

Electronic Supplementary Information

**Heavy-element-free triplet accessibility in pyrene-core compounds at room temperature  
by microcrystal engineering**

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## 1. Materials

All materials were used without any prior purification. 1-Pyrenecarboxaldehyde (PyCHO) and phenylboronic acid and 9-H carbazole, Ru-Phos and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. Bromine, cesium carbonate and piperidine were purchased from Spectrochem, India. Tetrakis(triphenylphosphine)palladium(0) was purchased from TCI Chemicals. Palladium acetate was purchased from Alfa Aesar. Spectroscopic grade solvents from Merck were used for synthesis and other experiments.

## 2. Instrumental Methods

<sup>1</sup>H-NMR spectra were recorded using a 400 MHz JEOL and a 500 MHz Bruker Avance NMR spectrometer with CDCl<sub>3</sub> as solvent. Tetramethylsilane (TMS) was used as an internal standard.

The dynamic light scattering (DLS) data were obtained on a Malvern Zetasizer Nano, equipped with a 4.0 mW HeNe laser operating at  $\lambda = 633$  nm at a 173° scattering angle.

Transmission electron microscope (TEM) images and HAADF-STEM mapping were obtained with a DST-FIST facility, IISER Kolkata, JEOL, JEM-2100F. Field emission scanning electron microscope (FE-SEM) images were recorded using a Carl Zeiss SUPRA 55VP FESEM.

Powder XRD measurements were performed with a Rigaku X-ray diffractometer (Cu K $\alpha$  irradiation,  $\lambda = 1.541$  Å).

Single crystal X-ray diffraction (SCXRD): SCXRD data was collected at 279 K for the crystal of CzPyCHO and PhPyCHO on a Rigaku (dual, Cu/Mo at zero Eos) diffractometer using monochromatic Cu-K $\alpha$  radiation having a 100  $\mu$ m beam size. The structure was solved by Olex2 (1.2.9 version) with the SHELXT structure solution program via intrinsic phasing algorithm and the ShelXL refinement package using Least Squares minimization was utilized to refine the structure. 1-2 Displacement parameters of all non-hydrogen atoms were refined

anisotropically. Mercury (3.10.1 version) software was used to prepare all the crystal packing diagrams.

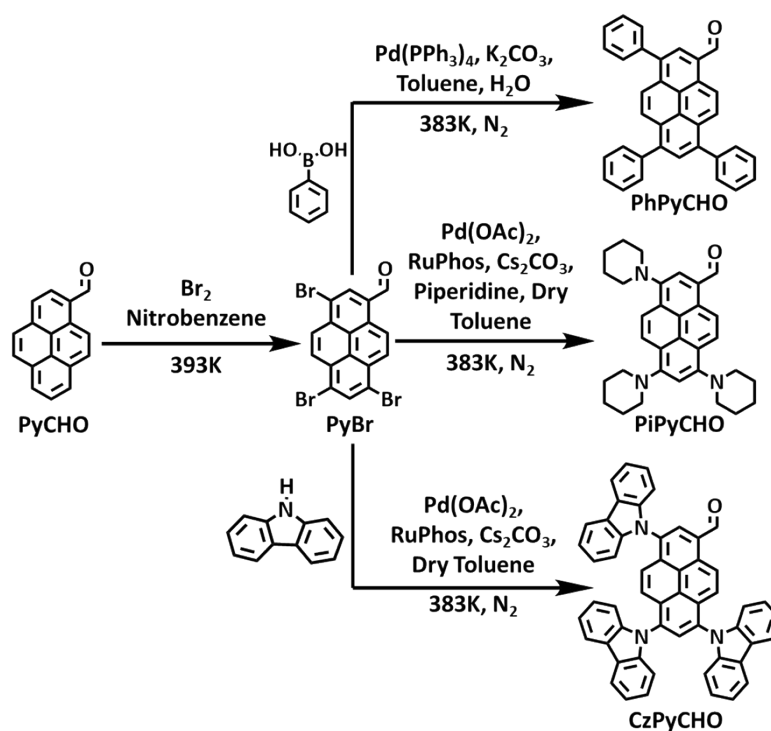
### **3. Optical Measurements**

UV-VIS spectroscopy was done in a U2900 spectrophotometer from HITACHI using a quartz cuvette (path length of 1 cm) for solutions and 1 cm × 1 cm quartz plate for film state. Steady-state and time resolved PL measurement were performed in a QuantaMaster 40 machine from PTI (Xe-lamp), time-correlated single-photon counting (TCSPC) methods with HORIBA JOBIN S3 YVON (single photon counting controller: Fluorohub, precision photo multiplayer power supply: Fluoro3PS), and FLS 1000 Photoluminescence Spectrometer (Xe-400 lamp,  $\mu$ F-400-microsecond flashlamp, PMT-900 detector) from Edinburgh Instruments. PL spectra of solid-state (film/crystal) were recorded in a front-face geometry. Temperature-dependent PL experiment in solid-state is performed in FLS1000 with the cryostat (Oxford Instruments Optistat DN model) setup using liquid nitrogen as a cryogen. Absolute quantum yields were measured using an integrating sphere (using Xe-400 lamp and PMT-900 + Integrating sphere detector)

### **4. Computational Methodologies**

The ground state and time-dependent density functional theory (DFT) was used to optimize the structures. The calculations were performed using B3LYP/6-31G(d,p)<sup>1</sup> as basis sets using Gaussian 16 program for geometry optimization. The spin orbit coupling (SOC) constants were calculated with TD-DFT using B3LYP/TZVP basis set in a PySOC package.

