectra of **TT-Py** (10^{-5}M) in of deaerated CH_2Cl_2 at 298 K, λ_{exc}=300nm (blue line, delay 50 μs, window 100 μs; black line, delay 100 μs, window 200 μs; red line, delay 200 μs, window 5 ms). The spectra are normalized.

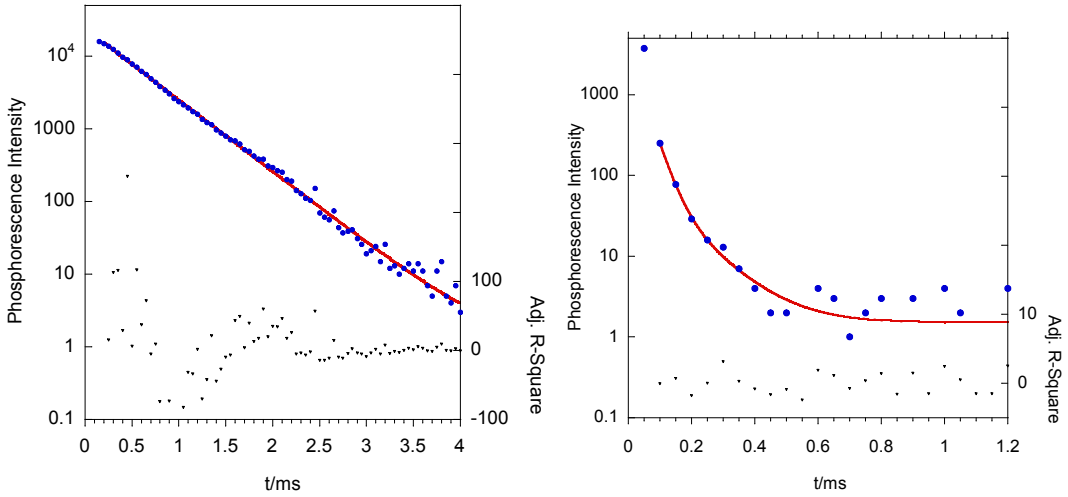


Figure S13. Phosphorescence decays of **TT-Py** (10^{-5}M) in CH_2Cl_2 deaerated solution (blue points) at 298 K, λ_{exc}=300nm. Left, λ_{em}=520nm (mono-exp fit, red line τ=441µs; Adj. R-Square= 0,99966); Right , λ_{em}=400nm (bi-exp fit, red line : biexp fit; τ_{av}=40µs A1=0.03, τ_1=116µs ; A2=0.97, τ_1=34µs, . R-Square= 0,99896)).

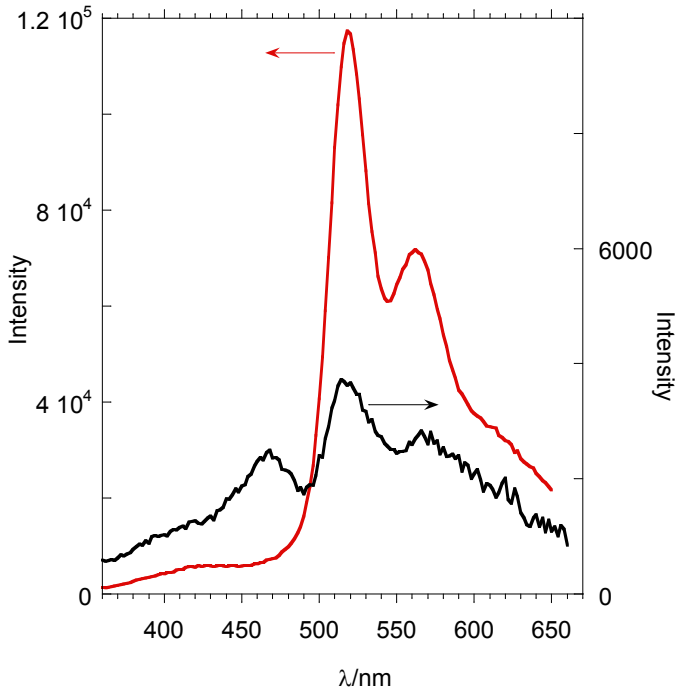


Figure S14. Phosphorescence spectra of **TT-Py** (10^{-5}M) in CH_2Cl_2 deaerated solution before (red) and after (black) air diffusion in the cell, at 298 K. λ_{exc}=300nm; delay 50 µs, window 100 µs.

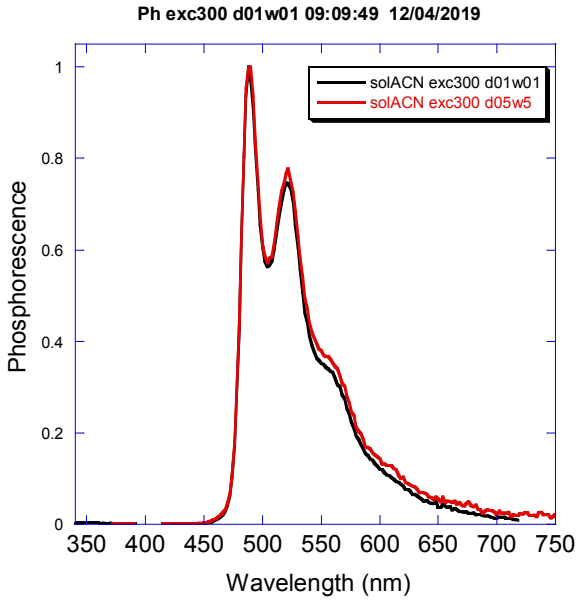


Figure S15. Phosphorescence spectra of **TT-Py** (10^{-5}M) in CH_3CN deareated solution at 298 K. λ_{exc}=300nm (black line, delay 100 µs, window 100 µs; red line, delay 500 µs, window 5ms).

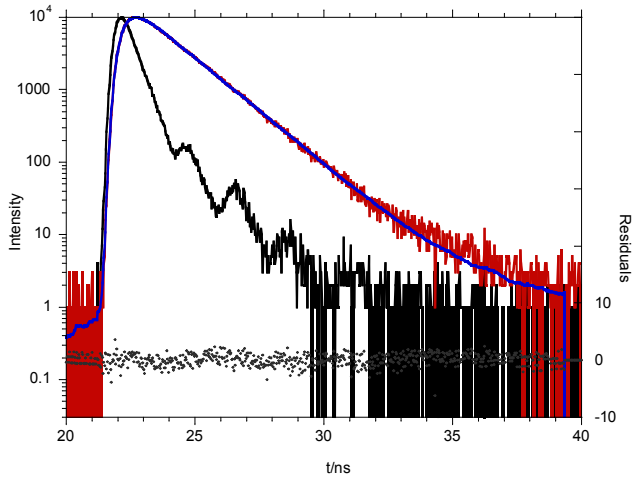


Figure S16 Decay of **TT-Py** (10^{-5}M) in CH_3CN deaerated solution (red line) at 298 K, λ_{exc}=300nm, λ_{em}=350nm. Bi-exp fit, blue line: τ_{av}=1.36ns A1=0.0815, τ_1=0.6848ns ; A2=0.9185, τ_2=1.3930ns, CHISQ = 1.084949). Similar decay is recorded after O_2 diffusion into the cell.

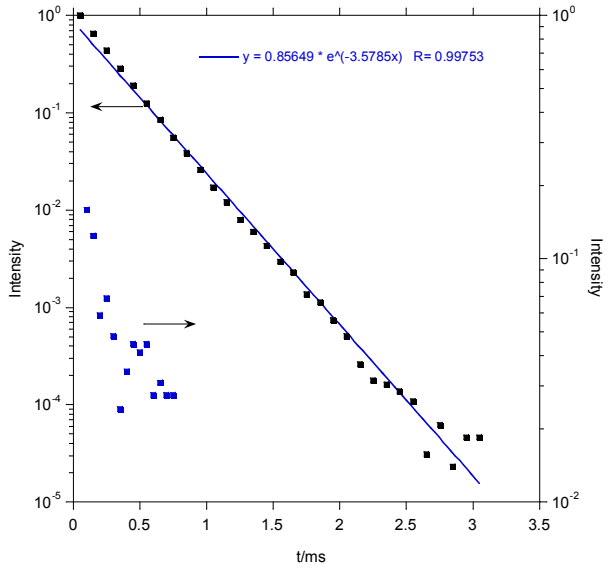


Figure S17 Phosphorescence decay of **TT-Py** (10^{-5}M) in CH_3CN deaerated solution (black points) and after O_2 diffusion into the cell (blue points) at 298 K, λ_{exc}=300nm, λ_{em}=490nm. Mono-exp fit (blue line).

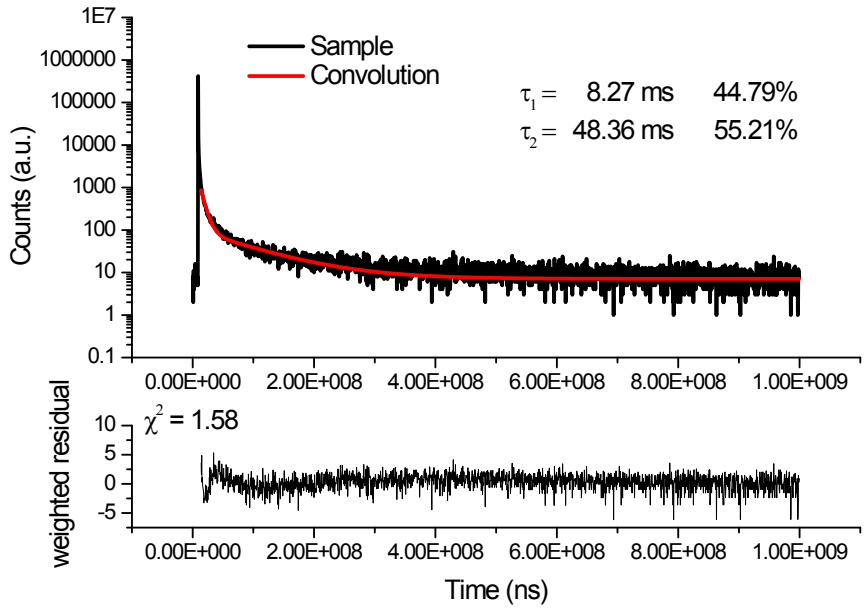


Figure S18. Lifetime measurement (λ_{exc}=300nm, λ_{em}=350nm) of **TT-Py** in CH_3CN deareated solution (10^{-5} M) at 298 K. τ_{av} = 43.47 ms

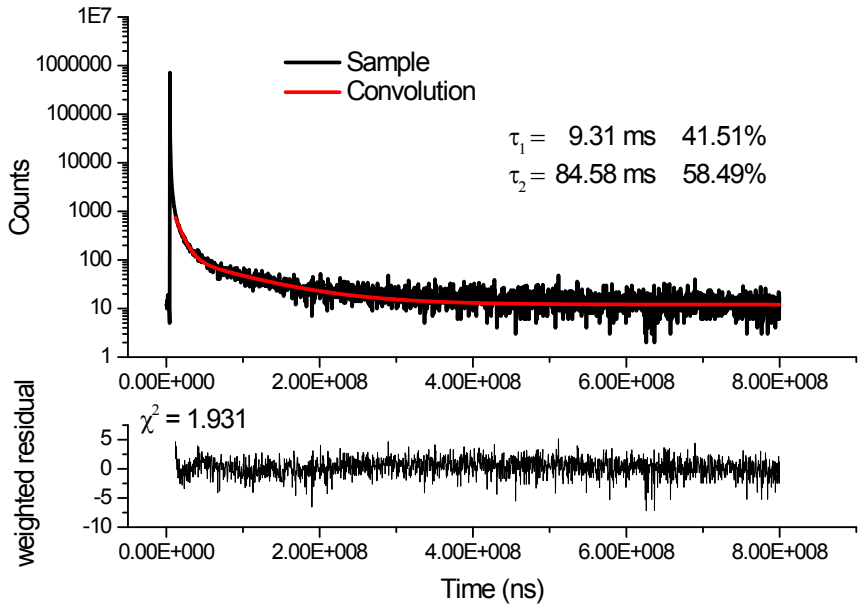


Figure S19. Lifetime measurement (λ_{exc}= 300 nm, λ_{em}=360 nm) of **TT-Py** (10^{-4}M) in deareated CH_3CN/H_2O (50/50) solution at 298 K. τ_{av} = 79.13 ms.

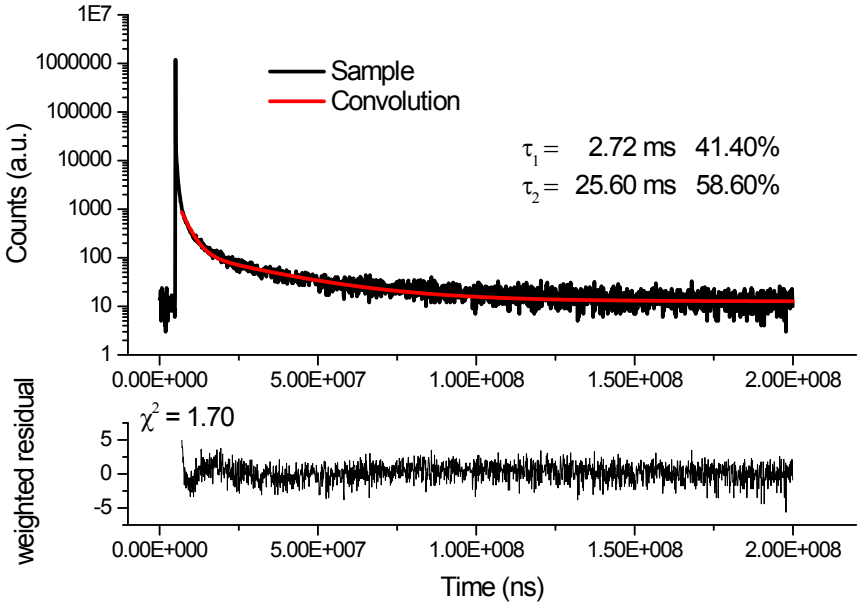


Figure S20. Lifetime measurement (λ_{exc}= 300 nm, λ_{em}=488 nm) of **TT-Py** (10^{-4}M) in deareated CH_3CN/H_2O (50/50) solution at 298 K. τ_{av} = 24.00 ms.

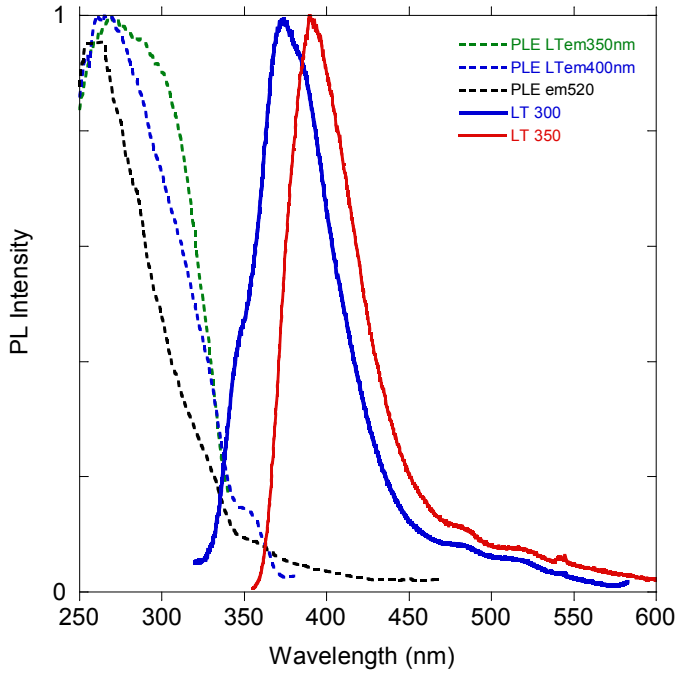


Figure S21. PL (solid line) and PLE (dotted line) of **TT-Py** (10^{-5}M) in CH_2Cl_2 solution at 77 K. λ_{em}=350nm, green line; λ_{em}=400nm, blue line; λ_{em}=520nm, black line; λ_{exc}=300nm, blue line; λ_{exc}=350nm, red line.

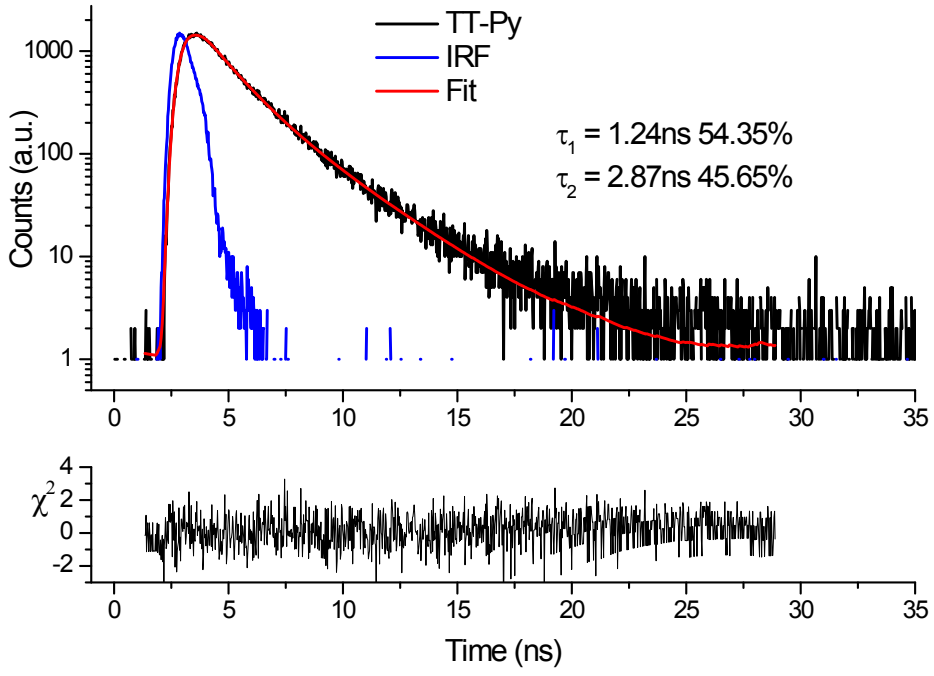


Figure S22. Lifetime measurement (λ_{exc}=300nm, λ_{em}=343nm) of **TT-Py** (10^{-5}M) in CH_2Cl_2 solution at 77 K. τ_{av} = 2.32ns.

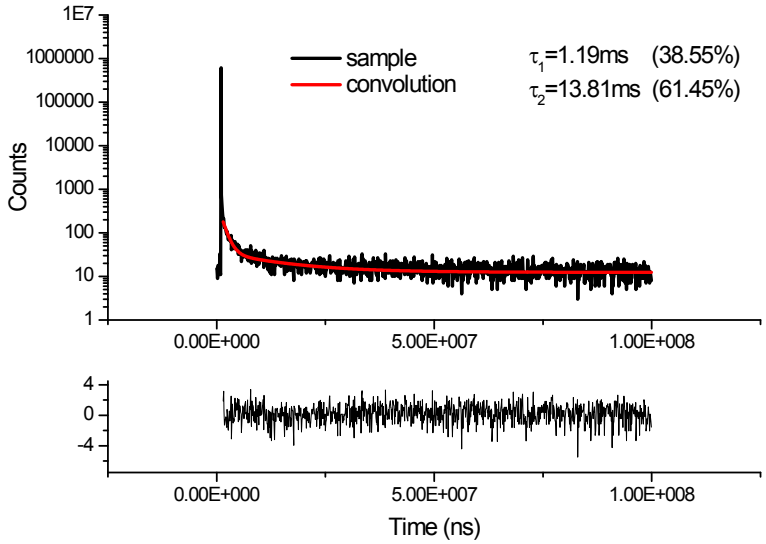


Figure S23. Lifetime measurement (λ_{exc}= 350 nm, λ_{em}=388 nm) of **TT-Py** (10^{-5}M) in CH_2Cl_2 solution at 77 K. τ_{av} = 13.16ms

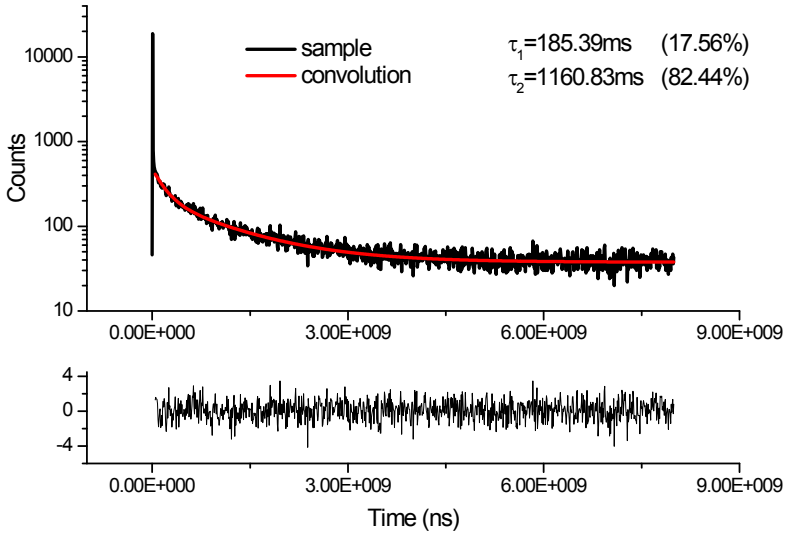


Figure S24. Lifetime measurement (λ_{exc}= 350 nm, λ_{em}=550 nm) of **TT-Py** (10^{-5}M) in CH_2Cl_2 solution at 77 K. τ_{av} = 1.31 s

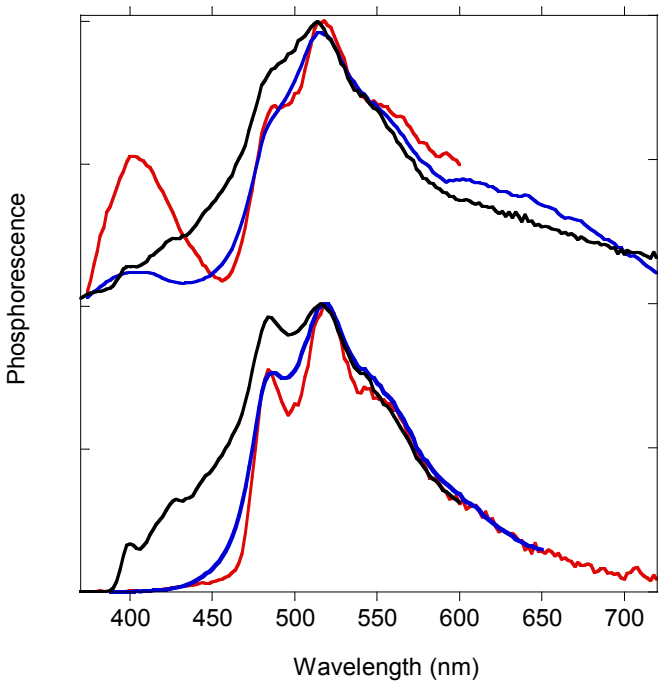


Figure S25. Phosphorescence spectra of **TT-Py** (10^{-5}M) in CH_2Cl_2 solution at 77 K. λ_{exc}=300nm, black line; λ_{exc}=325nm, blue line; λ_{exc}=350nm, red line; Top, delay 200 μs, window 400 μs; Bottom, delay 10ms, window 20ms.

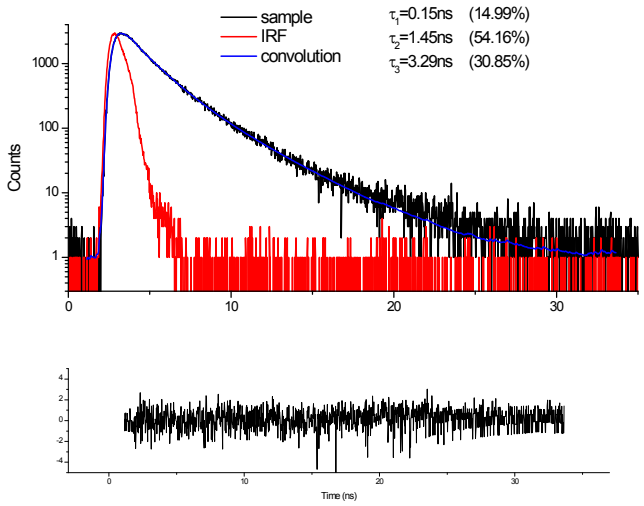


Figure S26. Lifetime measurement (λ_{exc}= 300 nm, λ_{em}=343 nm) of **TT-Py** (10^{-5}M) in CH_3CN solution at 77 K. τ_{av} = 2.46 ns

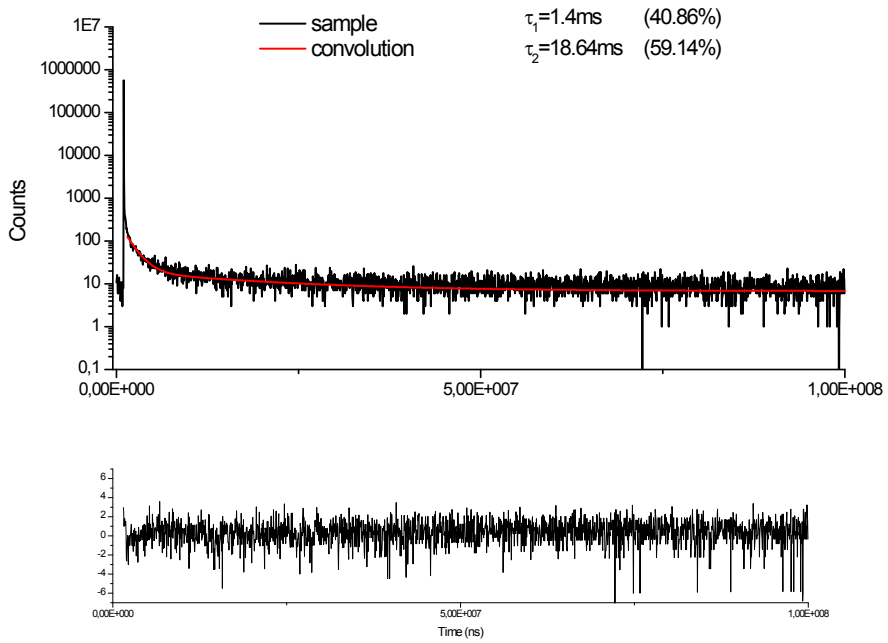


Figure S27. Lifetime measurement (λ_{exc}= 300 nm, λ_{em}=388 nm) of **TT-Py** (10^{-5}M) in CH_3CN solution at 77 K. τ_{av} = 17.79 ms

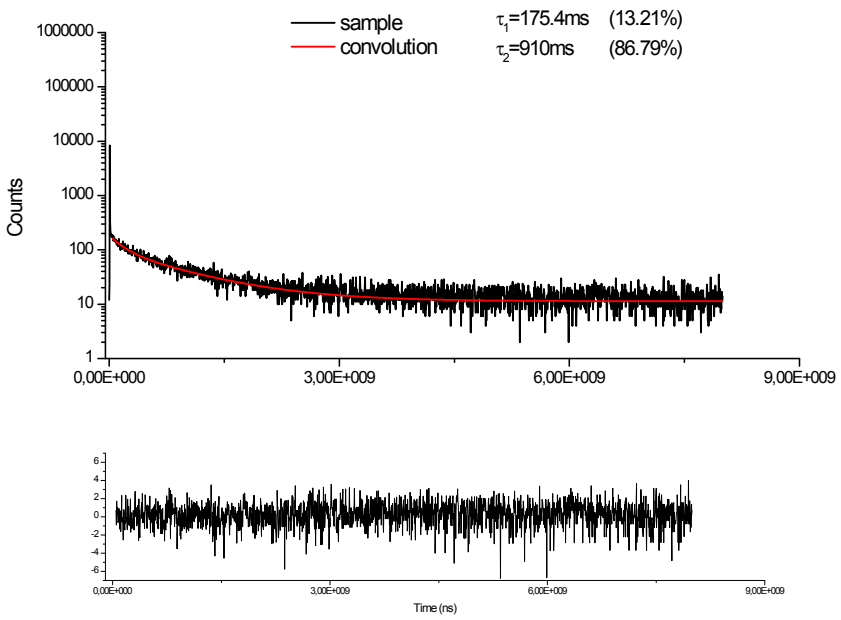


Figure S28. Lifetime measurement (λ_{exc}= 300 nm, λ_{em}=500 nm) of **TT-Py** (10^{-5}M) in CH_3CN solution at 77 K. τ_{av} =889 ms

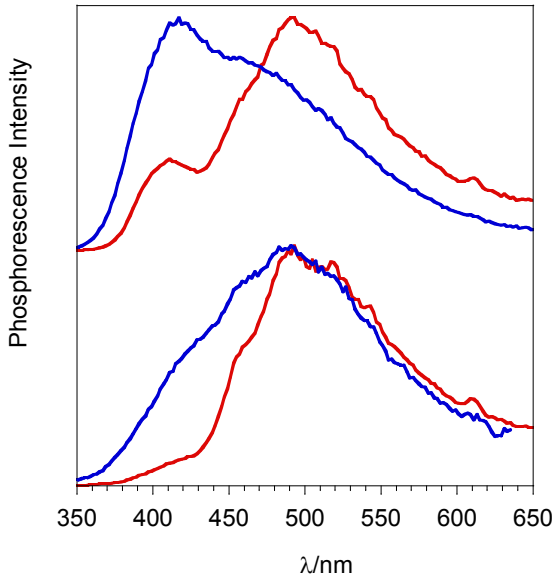


Figure S29. Phosphorescence spectra of **TT-Py** (10^{-5}M) in CH_3CN solution at 77 K. Top, λ_{exc}=270nm,; Bottom, λ_{exc}=300nm (blue line delay 200 μs, window 500 μs; red line delay 2ms window 5ms).

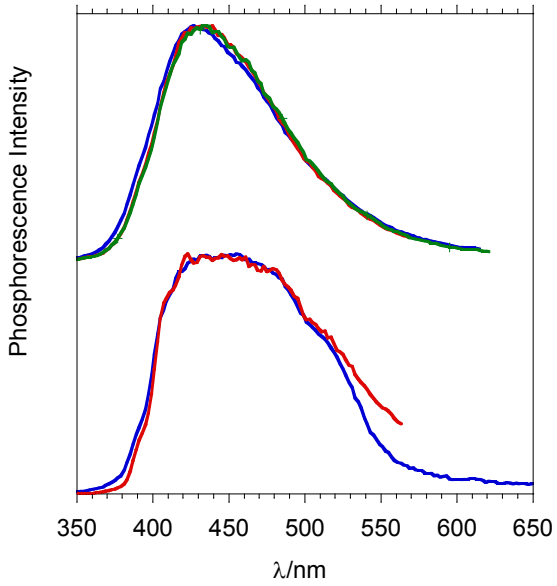


Figure S30. Phosphorescence spectra of **TT-Py** (10^{-5}M) in CH_3OH/CH_3CH_2OH (v/v = 20/80), solution at 77 K. Top, λ_{exc}=270nm; Bottom, λ_{exc}=300nm; blue line delay 200 μs, window 500 μs; red line delay 2ms window 5ms; green line delay 20ms, window 10ms.