## 5. Synthetic Procedures



**Scheme 1** Synthetic Route of the Molecules

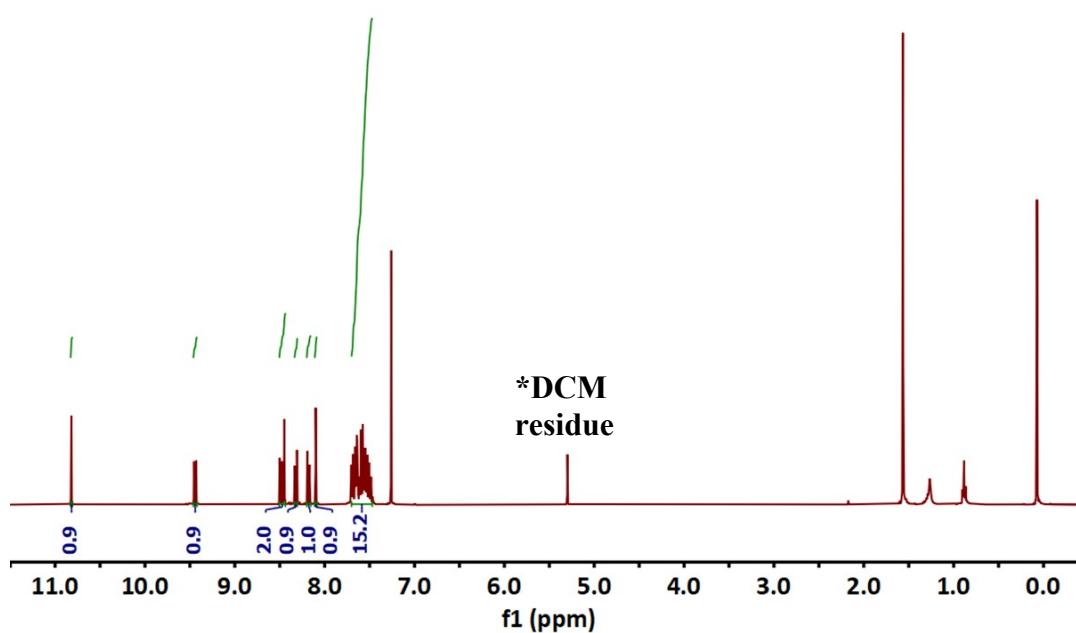
### Synthesis of PyBr

Briefly, 2.4 g (10.2 mmol) of 1-pyrenecarboxaldehyde was dissolved in 30 mL of nitrobenzene followed by 2.1 mL (40 mmol) of bromine to the solution, and the mixture was heated at 120 °C for 5 h. The reaction was accompanied by precipitation of PyBr. After the reaction mixture was cooled down to room temperature, the crude product was filtered out and washed with different organic solvents, such as, dichloromethane, chloroform, ethyl acetate, and acetone to remove bromine and any unreacted 1-pyrenecarboxaldehyde. The precipitate was dried, weighed (4.5 g), and stored for further reactions. Due to its extremely poor solubility, it was used for further reactions without any purification.

### Synthesis of PhPyCHO

1 g (2.14 mmol) of PyBr, 0.85 g (7 mmol) of phenylboronic acid and 2.7 g (8.3 mmol) cesium carbonate were added to a mixture of 20 mL toluene, 5 mL water and 5 mL ethanol in a pressure tube. The mixture was vigorously purged with nitrogen and stirred at room temperature.