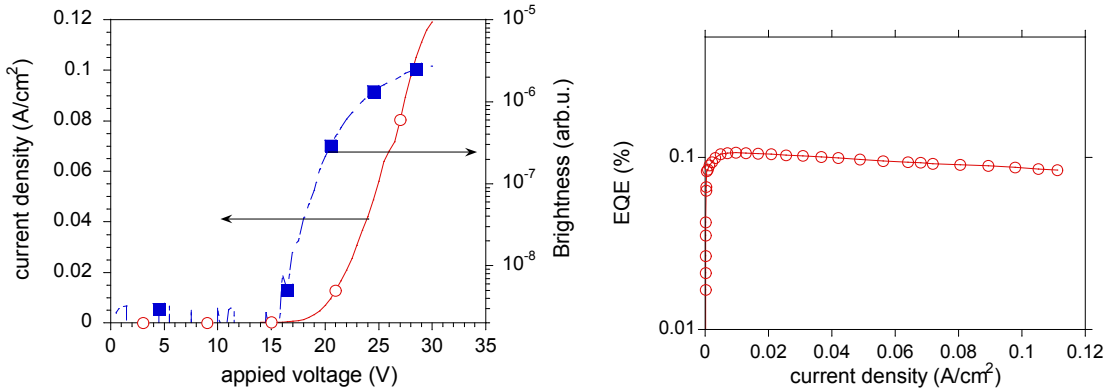


Figure S31. Current-Voltage-Brightness characteristics (left) and external quantum efficiency (right) of a **TT-Py** based OLED with device structure ITO/PEDOT:PSS/PVK:PBD:**TT-Py** (10 wt.%)/TPBI/Ba/Al.

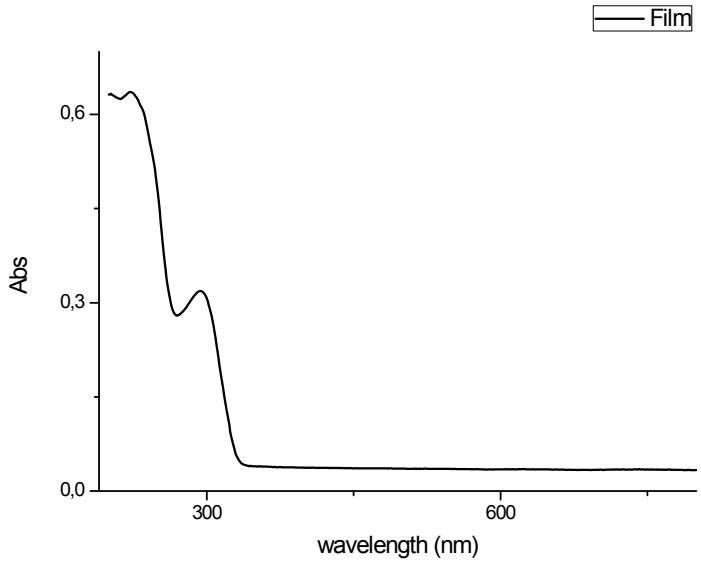


Figure S32. Absorption spectrum of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K.

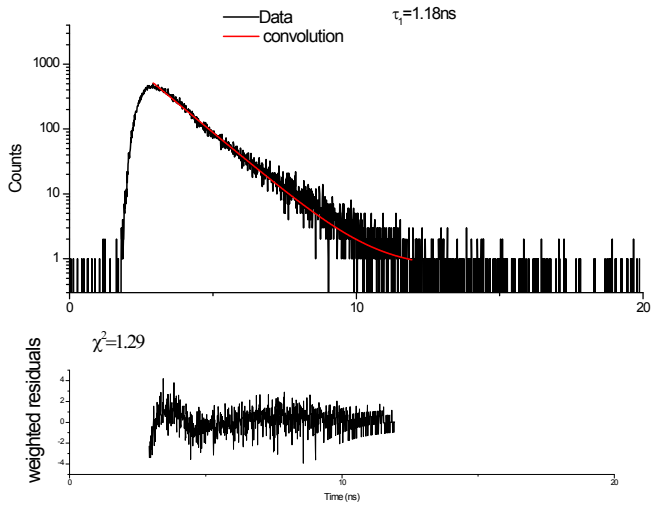


Figure S33. Decay of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K. λ_{exc}=300nm , λ_{em}=350nm

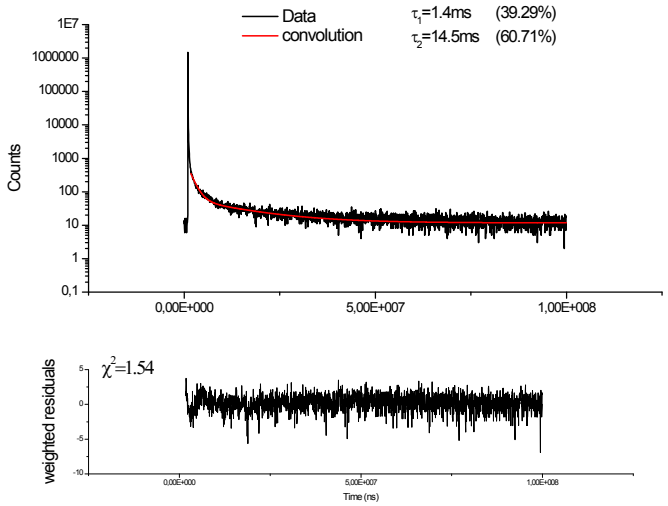


Figure S34. Decay of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K. λ_{exc}=350nm , λ_{em}=400nm

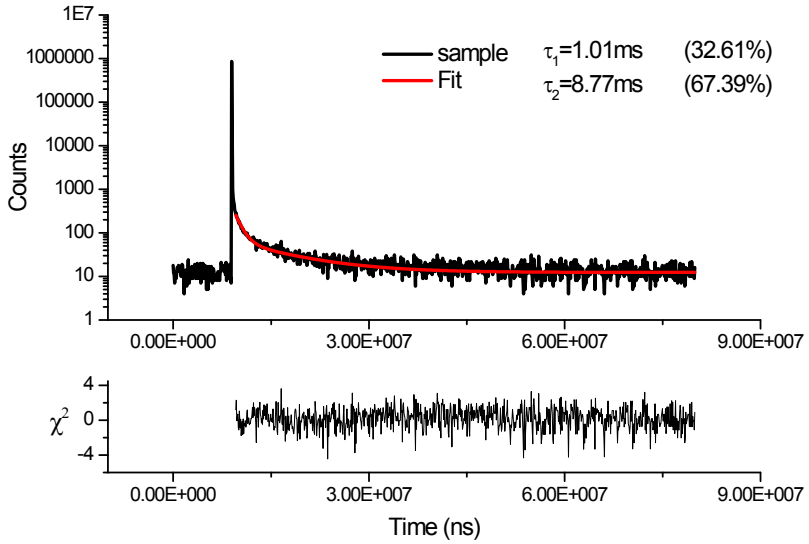


Figure S35-A. TT-Py in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K. λ_{exc}=330nm; λ_{em}=450nm

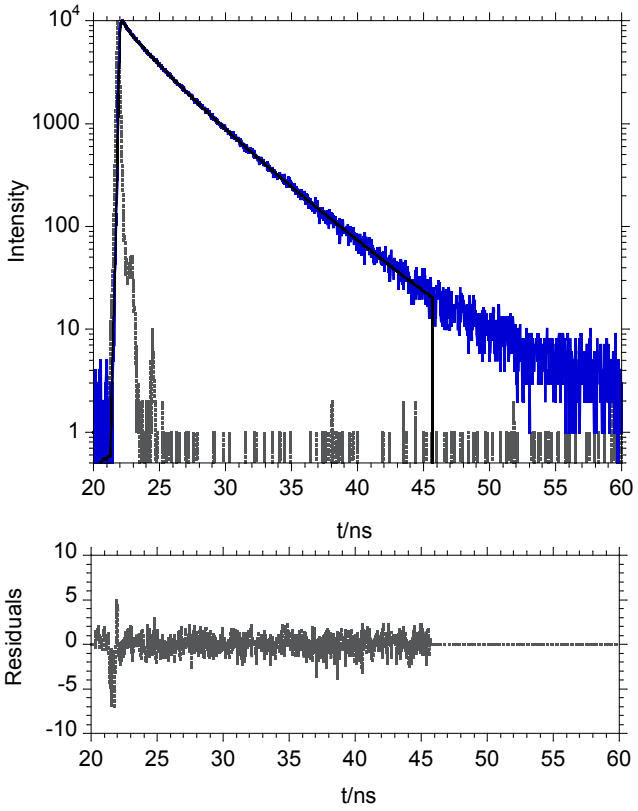


Figure S35-B. Decay of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K. λ_{exc}=408nm , λ_{em}=450nm. 3-exp fit, black line: τ_{av}=3.47ns A1=0.4402, τ_1=2.4769ns ; A2=0.2345, τ_2=0.330661ns, A3=0.3252, τ_3=4.39950ns, CHISQ =1.1313259)

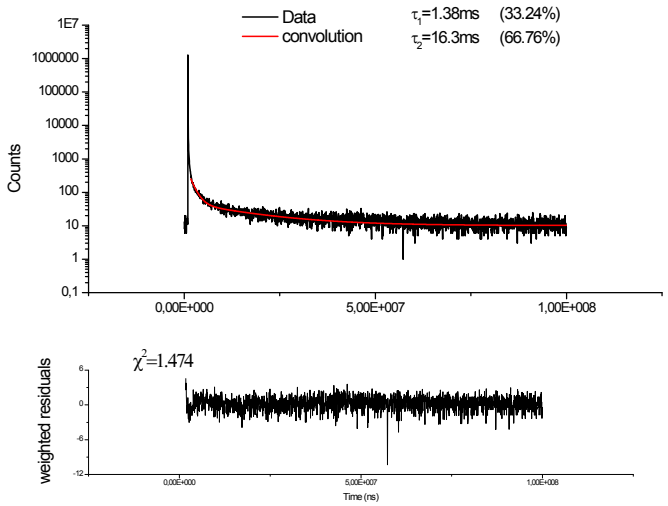


Figure S36. Decay of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K. λ_{exc}=400nm , λ_{em}=500nm.

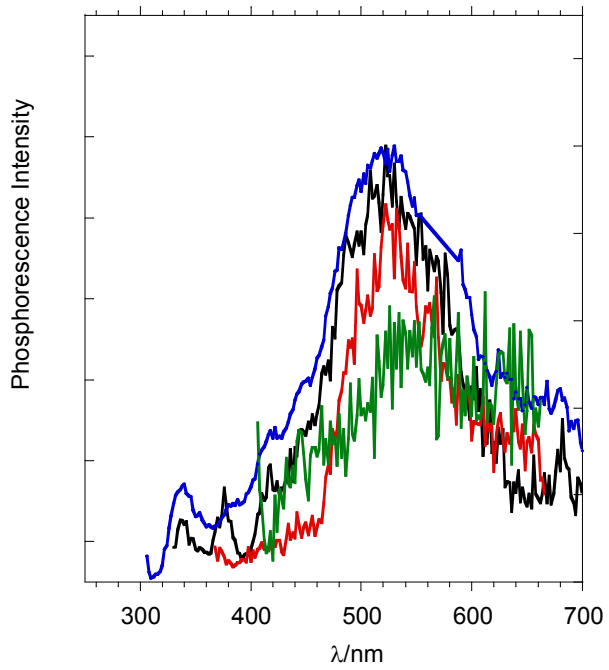


Figure S37. Phosphorescence spectra of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K. λ_{exc}=290nm (blue line, delay 100 μs, window 500 μs); λ_{exc}=300nm (black line, delay 1ms, window 5ms); λ_{exc}=350nm (red line, delay 1ms window 5ms; λ_{exc}=390nm (green line, delay 1ms, window 5ms).

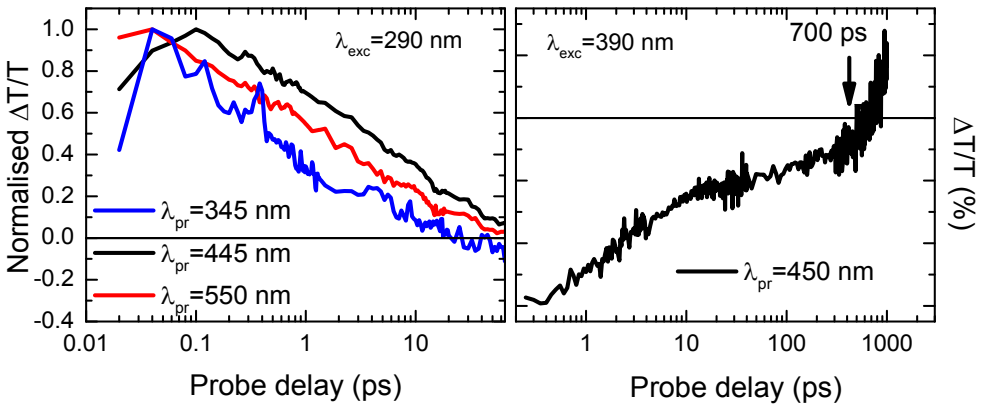


Figure S38. Ultrafast spectroscopy dynamics selected at different probe wavelengths. Left panel: 290 nm excitation. Right panel: 390 nm excitation.

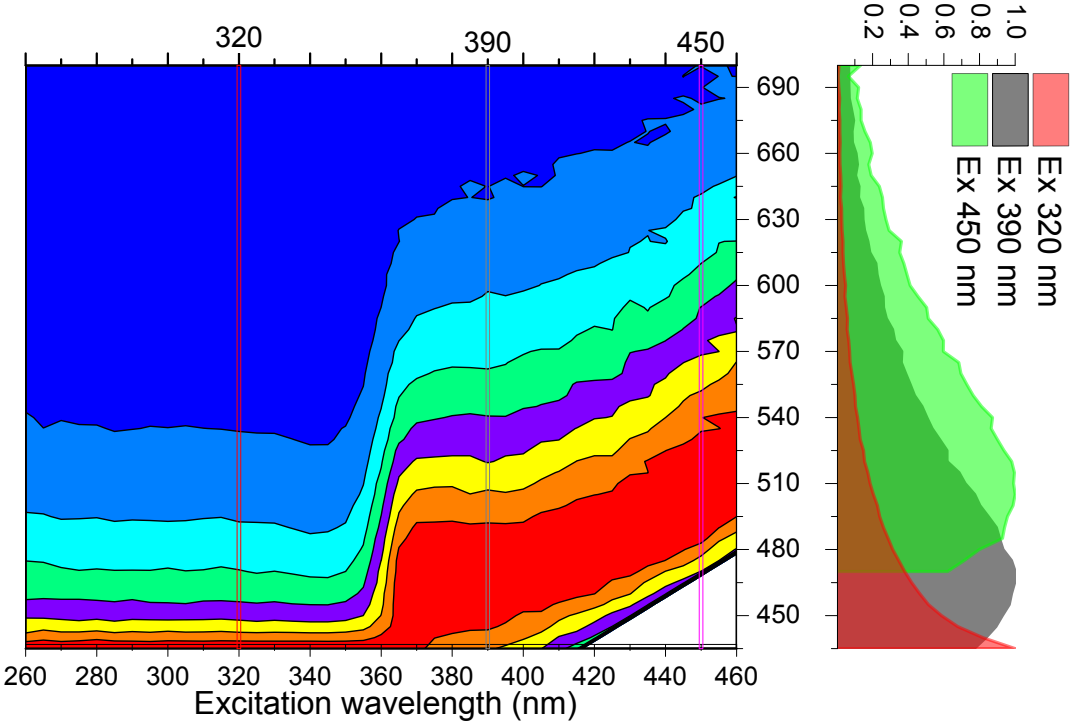


Figure S39. Normalized excitation-emission mapping of **TT-Py-A** crystals.

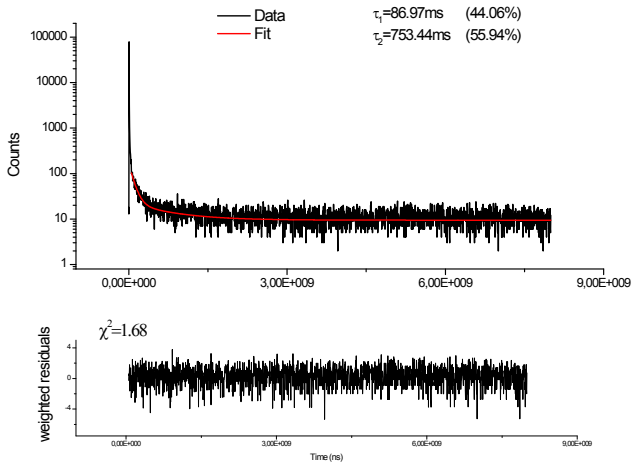
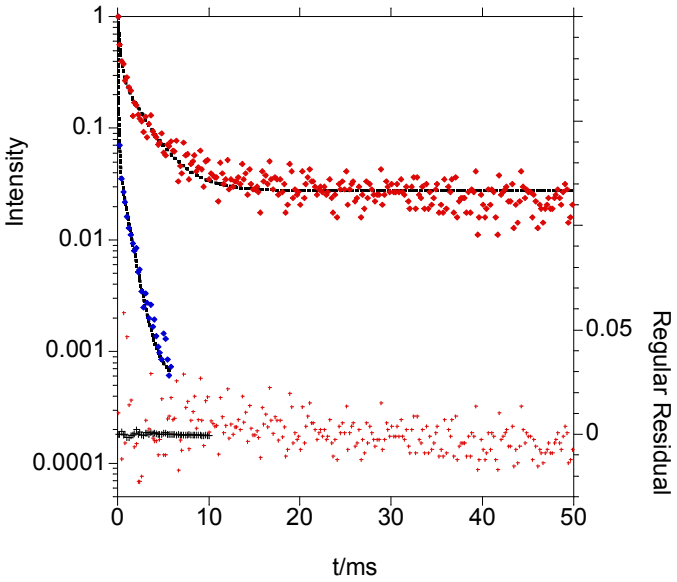


Figure S40. Decay of **TT-Py-A** crystals at 298 K. λ_{exc}=300nm, λ_{em}=360nm



	A1	t1	A2	t2	Adj. R-Square	τ_{av}	<t>
410nm	0,05346	0,92075	2,26981	0,05732	0,99998	0.29	0.08
615nm	0,81543	0,24181	0,30478	2,55486	0,98135	2.09	0.87

Figure S41. Phosphorescence decay of **TT-Py-A** crystals at 298 K. λ_{exc}=290nm, λ_{em}=410nm (blue point) with biexponential fit (black dotted); λ_{exc}=360nm, λ_{em}=615nm (red point) with biexponential fit (black dotted); see parameters above.

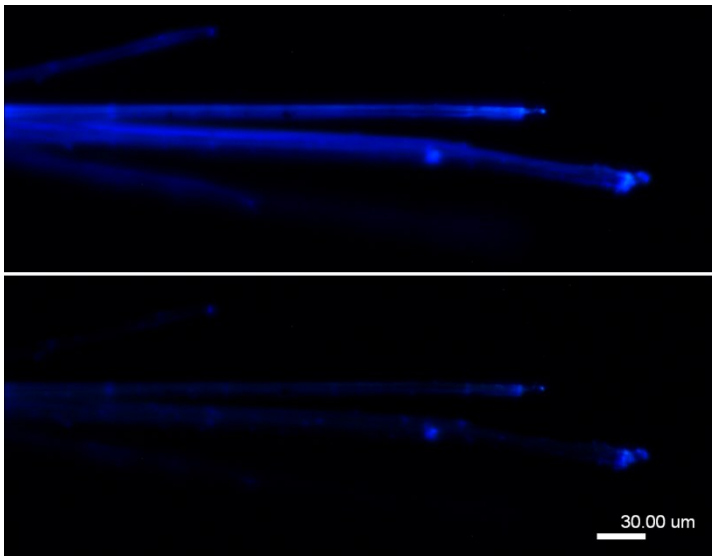


Figure S42. Fluorescence microscopy images of **TT-Py-H** crystals at 298 K. λ_{exc}=360-400nm, with vertical (top) and orizontal (bottom) polarized emission.

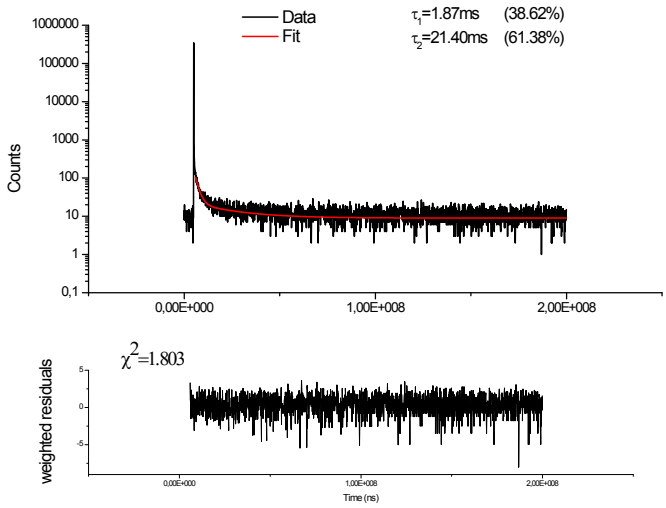


Figure S43. Decay of **TT-Py-H** crystals at 298 K. λ_{exc}=300nm, λ_{em}=360nm

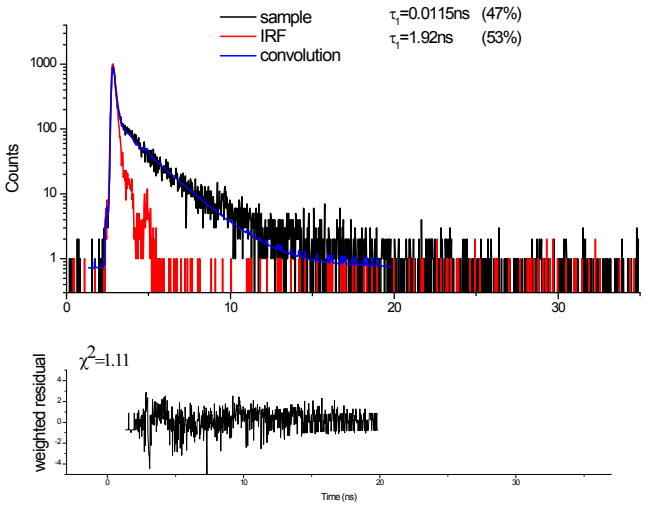


Figure S44. Decay of **TT-Py-H** crystals at 298 K. λ_{exc}=404nm , λ_{em}=450nm

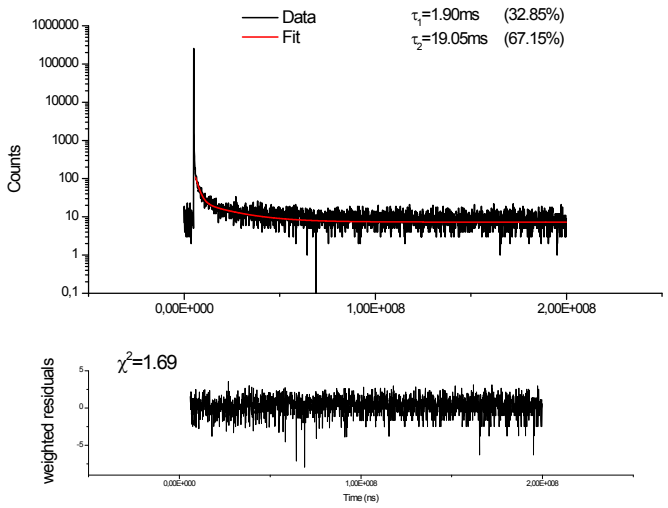


Figure S45. Decay of **TT-Py-H** crystals at 298 K. λ_{exc}=300nm , λ_{em}=500nm

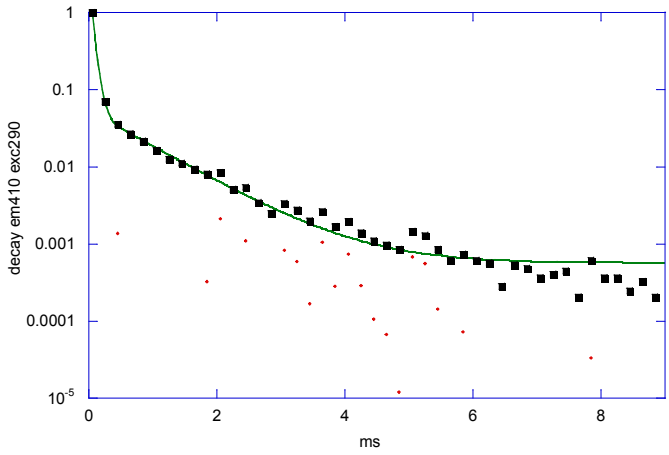


Figure S46. Decay of **TT-Py-H** crystals at 298 K. λ_{exc}=290nm, λ_{em}=410nm. 2exp fit, A1=0.0379, t1=1.047ms, A2=0.9548, t2=0.05846ms. τ_{av}=0.47 ms. R= 0,99972

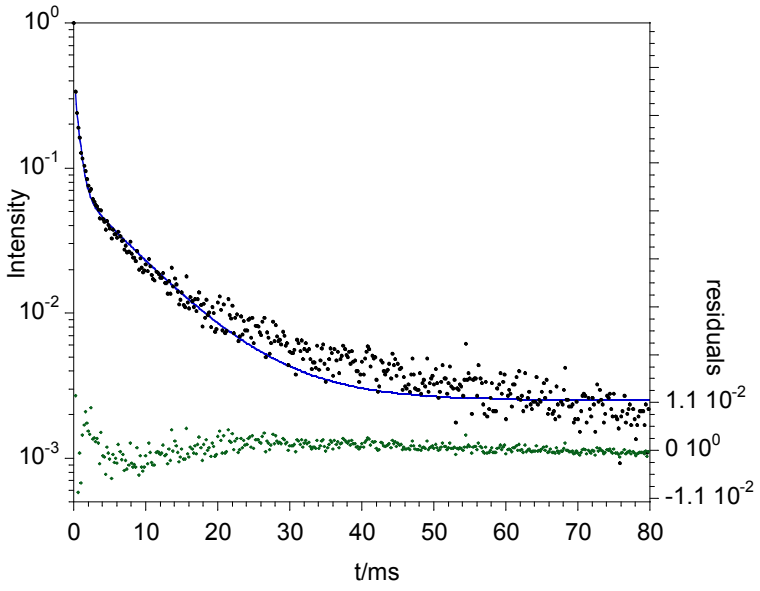


Figure S47. Decay of **TT-Py-H** crystals at 298 K. λ_{exc}=272nm, λ_{em}=570nm. 2exp fit, A1=0.8434, t1=0.6272ms, A2=0.1566, t2=8.189ms. τ_{av}=5.98 ms. R= 0,99341

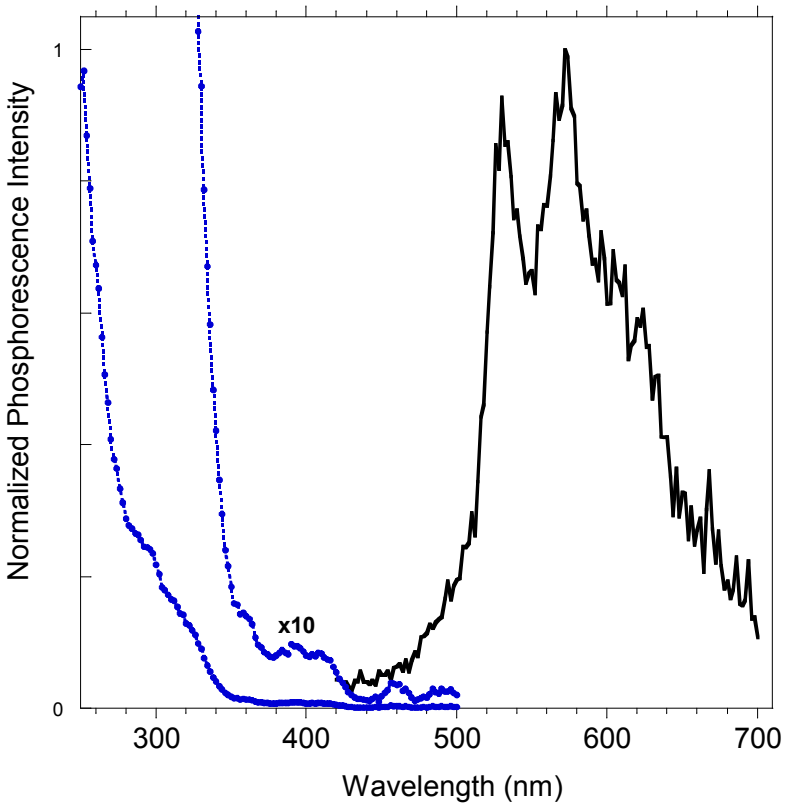


Fig. S48. Phosphorescence of **TT-Py-H** at 86 K. Emission (exc 400nm) and excitation profile of the 530nm emission. (delay 200μs, window 500μs)

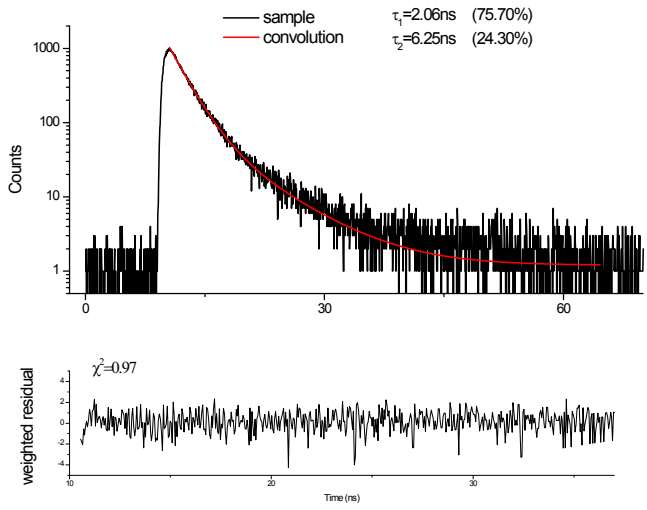


Figure S49. Decay of **TT-Py-X** crystals at 298 K. λ_{exc}=300nm , λ_{em}=450nm

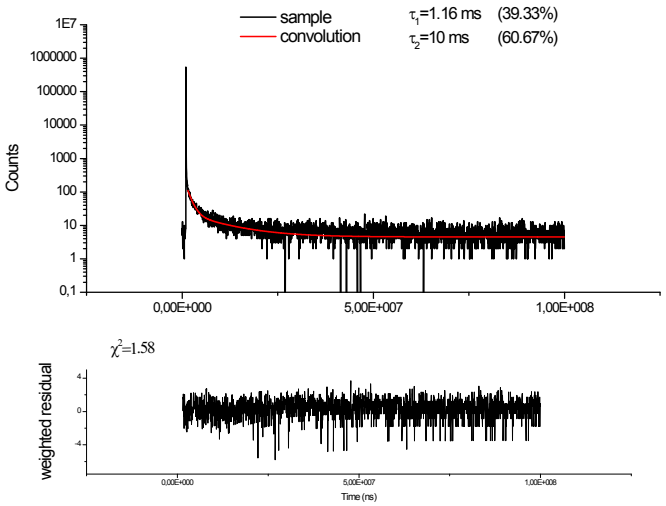


Figure S50. Decay of **TT-Py-X** crystals at 298 K. λ_{exc}=300nm , λ_{em}=570nm

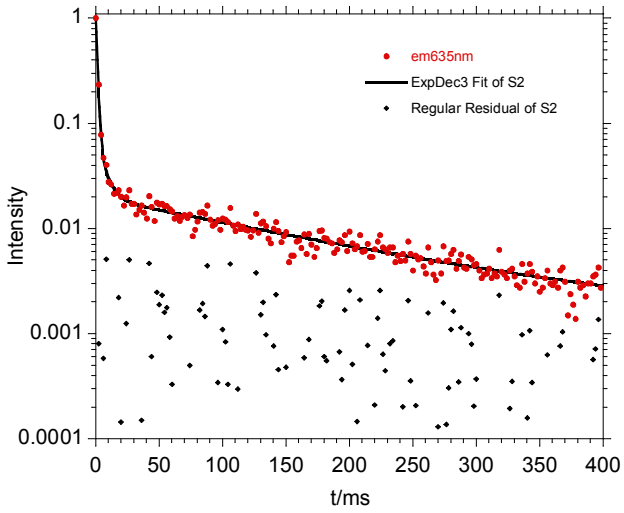


Figure S51. Decay of **TT-Py-X** crystals at 298 K. λ_{exc}=370nm, λ_{em}=634nm. 3exp fit, A1=0.0477, t1=6.34841ms, A2=0.9363, t2=1.19579, A3=0.0159, t3=168.6882. τ_{av}=111.07 ms. R= 0,99954