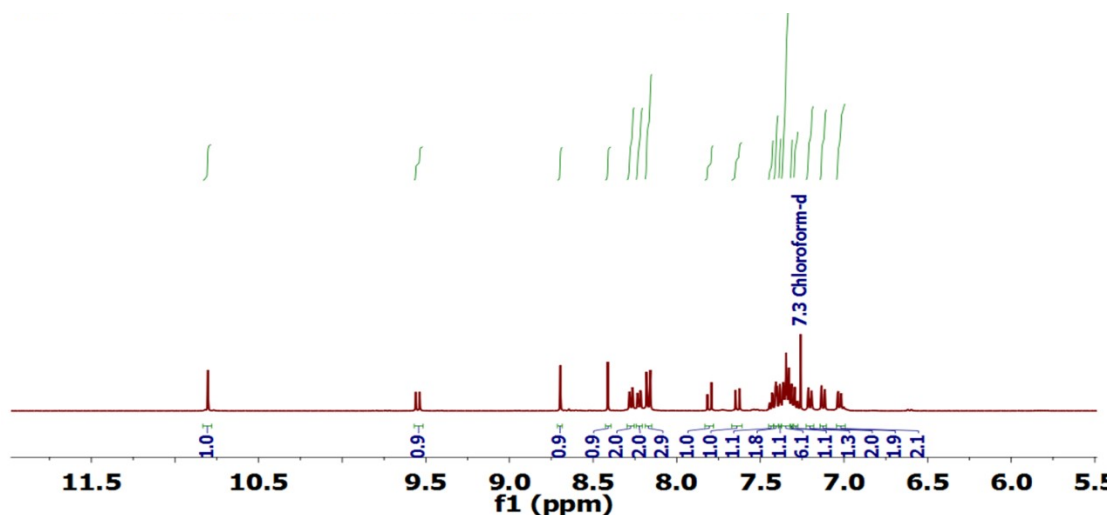
Finally, 180 mg (0.16 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> were added, and the pressure tube was sealed and heated overnight at 80 °C. After completion of the reaction, the solvents are first evaporated, and the mixture was worked up with ethyl acetate and water to get rid of cesium carbonate and Pd-catalyst. Column chromatography in silica using hexane and ethyl acetate yields 450 mg (45% yield) PhPyCHO as a yellow solid.  $\delta$  (<sup>1</sup>H NMR CDCl<sub>3</sub>): 10.82 (s, 1H), 9.44 (d, 9.6 Hz, 1H), 8.51 – 8.44 (m, 2H), 8.32 (d, J = 9.5 Hz, 1H), 8.20 – 8.16 (m, 1H), 8.10 (s, 1H), 7.71 – 7.46 (m, 15H)



**Fig. S1.** <sup>1</sup>H NMR spectrum of PhPyCHO in CDCl<sub>3</sub>.

### Synthesis of CzPyCHO

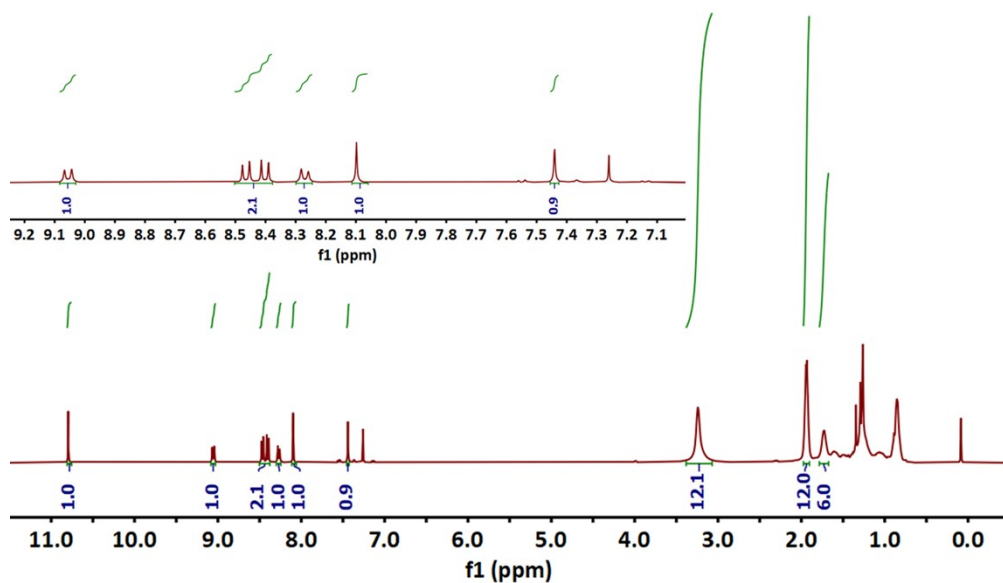
Similar procedure was followed with 0.92 g (5.5 mmol) of carbazole. The obtained solid was yellowish orange (250 mg, 23% yield).  $\delta$  (<sup>1</sup>H NMR CDCl<sub>3</sub>): 10.8 (s, 1H), 9.55 (d, J = 9.5 Hz, 1H), 8.7 (s, 1H), 8.41 (s, 1H), 8.27 (dd, J = 7.1, 1.3 Hz, 2H), 8.22 (dd, J = 6.4, 2.3 Hz, 2H), 8.17 (d, J = 9.5 Hz, 3H), 7.8 (d, J = 9.6 Hz, 1H), 7.64 (d, J = 9.5 Hz, 1H), 7.45 – 7.27 (m, 12H), 7.2 (d, J = 7.6 Hz, 2H), 7.12 (d, 8.0 Hz, 2H), 7.04 – 7.00 (m, 2H)



**Fig. S2.**  $^1\text{H}$  NMR spectrum of CzPyCHO in  $\text{CDCl}_3$ .

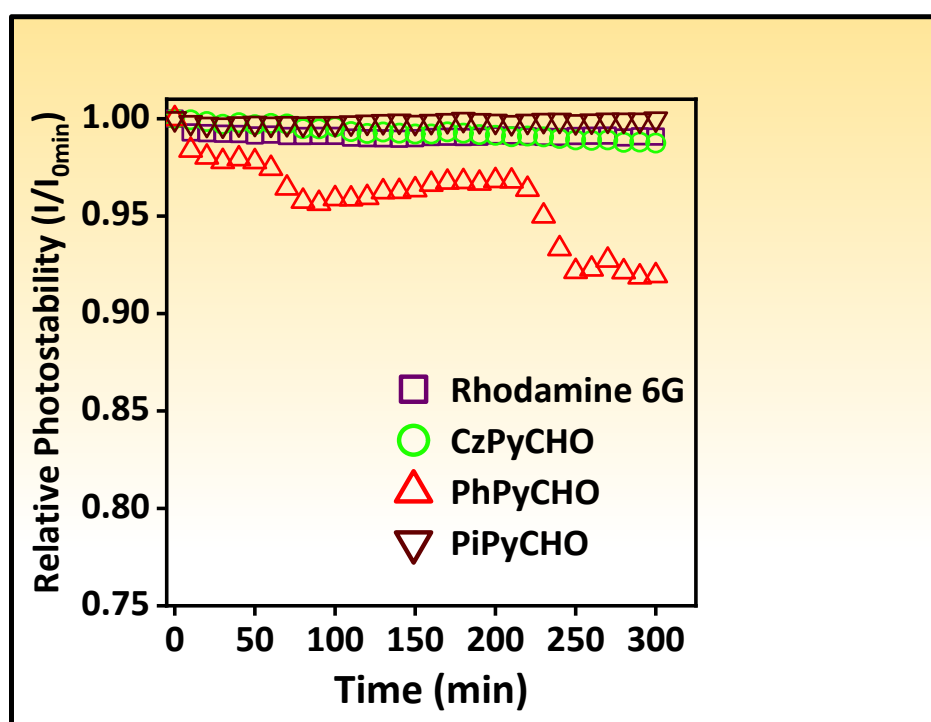
### Synthesis of PyPiCHO

This compound was synthesized by following a reported protocol.<sup>2</sup> 0.7 g (1.5 mmol) PyBr, 2.1 g cesium carbonate (6.3 mmol), 0.21 g (0.45 mmol) RuPhos mixed with 25 mL anhydrous toluene and 5 mL anhydrous ethanol and the mixture was stirred in a pressure tube at room temperature for 10 min under continuous nitrogen purging. Lastly, 50 mg (0.23 mmol)  $\text{Pd}(\text{OAc})_2$  and 0.53 mL (5.4 mmol) piperidine was added, and the pressure tube was sealed. The reaction was maintained at 80 °C overnight. After cooling the reaction mixture, the insoluble PyBr is filtered out and the resulting solution was dried over  $\text{MgSO}_4$ . Column chromatography in silica using hexane and dichloromethane was carried out to purify and obtain the desired product as a red solid (175 mg, 25% yield).  $\delta$  ( $^1\text{H}$  NMR  $\text{CDCl}_3$ ): 10.8 (s, 1H); 9.06 (d,  $J = 9.5\text{Hz}$ , 1H); 8.43 (dd,  $J = 25.2, 9.4\text{Hz}$ , 2H); 8.27 (d,  $J = 9.3\text{Hz}$ , 1H); 8.10 (s, 1H); 7.43 (s, 1H); 3.24 (m, 12H); 1.94 (d,  $J = 4.7\text{ Hz}$ , 12H); 1.73 (s, 6H)



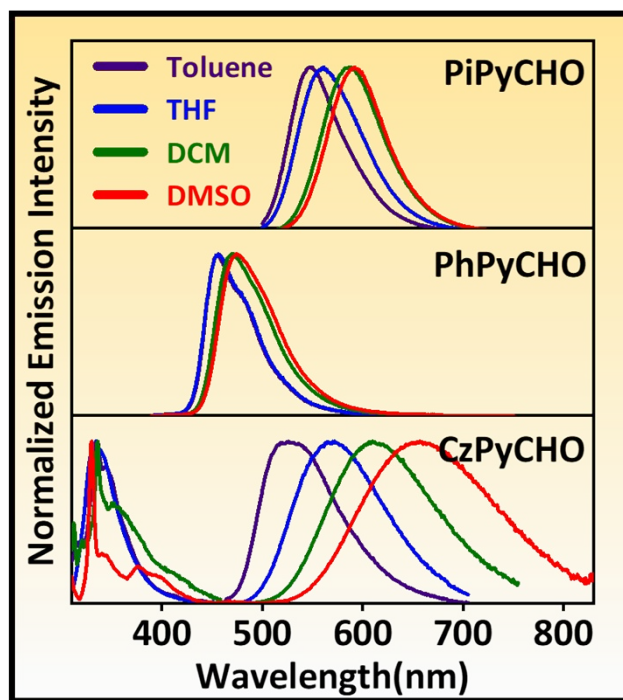
**Fig. S3.**  $^1\text{H}$  NMR spectrum of PiPyCHO in  $\text{CDCl}_3$ .