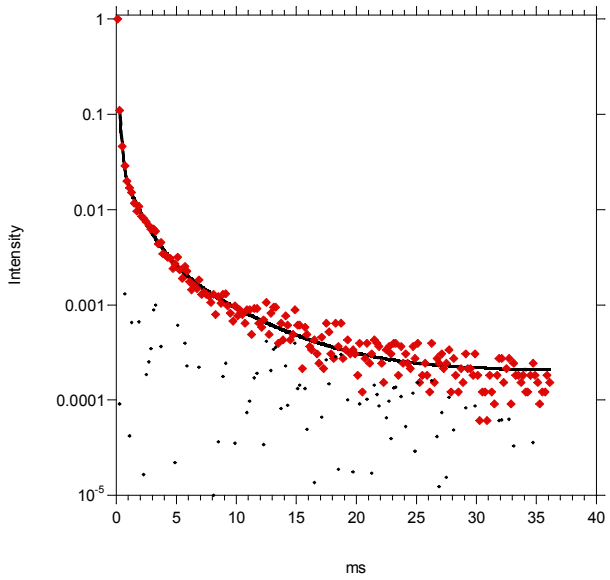


Figure S52. Decay of **TT-Py-X** crystals at 298 K. λ_{exc}=270nm, λ_{em}=408nm. 3exp fit, A1=0.94, t1=0.1578ms, A2=0.05, t2=1.2876, A3=0.01, t3=5.36276. τ_{av}=1.31 ms. R= 0,99912

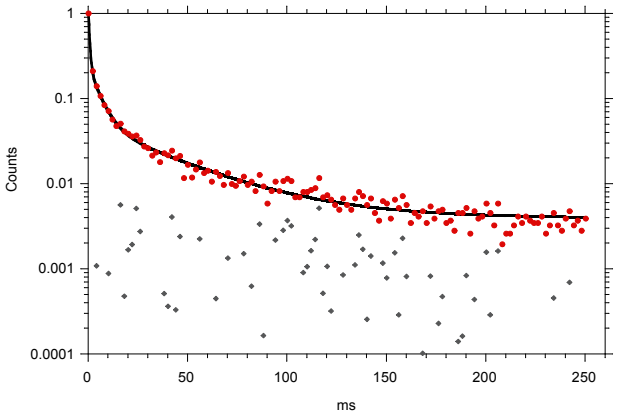


Figure S53. Decay of **TT-Py-X** crystals at 298 K. λ_{exc}=360nm, λ_{em}=532nm. 3exp fit, A1=0.1538, t1=5.45086ms, A2=0.8098, t2=0.61944, A3=0.0363, t3=40.02115. τ_{av}=22.60 ms. R= 0,99956

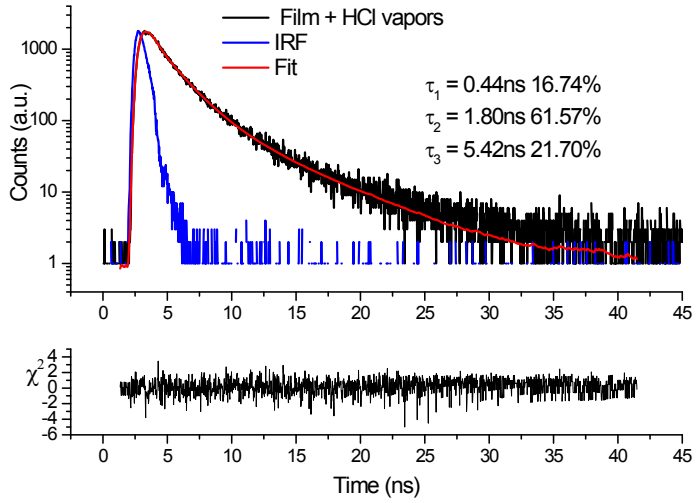


Figure S54. Lifetime measurement (λ_{exc}=300nm, λ_{em}=421nm) of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K exposed to HCl vapors for 45min τ_{av}= 3.56 ns.).

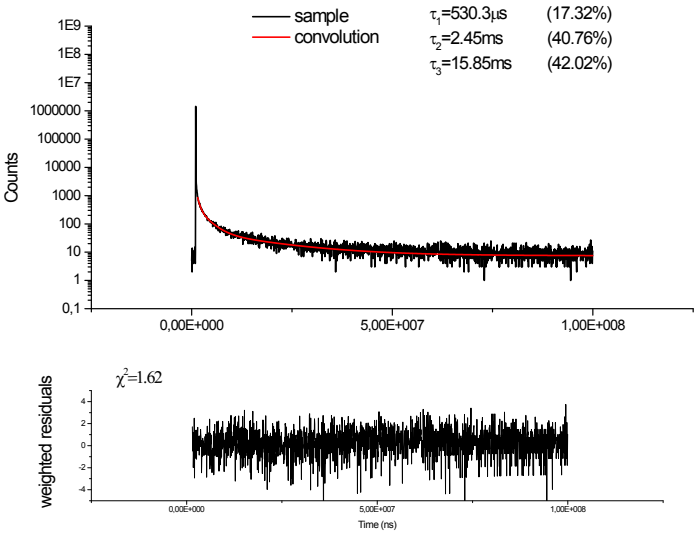


Figure S55. Lifetime measurement (λ_{exc}=340nm, λ_{em}=426nm) of **TT-Py** in PMMA (w/w **TT-Py**/PMMA 10%) at 298 K exposed to HCl vapors for 45min τ_{av}= 13.94 ms.

4. Crystal structures

Table S1. Crystallographic data and structure refinement details for **TT-Py-A**, **TT-Py-H·1.7H_2O** and **TT-Py-X** polymorphs**.**

	TT-Py-A	**TT-Py-H·1.7H_2O**	**TT-Py-X**
Chemical Formula	$C_{14}H_9N_7$	$(C_{14}H_9N_7),O_{1.7}$	$C_{14}H_9N_7$
Molecular weight	275.28	307.28	275.28
T(K)	293(2)	120(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	*Pbcn*	$P2_1/c$	$P2_1/c$
a(Å)	33.189(8)	3.7357(18)	18.0949(7)
b(Å)	10.162(3)	14.805(7)	8.8509(4)
c(Å)	7.2434(18)	23.784(11)	17.3684(7)
α(°)	90	90	90
β(°)	90	90.284(7)	117.796(1)
γ(°)	90	90	90
V(Å^3)	2443.0(10)	1315.4(11)	2460.69(18)
Z	8	4	8
D_{calcd} (g cm^{-3})	1.497	1.552	1.486
μ (mm^{-1})	0.099	0.112	0.099
Crystal size (mm)	0.55 x 0.07 x 0.01	0.45 x 0.04 x 0.04	0.35 x 0.27 x 0.18
2θmax, °	55.00	55.32	61.0
No. of measured, independent and observed [I >2σ(I)] reflections	66937 / 2803 / 1742	19094 / 3031 / 1577	47901 / 7501 / 5146
(R_{int})/(R_σ)	0.1067 / 0.0384	0.1709 / 0.1332	0.0285 / 0.0201
data/restraints/params	2803 / 0 / 190	3031 / 6 / 220	7501 / 0 / 379
R[F^2 > 2σ(F^2)], wR(F^2), S	0.0497, 0.1122, 1.059	0.0665, 0.1518, 1.000	0.0468, 0.1245, 1.028
Δρmax, Δρmin (e Å^{-3})	0.185, -0.204	0.303, -0.349	0.166, -0.220

5. Theoretical studies

In Tables S2-S4 we report the first singlet and triplet excitation energies as computed *in vacuo* at ωB97X/6-311++G(d,p) level for the optimized geometry of **TT-Py** in its absolute (**A**, Table S2) and relative (**D**, Table S3) minima and in the maximum energy state (**E**, Table S4). The simulated absorption spectrum computed at the minimum energy geometry (state **A**) is shown in Figure S52, together with that of the protonated species (**TT-PyH$^+$**) in its absolute minimum. The computed maxima positions are slightly blue-shifted with respect to the experimental ones principally as a consequence of the functional choice (see Computational details).
A schematic representation of the computed levels for the optimized monomers of **TT** and **TT-Py** (state **A**) is shown in Figure S53, while Figure S54 displays isodensity surface plots of the frontier orbitals mainly involved in the computed transitions of **TT-Py**.

Tables S5-S7 summarize the first singlet and triplet excitation energies as computed *in vacuo* at ωB97X/6-311++G(d,p) level for the optimized geometries of dimers of **TT-Py** starting from the X-ray structures of **TT-Py-A** (Table S5), **TT-Py-H** (Table S6) and **TT-Py-X** (Table S7).
Table S8 reports the first singlet and triplet excitation energies as computed *in vacuo* at ωB97X/6-311++G(d,p) level for the optimized geometries of **TT-PyH**$^+$ in its absolute minimum.

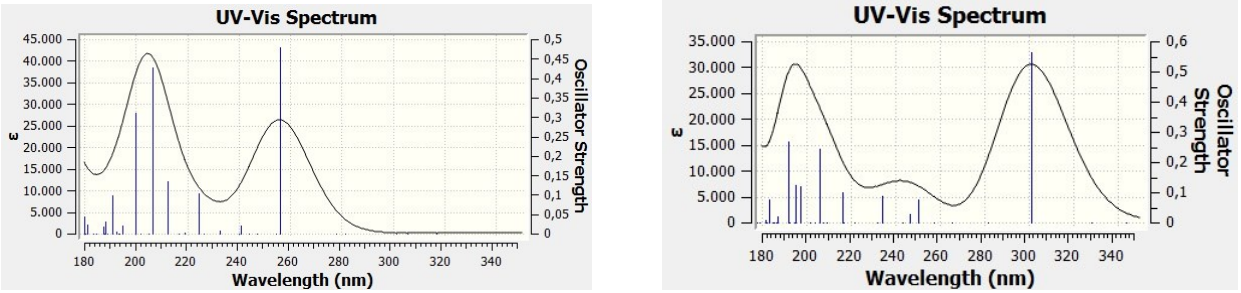


Figure S56. ωB97X/6-311++G(d,p) computed absorption spectrum of **TT-Py** (left) and **TT-PyH**$^+$ (right) in their absolute minimum, resulting from convolution of the excitation energies (blue sticks) with 0.25 eV of half-bandwidth.

Figure S57. Electronic levels computed for **TT** and **TT-Py** (state **A**) at molecular level. In blue are reported the singlet levels with oscillator strength $f \geq 0.0001$ and the corresponding values of f (see detailed information in Table S3).

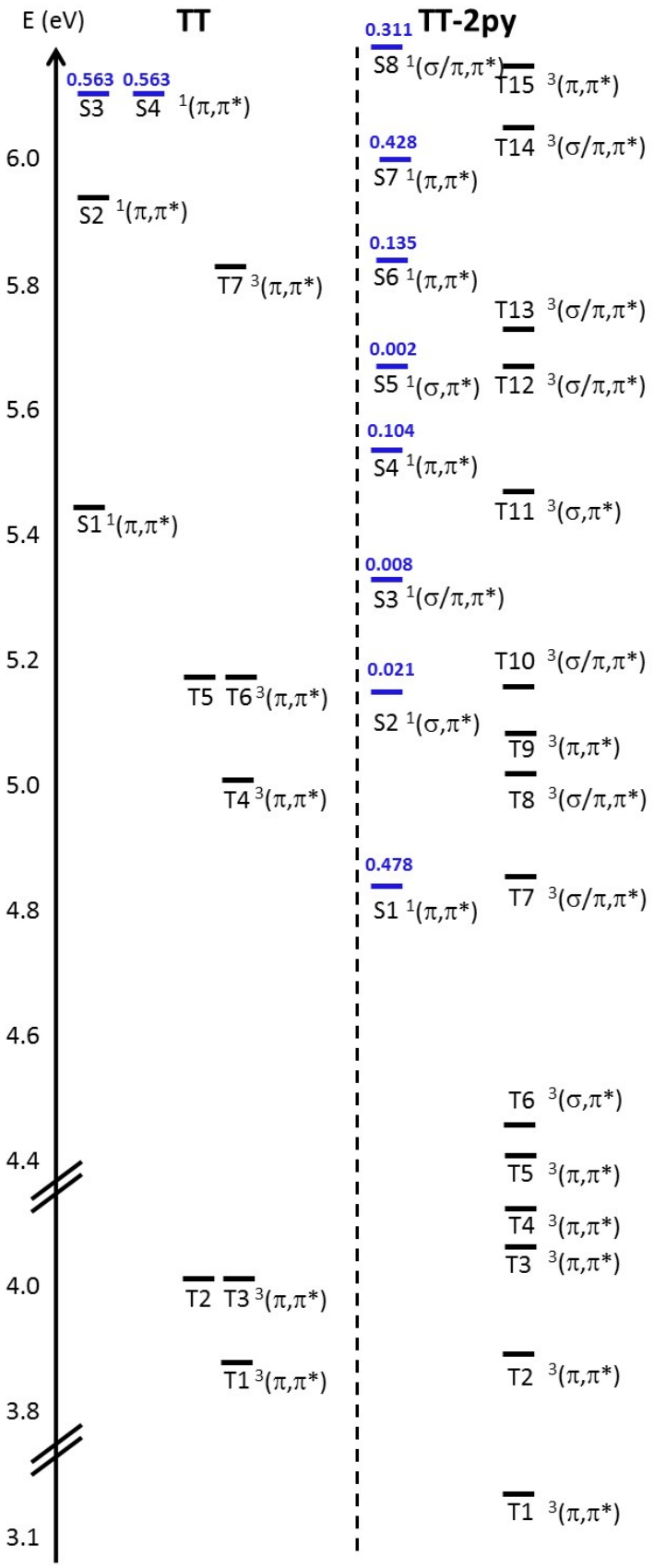
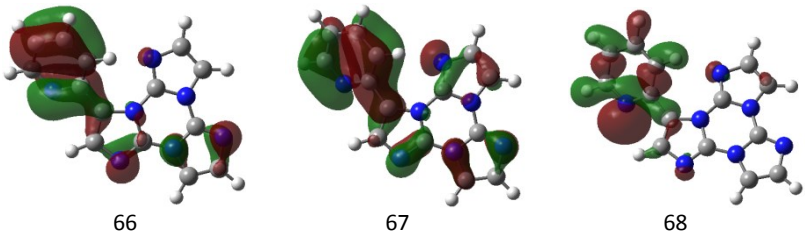


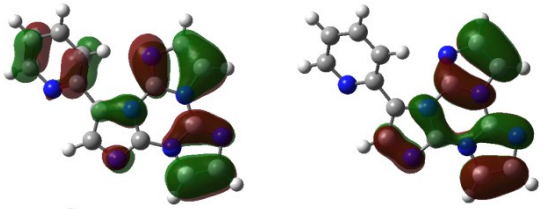
Figure S58. Isodensity surface plots of the frontier orbitals of monomeric **TT-Py** mainly involved in the computed transitions (isosurface values: 0.025, energies in a.u.).