## 6. Additional Information in Solution Phase

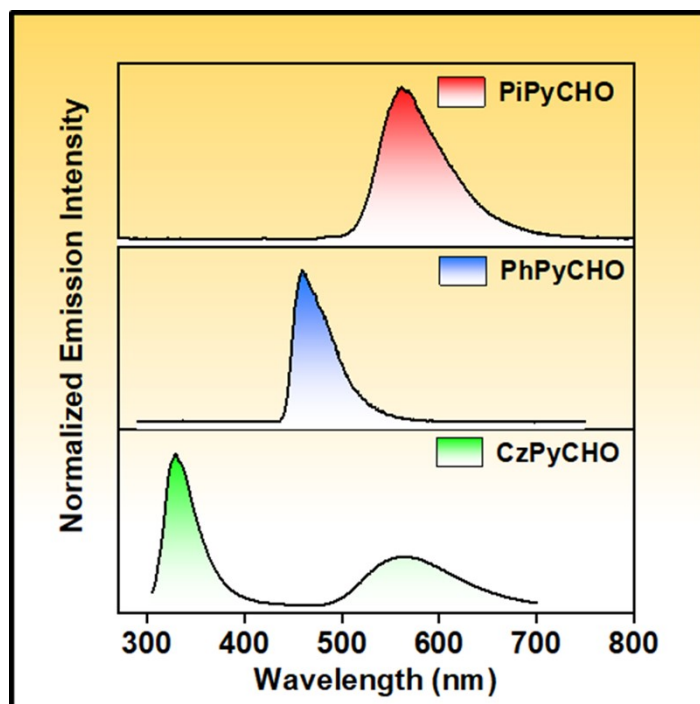


**Fig. S4.** Photostability of Rhodamine 6G, PiPyCHO, PhPyCHO and CzPyCHO dissolved in THF ( $10^{-5}$  M) for over 300 minutes.