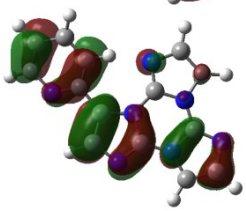
Highest Occupied MOs

MO	E(a.u.)	symmetry
66	-0.39632	π
67	-0.37928	mixed σ/π
	(σ contribution on one TT's N)	
68	-0.37198	σ
69	-0.34920	π
70	-0.33226	π
71	-0.31405	π



66 67 68

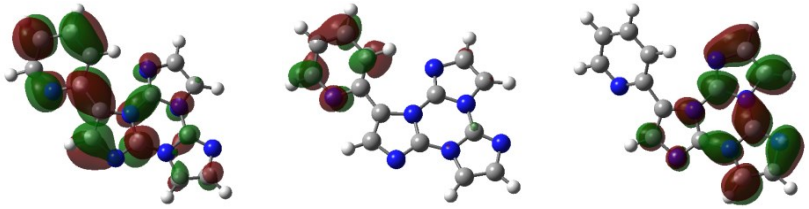




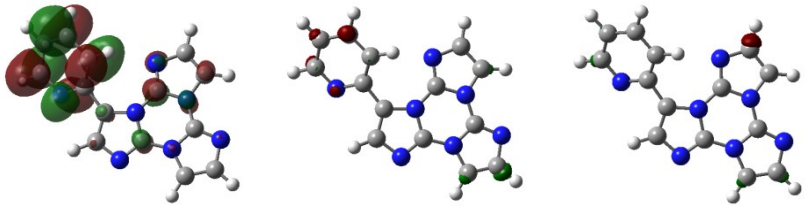
69 70 71

Lowest Unoccupied MOs

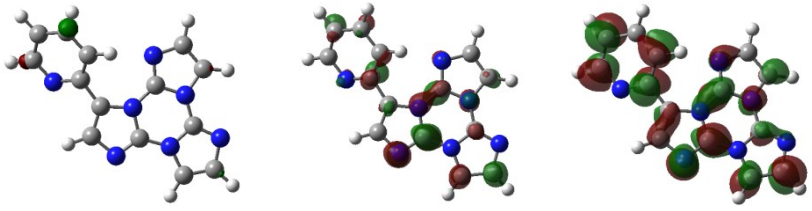
72	0.02046	π
73	0.04168	π
74	0.04628	π
75	0.04698	π
76	0.04858	mixed σ/π
		(σ on TT, π on py)
77	0.05238	σ
78	0.06064	σ
79	0.06217	π
80	0.06672	π



72 73 74



75 76 77



78 79 80

Table S2. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the optimized geometry of **TT-Py** (state **A**).

```
T1  Excited State   1:      Triplet-A      3.1469 eV  393.98 nm  f=nd  <S**2>=2.000
      66 -> 72        -0.12578
      66 -> 75        -0.10762
      67 -> 75        -0.10620
      67 -> 80        -0.10543
      69 -> 72         0.11322
      71 -> 72         0.58886
      71 -> 75        -0.10734

T2  Excited State   2:      Triplet-A      3.9108 eV  317.03 nm  f=nd  <S**2>=2.000
      66 -> 72        -0.16448
      67 -> 75        -0.17145
      69 -> 72         0.18436
      69 -> 75        -0.10937
      70 -> 74         0.42171
      71 -> 72        -0.11469
      71 -> 79         0.11748
      71 -> 80        -0.20702

T3  Excited State   3:      Triplet-A      4.0599 eV  305.39 nm  f=nd  <S**2>=2.000
      66 -> 72         0.19300
      67 -> 73        -0.12774
      67 -> 75         0.26688
      69 -> 80         0.15806
      70 -> 74         0.33476
      71 -> 72         0.17903
      71 -> 75         0.10862
      71 -> 80         0.12362
      71 -> 86         0.13503

T4  Excited State   4:      Triplet-A      4.1178 eV  301.10 nm  f=nd  <S**2>=2.000
      69 -> 74         0.42389
      70 -> 72         0.21543
      70 -> 75        -0.10631
      70 -> 79        -0.15052
      70 -> 80         0.22917
      70 -> 81        -0.10015
      70 -> 86        -0.14112
      71 -> 74        -0.17828

T5  Excited State   5:      Triplet-A      4.4072 eV  281.32 nm  f=nd  <S**2>=2.000
      66 -> 72        -0.15488
      67 -> 72         0.25881
      67 -> 73        -0.10053
      67 -> 75         0.20379
      69 -> 72         0.12081
      69 -> 75         0.14212
      71 -> 73        -0.18919
      71 -> 75         0.38143
      71 -> 79         0.14462
      71 -> 80        -0.12042

T6  Excited State   6:      Triplet-A      4.4628 eV  277.82 nm  f=nd  <S**2>=2.000
      68 -> 72         0.49664
      68 -> 73        -0.18725
      68 -> 75         0.37303

S1  Excited State   7:      Singlet-A      4.8401 eV  256.16 nm  f=0.4782  <S**2>=0.000
      69 -> 72         0.10809
      71 -> 72         0.64888

T7  Excited State   8:      Triplet-A      4.8747 eV  254.34 nm  f=nd  <S**2>=2.000
      66 -> 72         0.25117
      66 -> 73        -0.15808
      66 -> 75         0.31080
      67 -> 72         0.34657
      69 -> 72         0.10076
      71 -> 75        -0.20577
      71 -> 80        -0.17270

T8  Excited State   9:      Triplet-A      5.0156 eV  247.20 nm  f=nd  <S**2>=2.000
      67 -> 72        -0.15285
      67 -> 74        -0.11905
      67 -> 80         0.11782
      70 -> 72         0.14404
      70 -> 80         0.14253
      71 -> 74         0.43334
      71 -> 80        -0.11016
      71 -> 97        -0.13366

T9  Excited State  10:      Triplet-A      5.0810 eV  244.02 nm  f=nd  <S**2>=2.000
      69 -> 72         0.16870
      69 -> 74        -0.24116
```

```
      69 -> 86         0.18083
      70 -> 72         0.33677
      70 -> 75        -0.10153
      70 -> 80         0.12425
      70 -> 86         0.18908
      70 -> 94         0.10296
      71 -> 80         0.13441

S2  Excited State  11:      Singlet-A      5.1458 eV  240.94 nm  f=0.0209  <S**2>=0.000
      68 -> 72         0.57418
      68 -> 73        -0.14131
      68 -> 75         0.27474
      68 -> 79         0.10097
      68 -> 80        -0.10013

T10 Excited State  12:      Triplet-A      5.1663 eV  239.99 nm  f=nd  <S**2>=2.000
      62 -> 74         0.11105
      67 -> 72        -0.14923
      69 -> 72         0.21157
      69 -> 74         0.17311
      69 -> 75        -0.12814
      69 -> 79        -0.13306
      69 -> 80         0.20532
      70 -> 74        -0.21725
      70 -> 86         0.22464
      70 -> 87         0.11087

S3  Excited State  13:      Singlet-A      5.3272 eV  232.74 nm  f=0.0081  <S**2>=0.000
      66 -> 75        -0.11748
      66 -> 80        -0.10059
      67 -> 72         0.23000
      69 -> 72         0.17092
      70 -> 72         0.11492
      70 -> 74         0.21907
      71 -> 73        -0.22788
      71 -> 74         0.17570
      71 -> 75         0.37599
      71 -> 79         0.10016

T11 Excited State  14:      Triplet-A      5.4751 eV  226.45 nm  f=nd  <S**2>=2.000
      68 -> 72        -0.37076
      68 -> 73        -0.19978
      68 -> 75         0.40806
      68 -> 80         0.26248
      68 -> 81        -0.15390

S4  Excited State  15:      Singlet-A      5.5278 eV  224.29 nm  f=0.1043  <S**2>=0.000
      67 -> 72        -0.11363
      69 -> 72         0.17970
      69 -> 75        -0.11456
      70 -> 72         0.26849
      70 -> 74         0.27324
      70 -> 75        -0.12398
      70 -> 80         0.13240
      71 -> 73         0.10750
      71 -> 74         0.19630
      71 -> 75        -0.25057
      71 -> 80        -0.15996

S5  Excited State  16:      Singlet-A      5.6568 eV  219.18 nm  f=0.0017  <S**2>=0.000
      68 -> 72        -0.23119
      68 -> 73        -0.24021
      68 -> 75         0.48370
      68 -> 80         0.24022
      68 -> 81        -0.14578

T12 Excited State  17:      Triplet-A      5.6616 eV  218.99 nm  f=nd  <S**2>=2.000
      66 -> 72         0.26172
      66 -> 73         0.12084
      66 -> 75        -0.27633
      66 -> 80        -0.18137
      66 -> 81         0.10714
      67 -> 72         0.23065
      67 -> 75        -0.14852
      67 -> 80        -0.14563
      71 -> 74         0.15499
      71 -> 80         0.13741

T13 Excited State  18:      Triplet-A      5.7267 eV  216.50 nm  f=nd  <S**2>=2.000
      60 -> 74         0.16641
      61 -> 72         0.12322
      66 -> 72         0.21828
      66 -> 75        -0.11774
      66 -> 80        -0.14460
      67 -> 75        -0.12082
      69 -> 86         0.18958
      70 -> 72        -0.13607
      70 -> 90         0.10369
      70 -> 92         0.12999
```

```
      70 -> 94         0.10429
      71 -> 74        -0.16675
      71 -> 75         0.12567
      71 -> 94        -0.10878
      71 -> 97        -0.10927

S6  Excited State  19:      Singlet-A      5.8424 eV  212.21 nm  f=0.1352  <S**2>=0.000
      69 -> 72         0.14195
      69 -> 80         0.10798
      70 -> 72        -0.27104
      70 -> 74         0.40095
      70 -> 80        -0.11212
      71 -> 74        -0.34906

S7  Excited State  20:      Singlet-A      6.0009 eV  206.61 nm  f=0.4276  <S**2>=0.000
      69 -> 74        -0.33687
      70 -> 72        -0.32804
      70 -> 74         0.18705
      70 -> 80        -0.11512
      71 -> 74         0.34953

T14 Excited State  21:      Triplet-A      6.0497 eV  204.94 nm  f=nd  <S**2>=2.000
      62 -> 74         0.15120
      66 -> 74         0.10305
      67 -> 74        -0.10057
      69 -> 74         0.15572
      69 -> 86         0.16460
      70 -> 72        -0.21380
      71 -> 74         0.23609
      71 -> 75        -0.10703
      71 -> 79        -0.12484
      71 -> 80         0.15647

T15 Excited State  22:      Triplet-A      6.1469 eV  201.70 nm  f=nd  <S**2>=2.000
      60 -> 72         0.10143
      62 -> 72         0.14938
      62 -> 80         0.10497
      69 -> 72         0.28807
      69 -> 74        -0.12102
      69 -> 90        -0.11304
      69 -> 92        -0.13042
      70 -> 74        -0.17292
      70 -> 86        -0.25970
      70 -> 87        -0.12666
      70 ->110        -0.10372

S8  Excited State  23:      Singlet-A      6.1977 eV  200.05 nm  f=0.3114  <S**2>=0.000
      66 -> 72         0.11703
      67 -> 75         0.10643
      70 -> 72         0.18972
      70 -> 74         0.22332
      71 -> 73        -0.12727
      71 -> 74        -0.12173
      71 -> 79        -0.33491
      71 -> 80         0.34113
```

Table S3. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the local minimum of **TT-Py** (state **D**).

```
T1  Excited State   1:      Triplet-A      3.4850 eV  355.76 nm  f=nd  <S**2>=2.000
      66 -> 72         0.18891
      66 -> 74         0.16568
      67 -> 72        -0.12062
      67 -> 74         0.16412
      67 -> 80         0.19162
      69 -> 72        -0.20076
      71 -> 72         0.43137
      71 -> 74        -0.16506

T2  Excited State   2:      Triplet-A      3.8757 eV  319.90 nm  f=nd  <S**2>=2.000
      66 -> 72        -0.13285
      66 -> 74        -0.10361
      67 -> 72         0.11880
      67 -> 74        -0.15194
      69 -> 72         0.11925
      70 -> 75         0.12600
      70 -> 76         0.40130
      71 -> 72         0.16538
      71 -> 80         0.26658

T3  Excited State   3:      Triplet-A      4.0664 eV  304.90 nm  f=nd  <S**2>=2.000
      66 -> 72         0.14421
      66 -> 74         0.10214
      67 -> 72        -0.13267
      67 -> 74         0.19754
```

```
      69 -> 80         0.19972
      70 -> 75         0.10596
      70 -> 76         0.33450
      71 -> 72        -0.22519
      71 -> 80        -0.16920
      71 -> 86         0.13818

T4  Excited State   4:      Triplet-A      4.0960 eV  302.70 nm  f=nd  <S**2>=2.000
      69 -> 75         0.11976
      69 -> 76         0.38329
      70 -> 72         0.17735
      70 -> 74        -0.11202
      70 -> 80         0.26874
      70 -> 86         0.11174
      71 -> 76         0.25265

T5  Excited State   5:      Triplet-A      4.4338 eV  279.64 nm  f=nd  <S**2>=2.000
      68 -> 72         0.53450
      68 -> 73        -0.14566
      68 -> 74         0.33539

T6  Excited State   6:      Triplet-A      4.5196 eV  274.33 nm  f=nd  <S**2>=2.000
      67 -> 72         0.36608
      67 -> 73        -0.13950
      67 -> 74         0.31010
      69 -> 72         0.16123
      69 -> 74         0.17260
      71 -> 72        -0.17278
      71 -> 73         0.13195
      71 -> 74        -0.28045
      71 -> 80         0.10966

T7  Excited State   7:      Triplet-A      4.9251 eV  251.74 nm  f=nd  <S**2>=2.000
      65 -> 72         0.11665
      66 -> 72         0.37288
      66 -> 73        -0.11482
      66 -> 74         0.26487
      67 -> 72         0.25696
      67 -> 74        -0.12314
      67 -> 80        -0.12580
      69 -> 74        -0.13864
      71 -> 74         0.16998
      71 -> 80         0.14962

T8  Excited State   8:      Triplet-A      5.0528 eV  245.38 nm  f=nd  <S**2>=2.000
      67 -> 72        -0.13959
      67 -> 76         0.12416
      67 -> 80         0.10515
      69 -> 86        -0.10485
      69 -> 87         0.10760
      70 -> 72        -0.17291
      70 -> 80        -0.19144
      71 -> 75         0.12745
      71 -> 76         0.40811
      71 -> 95        -0.10848

T9  Excited State   9:      Triplet-A      5.1291 eV  241.73 nm  f=nd  <S**2>=2.000
      69 -> 72         0.14767
      69 -> 76         0.23429
      69 -> 86        -0.10897
      70 -> 72        -0.29471
      70 -> 80        -0.18228
      70 -> 86         0.15979
      70 -> 92        -0.11090
      70 -> 94         0.11384
      71 -> 80        -0.13367
      71 -> 87         0.10003

S1  Excited State  10:      Singlet-A      5.1403 eV  241.20 nm  f=0.0790  <S**2>=0.000
      68 -> 72         0.49261
      68 -> 73        -0.10078
      68 -> 74         0.23655
      69 -> 72         0.18564
      71 -> 72        -0.30048
```

Table S4. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for the maximum energy state of **TT-Py** (state **E**).

```
T1  Excited State   1:      Triplet-A      2.5339 eV  489.29 nm  f=nd  <S**2>=2.000
      66 -> 72         0.11051
      66 -> 80        -0.11232
      67 -> 77         0.13411
      68 -> 72         0.14850
      70 -> 72         0.64064
```

```
      70 <- 72         0.13955

T2  Excited State   2:      Triplet-A      2.8270 eV  438.58 nm  f=nd  <S**2>=2.000
      71 -> 72         0.61658
      71 -> 77         0.18820
      71 -> 80        -0.20458

S1  Excited State   3:      Singlet-A      3.2264 eV  384.28 nm  f=0.0003  <S**2>=0.000
      71 -> 72         0.66507
      71 -> 80        -0.16937
```