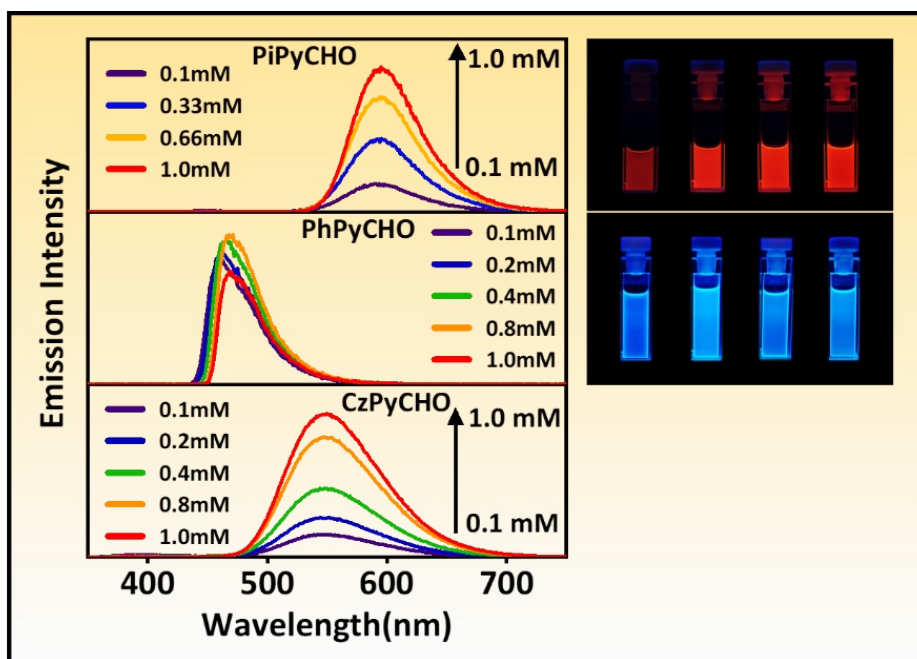




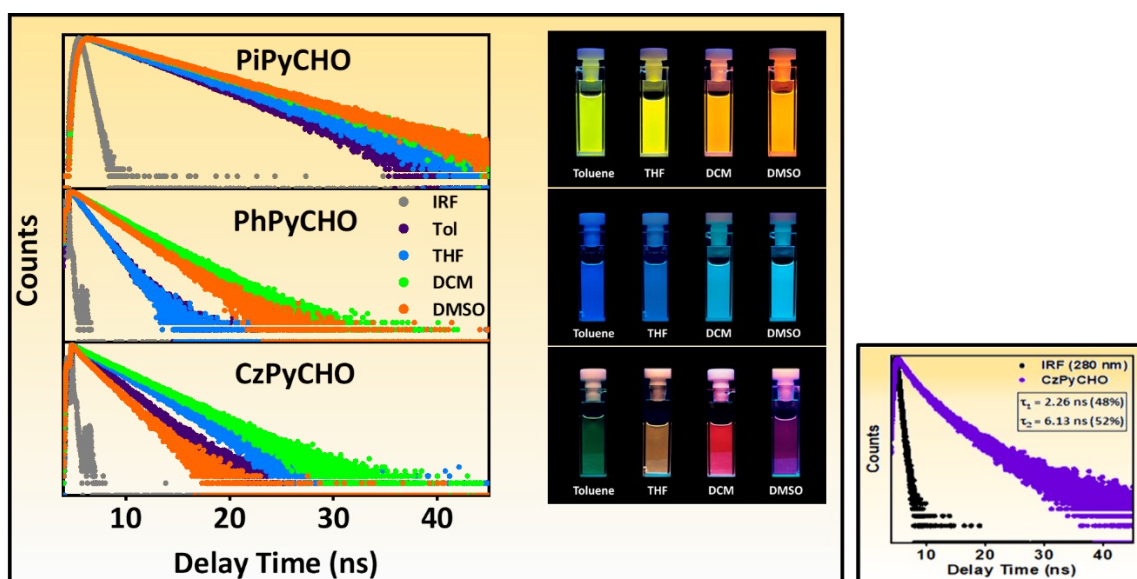
**Fig. S5.** Steady state PL spectra of PiPyCHO, PhPyCHO and CzPyCHO in various solvents ( $10^{-5}$  M) in ambient condition.



**Fig. S6.** Normalized steady state PL spectra of PiPyCHO, PhPyCHO and CzPyCHO in THF ( $10^{-5}$  M) in ambient condition exciting at 280 nm.



**Fig. S7.** Concentration dependent steady state PL spectra of PiPyCHO, PhPyCHO and CzPyCHO in THF in ambient condition.



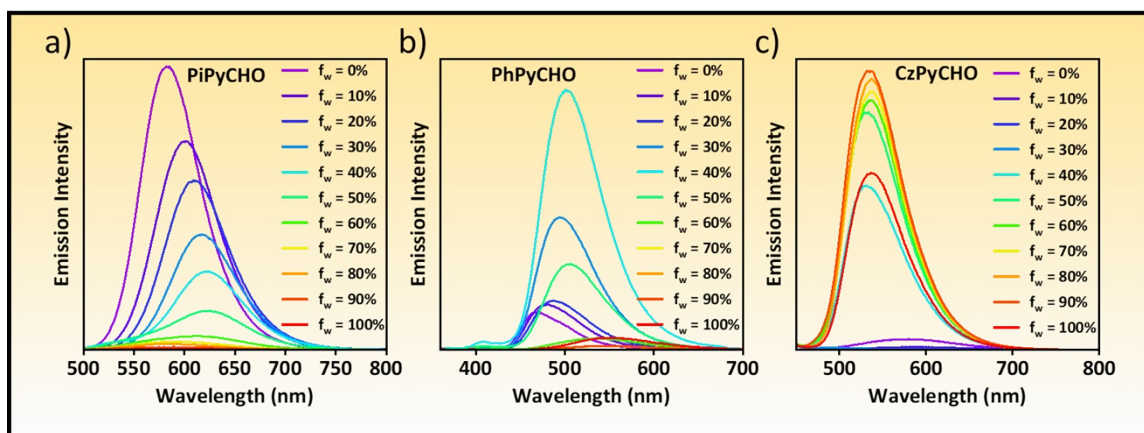
**Fig. S8.** Time-resolved PL decay profile of PiPyCHO, PhPyCHO and CzPyCHO in various solvents ( $10^{-5}$  M) in ambient condition. The samples were excited at 405 nm and the emissions were monitored at the respective maxima (see Table S1). The inset shows a double-exponential fit to the decay data obtained for CzPyCHO in THF on excitation at 280 nm monitoring the 330 nm emission.

**Table S1.** The photophysical parameters for the three compounds in various solvents and obtained by exciting the samples at 405 nm and monitoring the respective long-wavelength emission maxima at 25°C. The phosphorescence measurements were done at 78K obtained by using liquid nitrogen.

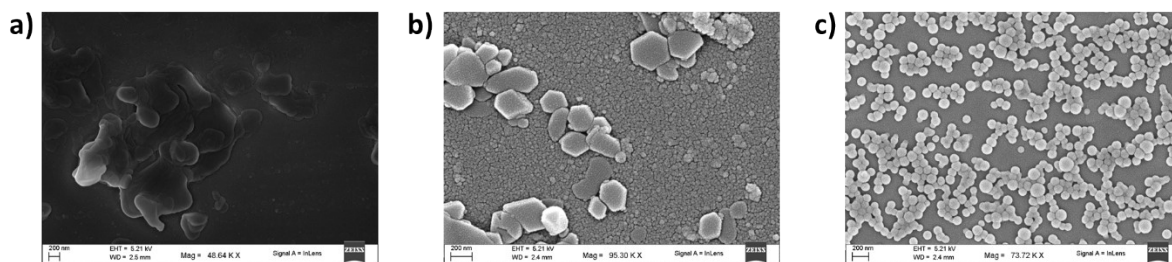
<b>Compound</b>	<b>Solvent</b>	$\lambda_{\text{abs}}^{\text{a}}$ (nm)	$\lambda_{\text{fl}}^{\text{a}}$ (nm)	$\tau_{\text{fl}}^{\text{a}}$ (ns)	$\lambda_{\text{phos}}^{\text{b}}$ (nm)	$\tau_{\text{phos}}^{\text{b}}$ ( $\mu\text{s}$ )	$\phi^{\text{a}}$ (%)
PiPyCHO	Toluene	308, 480	548	4.44			
	THF	307, 477	561	5.06	604	155.5	98 <sup>2</sup>
	DCM	305, 480	587	5.78			
	DMSO	307, 490	592	5.9			
PhPyCHO	Toluene	302, 425	450	1.31			
	THF	306, 428	452	1.31	545	111.2	35
	DCM	300, 426	470	3.04			
	DMSO	305, 423	471	2.54			
CzPyCHO	Toluene	300, 416	336, 526	2.13			
	THF	303, 421	334, 570	2.91	547	138.7	31
	DCM	301, 418	336, 610	3.5			
	DMSO	309, 416	330, 657	1.82			

**a:** measurement under ambient conditions

**b:** measured at 78K

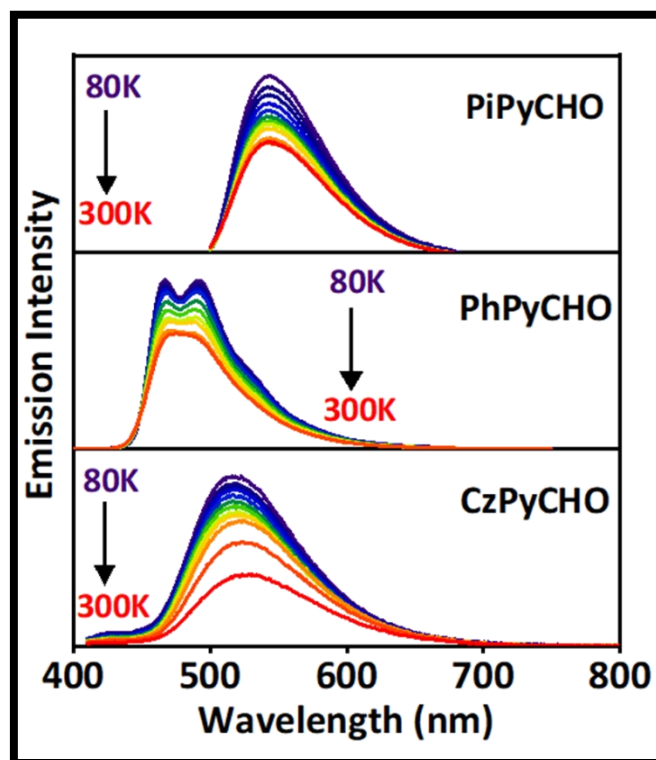


**Fig. S9.** Steady state PL spectra (excited at 390 nm) of (a) PiPyCHO, (b) PhPyCHO and (c) CzPyCHO in different DMF:water fractions in ambient condition.

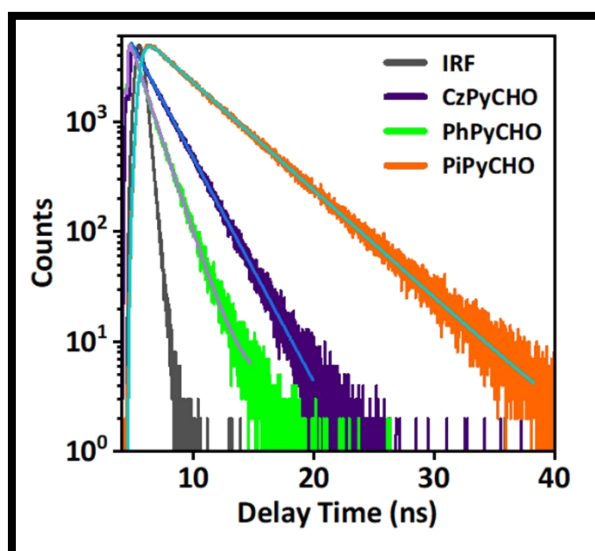


**Fig. S10.** Scanning electron microscopy (SEM) images of (a) PiPyCHO, (b) PhPyCHO, (c) CzPyCHO aggregates at water fraction ( $f_w$ ) = 80%, 40%, 90%, respectively in DMF at room temperature.