Table S5. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for dimeric **TT-Py** at its optimized geometry starting from the X-ray geometry of **TT-Py-A**.

```
T1  Excited State   1:      Triplet-A      3.1818 eV  389.67 nm  f=nd  <S**2>=2.000
     132 -> 144       -0.12322
     138 -> 144        0.11933
     142 -> 143        0.25955
     142 -> 144        0.49944

T2  Excited State   2:      Triplet-A      3.2425 eV  382.37 nm  f=nd  <S**2>=2.000
     131 -> 143       -0.14511
     134 -> 146        0.10640
     134 -> 155        0.11834
     137 -> 143        0.13874
     140 -> 143       -0.13406
     141 -> 143        0.48014
     141 -> 144       -0.21482
     141 -> 146       -0.13844

T3  Excited State   3:      Triplet-A      3.8876 eV  318.92 nm  f=nd  <S**2>=2.000
     131 -> 143        0.15316
     134 -> 145       -0.10995
     134 -> 146       -0.17875
     137 -> 143       -0.12380
     137 -> 146        0.10671
     139 -> 147       -0.13177
     139 -> 148        0.25714
     139 -> 149       -0.10172
     139 -> 150        0.17559
     141 -> 143        0.12689
     141 -> 155        0.23880

T4  Excited State   4:      Triplet-A      3.8945 eV  318.36 nm  f=nd  <S**2>=2.000
     132 -> 144       -0.15644
     135 -> 148       -0.10059
     135 -> 150        0.12171
     135 -> 151       -0.12771
     138 -> 144        0.13662
     140 -> 152        0.31604
     141 -> 152        0.10000
     142 -> 144       -0.12097
     142 -> 157        0.12059
     142 -> 158       -0.13499
     142 -> 159        0.10538
     142 -> 160        0.13458

T5  Excited State   5:      Triplet-A      4.0310 eV  307.58 nm  f=nd  <S**2>=2.000
     131 -> 143        0.14292
     134 -> 145       -0.13614
     134 -> 146       -0.22059
     137 -> 155        0.17256
     139 -> 147        0.11995
     139 -> 148       -0.22794
     139 -> 150       -0.16327
     140 -> 152       -0.10574
     141 -> 143        0.16628

T6  Excited State   6:      Triplet-A      4.0358 eV  307.21 nm  f=nd  <S**2>=2.000
     132 -> 144        0.12978
     135 -> 148        0.11367
     135 -> 150       -0.14030
     135 -> 151        0.14346
     140 -> 152        0.29728
     142 -> 144        0.13381
     142 -> 171       -0.10344

T7  Excited State   7:      Triplet-A      4.1054 eV  302.00 nm  f=nd  <S**2>=2.000
     137 -> 147        0.14439
     137 -> 148       -0.28541
     137 -> 149        0.11419
     137 -> 150       -0.19032
     139 -> 143        0.15702
     139 -> 155        0.26420
     141 -> 148        0.13922

T8  Excited State   8:      Triplet-A      4.1198 eV  300.95 nm  f=nd  <S**2>=2.000
     138 -> 152        0.37487
```

```
     139 -> 152       -0.12202
     140 -> 143        0.10620
     140 -> 144        0.15225
     140 -> 157       -0.11786
     140 -> 158        0.14316
     140 -> 160       -0.13526
     140 -> 171        0.11412
     142 -> 152       -0.15490

T9  Excited State   9:      Triplet-A      4.3818 eV  282.95 nm  f=nd  <S**2>=2.000
     131 -> 143       -0.10891
     134 -> 143       -0.30000
     134 -> 144        0.11291
     134 -> 145       -0.13045
     134 -> 146       -0.17896
     137 -> 143        0.14291
     137 -> 146        0.13678
     141 -> 143        0.10211
     141 -> 145        0.18874
     141 -> 146        0.29138
     141 -> 155       -0.19311

T10 Excited State  10:      Triplet-A      4.3881 eV  282.55 nm  f=nd  <S**2>=2.000
     132 -> 144       -0.11580
     135 -> 143       -0.10857
     135 -> 144       -0.21738
     135 -> 150       -0.11651
     135 -> 151        0.12259
     136 -> 144        0.13731
     138 -> 144        0.14648
     138 -> 150        0.11290
     138 -> 151       -0.11819
     142 -> 148       -0.18197
     142 -> 150        0.23158
     142 -> 151       -0.23256
     142 -> 158       -0.10621
     142 -> 160        0.11048

T11 Excited State  11:      Triplet-A      4.4800 eV  276.75 nm  f=nd  <S**2>=2.000
     135 -> 144        0.15965
     136 -> 143        0.21542
     136 -> 144        0.42061
     136 -> 148       -0.15051
     136 -> 150        0.23516
     136 -> 151       -0.25423

T12 Excited State  12:      Triplet-A      4.5346 eV  273.42 nm  f=nd  <S**2>=2.000
     133 -> 143        0.48210
     133 -> 144       -0.18056
     133 -> 145        0.21601
     133 -> 146        0.30266

S1  Excited State  13:      Singlet-A      4.8042 eV  258.07 nm  f=0.2231  <S**2>=0.000
     138 -> 144        0.10953
     141 -> 143        0.29620
     142 -> 143        0.28030
     142 -> 144        0.48198

S2  Excited State  14:      Singlet-A      4.8570 eV  255.27 nm  f=0.3873  <S**2>=0.000
     137 -> 143        0.13002
     140 -> 143       -0.10827
     141 -> 143        0.48721
     141 -> 144       -0.20161
     142 -> 143       -0.19626
     142 -> 144       -0.24819

T13 Excited State  15:      Triplet-A      4.8759 eV  254.28 nm  f=nd  <S**2>=2.000
     132 -> 143        0.13849
     132 -> 144        0.25651
     132 -> 148       -0.14170
     132 -> 150        0.20615
     132 -> 151       -0.22354
     135 -> 143       -0.12008
     135 -> 144       -0.25469
     138 -> 144        0.10314
     142 -> 148        0.10311
     142 -> 150       -0.14625
     142 -> 151        0.14564

T14 Excited State  16:      Triplet-A      4.8811 eV  254.01 nm  f=nd  <S**2>=2.000
     131 -> 143       -0.30113
     131 -> 144        0.10385
     131 -> 145       -0.18139
     131 -> 146       -0.26280
     134 -> 143        0.25167
     134 -> 144       -0.13124
     141 -> 145        0.12478
     141 -> 146        0.18800
     141 -> 155        0.13486
```

```
T15 Excited State  17:      Triplet-A      4.9711 eV  249.41 nm  f=nd  <S**2>=2.000
     135 -> 144        0.11839
     140 -> 144        0.11557
     142 -> 152        0.35508
     142 -> 171       -0.10177
     142 -> 184        0.14361

T16 Excited State  18:      Triplet-A      5.0091 eV  247.52 nm  f=nd  <S**2>=2.000
     134 -> 143       -0.15635
     134 -> 155        0.10916
     137 -> 169        0.11199
     139 -> 143       -0.17299
     139 -> 155       -0.19472
     140 -> 143       -0.12717
     141 -> 147       -0.12723
     141 -> 148        0.25926
     141 -> 150        0.19651

T17 Excited State  19:      Triplet-A      5.0432 eV  245.84 nm  f=nd  <S**2>=2.000
     138 -> 144        0.10964
     138 -> 152       -0.21651
     138 -> 171       -0.12224
     140 -> 143        0.18120
     140 -> 144        0.18964
     140 -> 152        0.11439
     141 -> 148        0.11857
     142 -> 158        0.10200
     142 -> 160       -0.10435

T18 Excited State  20:      Triplet-A      5.0592 eV  245.07 nm  f=nd  <S**2>=2.000
     137 -> 143        0.14587
     137 -> 148        0.15444
     137 -> 150        0.11220
     137 -> 169       -0.10376
     139 -> 143        0.24686
     139 -> 155        0.10251
     139 -> 169       -0.11251
     141 -> 155        0.18828
```

Table S6. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for dimeric **TT-Py** at its optimized geometry starting from the X-ray geometry of **TT-Py-H**.

```
T1  Excited State   1:      Triplet-A      3.2072 eV  386.58 nm  f=nd  <S**2>=2.000
     131 -> 143       -0.11193
     137 -> 143        0.10204
     141 -> 143        0.44432
     142 -> 143       -0.34532

T2  Excited State   2:      Triplet-A      3.3566 eV  369.37 nm  f=nd  <S**2>=2.000
     132 -> 144        0.13230
     138 -> 144        0.12276
     141 -> 144        0.25492
     142 -> 144        0.41860
     142 -> 147        0.13568

T3  Excited State   3:      Triplet-A      3.8558 eV  321.56 nm  f=nd  <S**2>=2.000
     132 -> 144        0.14842
     135 -> 152        0.11913
     138 -> 144        0.11966
     139 -> 150        0.11280
     140 -> 147        0.12159
     140 -> 150        0.27777
     141 -> 144       -0.12273
     142 -> 144       -0.14256
     142 -> 156       -0.11396
     142 -> 157        0.11777
     142 -> 158        0.13054

T4  Excited State   4:      Triplet-A      3.8833 eV  319.28 nm  f=nd  <S**2>=2.000
     131 -> 143        0.14479
     133 -> 143        0.13074
     133 -> 146       -0.10772
     137 -> 143       -0.16303
     139 -> 146       -0.19783
     139 -> 147       -0.18547
     139 -> 150        0.12731
     140 -> 146        0.11393
     141 -> 143        0.10247
     141 -> 157       -0.14460
     142 -> 143       -0.11489
     142 -> 157        0.10804

T5  Excited State   5:      Triplet-A      4.0217 eV  308.29 nm  f=nd  <S**2>=2.000
     135 -> 152       -0.11791
     138 -> 157       -0.11490
     139 -> 146        0.14154
```

```
     139 -> 147        0.17377
     140 -> 150        0.29675
     142 -> 144        0.13605

T6  Excited State   6:      Triplet-A      4.0331 eV  307.42 nm  f=nd  <S**2>=2.000
     133 -> 152        0.10051
     137 -> 157       -0.11648
     139 -> 146        0.20703
     139 -> 147        0.14273
     139 -> 150       -0.19341
     140 -> 146       -0.13313
     140 -> 147       -0.19267
     140 -> 150       -0.10085
     142 -> 143       -0.11556

T7  Excited State   7:      Triplet-A      4.1010 eV  302.33 nm  f=nd  <S**2>=2.000
     135 -> 150        0.10023
     137 -> 150       -0.14478
     138 -> 147        0.16467
     138 -> 150        0.30113
     140 -> 144        0.17882
     140 -> 150       -0.10401
     140 -> 156        0.11386
     140 -> 157       -0.15748
     140 -> 158       -0.14418
     142 -> 150       -0.14184

T8  Excited State   8:      Triplet-A      4.1219 eV  300.79 nm  f=nd  <S**2>=2.000
     137 -> 146       -0.24954
     137 -> 147       -0.22341
     137 -> 150        0.12666
     138 -> 146       -0.11708
     138 -> 150        0.11458
     139 -> 143       -0.18434
     139 -> 156        0.10748
     139 -> 157        0.15353
     140 -> 157       -0.10112
     141 -> 146        0.11708

T9  Excited State   9:      Triplet-A      4.3835 eV  282.85 nm  f=nd  <S**2>=2.000
     133 -> 143        0.26243
     133 -> 146        0.10746
     133 -> 147       -0.16200
     137 -> 143       -0.15247
     137 -> 146       -0.10211
     137 -> 147        0.11256
     141 -> 143       -0.10935
     141 -> 144       -0.10908
     141 -> 146       -0.15416
     141 -> 147        0.18313
     141 -> 152        0.17819
     142 -> 146        0.14592
     142 -> 147       -0.14682

T10 Excited State  10:      Triplet-A      4.4213 eV  280.42 nm  f=nd  <S**2>=2.000
     135 -> 144        0.28913
     135 -> 146        0.10765
     135 -> 151       -0.12849
     135 -> 152        0.16691
     138 -> 144       -0.14225
     138 -> 152       -0.11049
     141 -> 146       -0.12202
     142 -> 144       -0.10291
     142 -> 146       -0.14810
     142 -> 151        0.13764
     142 -> 152       -0.21071
     142 -> 157       -0.11387
T11 Excited State  11:      Triplet-A      4.4703 eV  277.35 nm  f=nd  <S**2>=2.000
     134 -> 143       -0.17968
     134 -> 147        0.10152
     136 -> 144        0.44423
     136 -> 146        0.18564
     136 -> 151       -0.19605
     136 -> 152        0.25095
     136 -> 157        0.10504

T12 Excited State  12:      Triplet-A      4.4766 eV  276.96 nm  f=nd  <S**2>=2.000
     134 -> 143        0.43306
     134 -> 144        0.12019
     134 -> 146        0.19795
     134 -> 147       -0.23648
     134 -> 152       -0.14230
     135 -> 143        0.14088
     136 -> 144        0.16668
     136 -> 152        0.12928

S1  Excited State  13:      Singlet-A      4.8331 eV  256.53 nm  f=0.1021  <S**2>=0.000
     137 -> 143       -0.10158
     141 -> 143       -0.42172
```

```
     141 -> 144        0.12627
     141 -> 147        0.10482
     142 -> 143        0.42483
     142 -> 144        0.19054

T13 Excited State  14:      Triplet-A      4.8642 eV  254.89 nm  f=nd  <S**2>=2.000
     131 -> 143        0.16110
     131 -> 147       -0.13056
     131 -> 152       -0.16174
     132 -> 143        0.22283
     132 -> 144        0.18001
     132 -> 146        0.16885
     132 -> 147       -0.13386
     133 -> 143       -0.15679
     133 -> 144        0.10002
     135 -> 144        0.13183
     141 -> 147        0.12195
     142 -> 147       -0.10418
     142 -> 150        0.12351

T14 Excited State  15:      Triplet-A      4.8947 eV  253.30 nm  f=nd  <S**2>=2.000
     131 -> 143       -0.11978
     131 -> 144       -0.15148
     131 -> 146       -0.14298
     132 -> 143       -0.15676
     132 -> 144        0.15573
     132 -> 151       -0.12156
     132 -> 152        0.21069
     133 -> 143        0.11004
     133 -> 144        0.12764
     135 -> 144        0.16315
     141 -> 147       -0.10810
     141 -> 150        0.12220
     142 -> 155        0.10296
     142 -> 156        0.11023

T15 Excited State  16:      Triplet-A      4.9712 eV  249.41 nm  f=nd  <S**2>=2.000
     135 -> 144       -0.13136
     140 -> 144        0.12877
     140 -> 157       -0.10304
     141 -> 150        0.21826
     142 -> 147        0.18407
     142 -> 150        0.24920
     142 -> 152       -0.12600
     142 -> 186       -0.12964

T16 Excited State  17:      Triplet-A      4.9867 eV  248.63 nm  f=nd  <S**2>=2.000
     133 -> 143        0.12816
     141 -> 146        0.22830
     141 -> 147        0.16822
     142 -> 146       -0.18996
     142 -> 147       -0.10636
     142 -> 150        0.18310

S2  Excited State  18:      Singlet-A      5.0056 eV  247.69 nm  f=0.5076  <S**2>=0.000
     138 -> 144        0.11120
     141 -> 143        0.20198
     141 -> 144        0.27679
     142 -> 143       -0.12242
     142 -> 144        0.48072
     142 -> 147        0.11216

T17 Excited State  19:      Triplet-A      5.0562 eV  245.21 nm  f=nd  <S**2>=2.000
     137 -> 143        0.11812
     137 -> 146       -0.12508
     137 -> 168       -0.13174
     138 -> 146       -0.10114
     138 -> 147       -0.10441
     139 -> 143        0.27378
     139 -> 157       -0.11248
     139 -> 168       -0.11313
     139 -> 177        0.11289
     140 -> 143       -0.13419

T18 Excited State  20:      Triplet-A      5.0828 eV  243.93 nm  f=nd  <S**2>=2.000
     138 -> 147        0.12599
     138 -> 150        0.19711
     138 -> 169        0.12341
     139 -> 144       -0.12085
     140 -> 144       -0.23128
     140 -> 146        0.11699
     140 -> 150        0.10587
     140 -> 157        0.10998
     140 -> 181        0.11829
```

Table S7. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for dimeric **TT-Py** at its optimized geometry starting from the X-ray geometry of **TT-Py-X**.

```
T1  Excited State   1:      Triplet-A      3.1255 eV  396.68 nm  f=0.0000  <S**2>=2.000
     131 -> 143         0.13266
     137 -> 143         0.13026
     141 -> 143         0.57049

T2  Excited State   2:      Triplet-A      3.2302 eV  383.83 nm  f=0.0000  <S**2>=2.000
     132 -> 144         0.13509
     132 -> 150         0.11558
     135 -> 150        -0.10649
     135 -> 160         0.10506
     138 -> 144        -0.11968
     142 -> 144         0.54986
     142 -> 150        -0.10656

T3  Excited State   3:      Triplet-A      3.8797 eV  319.57 nm  f=0.0000  <S**2>=2.000
     132 -> 144        -0.15355
     135 -> 150         0.16964
     138 -> 144         0.16013
     138 -> 150        -0.11082
     140 -> 146        -0.11468
     140 -> 150         0.10556
     140 -> 151         0.36736
     142 -> 144         0.12255
     142 -> 160        -0.19333

T4  Excited State   4:      Triplet-A      3.9091 eV  317.17 nm  f=0.0000  <S**2>=2.000
     131 -> 143        -0.15115
     133 -> 146         0.12620
     137 -> 143        -0.16712
     139 -> 147        -0.20867
     139 -> 148         0.37096
     141 -> 143         0.10480
     141 -> 155         0.14793
     141 -> 156        -0.15939

T5  Excited State   5:      Triplet-A      4.0267 eV  307.91 nm  f=0.0000  <S**2>=2.000
     132 -> 144        -0.17187
     135 -> 150         0.23493
     135 -> 151        -0.10912
     138 -> 160         0.13221
     140 -> 146         0.10109
     140 -> 150        -0.11339
     140 -> 151        -0.27920
     140 -> 160         0.11887
     142 -> 144         0.19474
     142 -> 160        -0.12977

T6  Excited State   6:      Triplet-A      4.0519 eV  305.99 nm  f=0.0000  <S**2>=2.000
     131 -> 143         0.17992
     133 -> 145         0.16494
     133 -> 146        -0.21063
     134 -> 146         0.11526
     137 -> 155        -0.10591
     137 -> 156         0.12915
     139 -> 143        -0.10343
     139 -> 147        -0.14341
     139 -> 148         0.25478
     141 -> 143        -0.17575
     141 -> 145        -0.10333
     141 -> 146         0.12319

T7  Excited State   7:      Triplet-A      4.1025 eV  302.22 nm  f=0.0000  <S**2>=2.000
     137 -> 147        -0.10985
     137 -> 148         0.21039
     138 -> 150         0.10621
     138 -> 151         0.29897
     139 -> 143        -0.11412
     139 -> 155        -0.11916
     139 -> 156         0.11886
     140 -> 144         0.16409
     140 -> 160        -0.16604
     142 -> 151         0.12839

T8  Excited State   8:      Triplet-A      4.1060 eV  301.96 nm  f=0.0000  <S**2>=2.000
     137 -> 147        -0.16416
     137 -> 148         0.28740
     138 -> 151        -0.20639
     139 -> 143        -0.16369
     139 -> 155        -0.16054
     139 -> 156         0.15422
     140 -> 144        -0.11948
     140 -> 160         0.11703
     141 -> 148        -0.11349
```

```
T9 Excited State   9:      Triplet-A      4.3791 eV  283.13 nm  f=0.0000  <S**2>=2.000
     131 -> 143       -0.17071
     133 -> 143        0.23139
     133 -> 145        0.10379
     133 -> 146       -0.12124
     134 -> 143       -0.11515
     137 -> 143       -0.13171
     137 -> 146        0.11995
     141 -> 145       -0.23901
     141 -> 146        0.30258
     141 -> 151        0.12717
     141 -> 155        0.13540

T10 Excited State  10:      Triplet-A      4.3968 eV  281.98 nm  f=0.0000  <S**2>=2.000
     132 -> 144        0.12860
     135 -> 144        0.27877
     135 -> 150        0.19620
     138 -> 144       -0.14612
     138 -> 150       -0.16762
     142 -> 149        0.10997
     142 -> 150        0.35975
     142 -> 160        0.13827

T11 Excited State  11:      Triplet-A      4.4811 eV  276.68 nm  f=0.0000  <S**2>=2.000
     136 -> 144        0.48821
     136 -> 149        0.12654
     136 -> 150        0.37040

T12 Excited State  12:      Triplet-A      4.5428 eV  272.92 nm  f=0.0000  <S**2>=2.000
     133 -> 143        0.18232
     133 -> 146       -0.11299
     134 -> 143        0.44999
     134 -> 144        0.10493
     134 -> 145        0.21316
     134 -> 146       -0.25561
     136 -> 143        0.12022

S1  Excited State  13:      Singlet-A      4.7592 eV  260.52 nm  f=0.1637  <S**2>=0.000
     137 -> 143        0.12785
     141 -> 143        0.60195
     142 -> 143        0.11101
     142 -> 144       -0.18530

T13 Excited State  14:      Triplet-A      4.8552 eV  255.36 nm  f=0.0000  <S**2>=2.000
     131 -> 143        0.24394
     131 -> 145        0.19983
     131 -> 146       -0.24437
     133 -> 143        0.33616
     141 -> 145        0.13484
     141 -> 146       -0.15616
     141 -> 155        0.10040
     141 -> 156       -0.12427

T14 Excited State  15:      Triplet-A      4.8892 eV  253.59 nm  f=0.0000  <S**2>=2.000
     132 -> 144       -0.28011
     132 -> 149       -0.10660
     132 -> 150       -0.31942
     135 -> 144        0.27200
     138 -> 144       -0.10646
     142 -> 150       -0.15077
     142 -> 151        0.20677
     142 -> 160        0.13580

S2  Excited State  16:      Singlet-A      4.9095 eV  252.54 nm  f=0.5765  <S**2>=0.000
     138 -> 144       -0.11652
     141 -> 143        0.19201
     142 -> 144        0.59653

T15 Excited State  17:      Triplet-A      4.9789 eV  249.02 nm  f=0.0000  <S**2>=2.000
     135 -> 144       -0.16156
     135 -> 151       -0.11367
     135 -> 160       -0.11697
     138 -> 144        0.11048
     140 -> 160        0.12882
     142 -> 146       -0.12273
     142 -> 150        0.18544
     142 -> 151        0.36199
     142 -> 171       -0.10343

T16 Excited State  18:      Triplet-A      5.0008 eV  247.93 nm  f=0.0000  <S**2>=2.000
     133 -> 143       -0.15088
     137 -> 148        0.10931
     137 -> 168        0.10561
     139 -> 143        0.29206
     139 -> 155        0.15622
     139 -> 156       -0.14416
     141 -> 147        0.16146
     141 -> 148       -0.29719
```

```
T17 Excited State  19:      Triplet-A      5.0398 eV  246.01 nm  f=0.0000  <S**2>=2.000
     137 -> 143       -0.18609
     137 -> 148        0.13852
     139 -> 143        0.22378
     139 -> 167        0.11501
     139 -> 168       -0.11307
     141 -> 147       -0.11531
     141 -> 148        0.20375
     141 -> 155       -0.12957
     141 -> 156        0.15353

T18 Excited State  20:      Triplet-A      5.0583 eV  245.11 nm  f=0.0000  <S**2>=2.000
     135 -> 144        0.10778
     138 -> 144        0.16062
     138 -> 151       -0.12152
     140 -> 144        0.34680
     140 -> 150       -0.11359
     140 -> 160       -0.11633
     140 -> 167        0.10070
     140 -> 170       -0.11450
     140 -> 171       -0.17502
```

Table S8. First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ and $T_0 \rightarrow T_n$ transitions computed for **TT-PyH$^+$** in its absolute minimum.

```
T1   Excited State   1:      Triplet-A      2.6923 eV  460.52 nm  f=0.0000  <S**2>=2.000
      67 -> 72         0.16067
      69 -> 72         0.21961
      70 -> 72         0.43902
      70 -> 73        -0.16167
      71 -> 72        -0.38161
      71 -> 73         0.13184

T2   Excited State   2:      Triplet-A      3.6012 eV  344.28 nm  f=0.0000  <S**2>=2.000
      61 -> 73        -0.14203
      63 -> 72        -0.12145
      65 -> 72        -0.12278
      65 -> 73        -0.19104
      67 -> 72         0.12457
      67 -> 73         0.29927
      69 -> 72         0.11823
      69 -> 73         0.25824
      70 -> 72         0.11519
      70 -> 73         0.30801
      71 -> 72        -0.12249
      71 -> 73        -0.28988

T3   Excited State   3:      Triplet-A      3.7777 eV  328.20 nm  f=0.0000  <S**2>=2.000
      69 -> 75         0.14053
      70 -> 72         0.16095
      70 -> 74         0.18491
      70 -> 75         0.19853
      71 -> 72         0.19571
      71 -> 74         0.20842
      71 -> 75         0.43626
      71 -> 82        -0.11545

S1   Excited State   4:      Singlet-A      4.1136 eV  301.40 nm  f=0.5642  <S**2>=0.000
      67 -> 72        -0.11587
      69 -> 72        -0.25874
      70 -> 72        -0.39177
      71 -> 72         0.48337

T4   Excited State   5:      Triplet-A      4.1143 eV  301.35 nm  f=0.0000  <S**2>=2.000
      63 -> 72         0.11440
      69 -> 72         0.21407
      69 -> 73        -0.11205
      69 -> 74        -0.32887
      70 -> 72        -0.17377
      70 -> 73         0.11427
      70 -> 74         0.39366
      70 -> 75        -0.11277
      71 -> 72        -0.13294

T5   Excited State   6:      Triplet-A      4.4009 eV  281.73 nm  f=0.0000  <S**2>=2.000
      61 -> 72        -0.16047
      63 -> 72         0.23827
      65 -> 72        -0.11212
      65 -> 73         0.10740
      67 -> 72         0.21697
      69 -> 72         0.16258
      69 -> 74         0.25630
      70 -> 72        -0.10438
      70 -> 74        -0.11698
      70 -> 75        -0.23679
      70 -> 82        -0.15377
```

```
      71 -> 74        -0.11633
      71 -> 75         0.17675

T6   Excited State   7:      Triplet-A      4.6674 eV  265.64 nm  f=0.0000  <S**2>=2.000
      62 -> 72        -0.18994
      63 -> 72        -0.18037
      63 -> 73        -0.13786
      67 -> 72        -0.10773
      69 -> 72         0.19323
      69 -> 74         0.11486
      69 -> 75         0.17760
      69 -> 82         0.14984
      70 -> 72        -0.24489
      71 -> 72        -0.18711
      71 -> 73         0.16406
      71 -> 74         0.29294

T7   Excited State   8:      Triplet-A      4.8172 eV  257.38 nm  f=0.0000  <S**2>=2.000
      62 -> 72         0.11331
      62 -> 73         0.11636
      63 -> 72         0.39379
      63 -> 73         0.23579
      65 -> 72         0.23336
      67 -> 72        -0.12571
      67 -> 73         0.10626
      69 -> 75         0.10412
      70 -> 73         0.13275
      70 -> 75         0.10501
      71 -> 72        -0.11258
      71 -> 74         0.24428
      71 -> 75        -0.11358

S2   Excited State   9:      Singlet-A      4.9470 eV  250.63 nm  f=0.0767  <S**2>=0.000
      69 -> 72        -0.22349
      70 -> 72         0.51517
      70 -> 73        -0.13774
      70 -> 75         0.17291
      71 -> 72         0.28598
      71 -> 74        -0.13444

S3   Excited State  10:      Singlet-A      5.0279 eV  246.59 nm  f=0.0294  <S**2>=0.000
      65 -> 72         0.11493
      67 -> 72        -0.12010
      67 -> 73        -0.15430
      69 -> 72        -0.16547
      69 -> 73        -0.18967
      70 -> 73        -0.39204
      71 -> 73         0.40927
      71 -> 75        -0.12749

T8   Excited State  11:      Triplet-A      5.0973 eV  243.24 nm  f=0.0000  <S**2>=2.000
      61 -> 72        -0.13938
      63 -> 72        -0.10177
      65 -> 74        -0.12147
      67 -> 72         0.14284
      69 -> 72        -0.26860
      69 -> 73         0.10857
      69 -> 74         0.21714
      69 -> 75        -0.18907
      70 -> 74         0.18253
      71 -> 72        -0.10034
      71 -> 74         0.27078
      71 -> 82         0.14190
      71 -> 91         0.13279

S4   Excited State  12:      Singlet-A      5.2901 eV  234.37 nm  f=0.0881  <S**2>=0.000
      69 -> 72         0.41729
      69 -> 73        -0.21077
      69 -> 75         0.11145
      70 -> 73        -0.16297
      70 -> 74         0.16645
      71 -> 72         0.27827
      71 -> 73         0.10943
      71 -> 75         0.28336

T9   Excited State  13:      Triplet-A      5.2939 eV  234.20 nm  f=0.0000  <S**2>=2.000
      61 -> 72        -0.13253
      65 -> 72        -0.14503
      67 -> 75        -0.21887
      69 -> 75         0.18178
      69 -> 87         0.11145
      70 -> 74         0.15195
      70 -> 75         0.26963
      70 -> 82        -0.16113
      70 -> 94        -0.11102
      71 -> 72         0.12889
      71 -> 74        -0.11172
      71 -> 75        -0.25826
      71 -> 82         0.13483
```

```
T10  Excited State  14:      Triplet-A      5.3507 eV  231.72 nm  f=0.0000  <S**2>=2.000
      69 -> 72         0.19382
      69 -> 74         0.13234
      69 -> 82        -0.21071
      69 -> 83         0.11256
      69 -> 87        -0.19037
      69 -> 91         0.10867
      70 -> 72        -0.21536
      70 -> 73        -0.10302
      70 -> 74        -0.17016
      70 -> 75         0.26340
      70 -> 82         0.11353
      70 -> 87         0.20141
      70 -> 91        -0.12273
T11  Excited State  15:      Triplet-A      5.5989 eV  221.44 nm  f=0.0000  <S**2>=2.000
      63 -> 73         0.14193
      65 -> 72        -0.11506
      69 -> 72         0.21739
      70 -> 74        -0.15418
      70 -> 82         0.14641
      71 -> 72         0.35075
      71 -> 74         0.20318
      71 -> 91         0.15607
      71 -> 94        -0.18983

T12  Excited State  16:      Triplet-A      5.7181 eV  216.83 nm  f=0.0000  <S**2>=2.000
      61 -> 72        -0.17023
      63 -> 73         0.14361
      65 -> 72        -0.11870
      65 -> 75         0.10236
      67 -> 72         0.27358
      69 -> 72        -0.17313
      69 -> 74        -0.17470
      71 -> 73         0.10537
      71 -> 74         0.17275
      71 -> 75        -0.15836
      71 -> 91        -0.12533
      71 -> 94         0.17863

S5   Excited State  17:      Singlet-A      5.7360 eV  216.15 nm  f=0.0993  <S**2>=0.000
      69 -> 72        -0.32497
      70 -> 72         0.14179
      70 -> 73         0.12400
      70 -> 74         0.33852
      71 -> 72        -0.10433
      71 -> 73         0.10795
      71 -> 74         0.36498
      71 -> 75         0.20153

T13  Excited State  18:      Triplet-A      5.9262 eV  209.21 nm  f=0.0000  <S**2>=2.000
      62 -> 73         0.16988
      62 -> 75         0.11109
      63 -> 72        -0.24569
      63 -> 73         0.45162
      63 -> 74        -0.10556
      65 -> 73         0.11666
      67 -> 74        -0.11711
      70 -> 74         0.10549
      71 -> 74        -0.13514

T14  Excited State  19:      Triplet-A      5.9794 eV  207.35 nm  f=0.0000  <S**2>=2.000
      66 -> 72         0.57668
      66 -> 73        -0.23427
      66 -> 74        -0.13329
      66 -> 75         0.12535
      68 -> 72         0.16700

S6   Excited State  20:      Singlet-A      6.0127 eV  206.20 nm  f=0.2447  <S**2>=0.000
      69 -> 73         0.15238
      69 -> 74         0.27891
      70 -> 74        -0.35314
      71 -> 74         0.44426
```

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