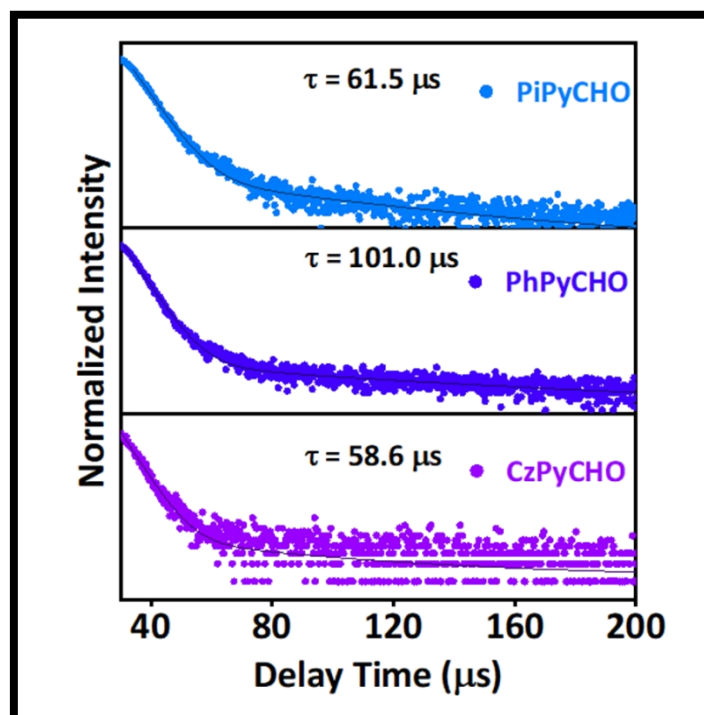
7. Additional Information in Solid State -



**Fig. S11.** Steady state PL spectra (excited at 390 nm) of PiPyCHO, PhPyCHO and CzPyCHO in PMMA matrix from room temperature to cryogenic conditions.



**Fig. S12.** Time-resolved fluorescence decay profiles of CzPyCHO, PhPyCHO and PiPyCHO in PMMA matrix at room temperature exciting the samples at 405 nm and monitoring at the respective emission maxima.



**Fig. S13.** Transient PL decay profile of PiPyCHO, PhPyCHO and CzPyCHO in PMMA matrix at 80K.

**Table S2.** The photophysical parameters for CzPyCHO, PhPyCHO and PiPyCHO in PMMA matrix and neat film obtained by exciting the samples at 405 nm and monitoring the respective long-wavelength emission maxima at 25°C. The phosphorescence measurements were done at 78K obtained by using liquid nitrogen.

<b>Compounds</b>	$\lambda_{\text{abs}}^{\text{a}}$ (nm)	$\lambda_{\text{em}}^{\text{a}}$ (nm)	$\tau_{\text{Fl}}^{\text{a}}$ (ns)	$\tau_{\text{Phos}}^{\text{c}}$ ( $\mu\text{s}$ )	$\phi_{\text{PMMA}}^{\text{a}}$ (%)	$\lambda_{\text{abs}}^{\text{b}}$ (nm)	$\lambda_{\text{em}}^{\text{b}}$ (nm)	$\tau_{\text{Fl}}^{\text{b}}$ (ns)	$\phi_{\text{Film}}^{\text{a}}$ (%)
CzPyCHO	417	530	2.23	58.6	54	431	600	2.41	3
PhPyCHO	424	479	1.31	101.0	75	451	516	3.64	27
PiPyCHO	474	545	4.56	61.5	66	480	614	2.78	1

a: measured for PMMA films under ambient conditions

b: measured in neat film under ambient conditions

c: measured for PMMA films at 78K

**Table S3.** The photophysical parameters for CzPyCHO and PhPyCHO in powdered sample and crystalline form obtained by exciting at 405 nm and monitoring the respective long-wavelength emission maxima at 25°C. The phosphorescence measurements were done at 78K obtained by using liquid nitrogen.

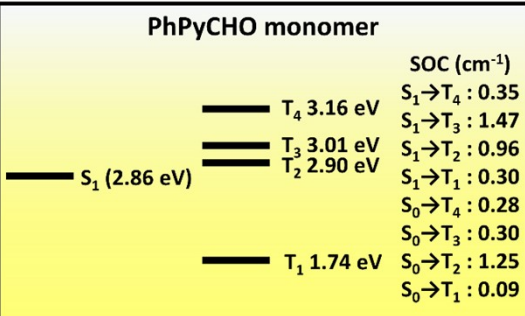
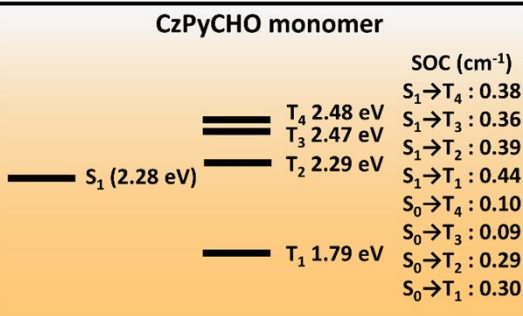
Compounds	$\lambda_{em}^a$ (nm)	$\tau_{Fl}^a$ (ns)	$\Phi_{Powder}^a$ (%)	$\lambda_{em}^b$ (nm)	$\tau_{Fl}^b$ (ns)	$\tau_{phos}^b$ ( $\mu$ s)	$\tau_{phos}^c$ (ms)	$\Phi_{Crystal}^a$ (%)
CzPyCHO	553	5.96	29	585	5.36	190	1.82	40
PhPyCHO	515	4.45	49	588	5.57	150	1.74	20

a: measured in powder under ambient conditions

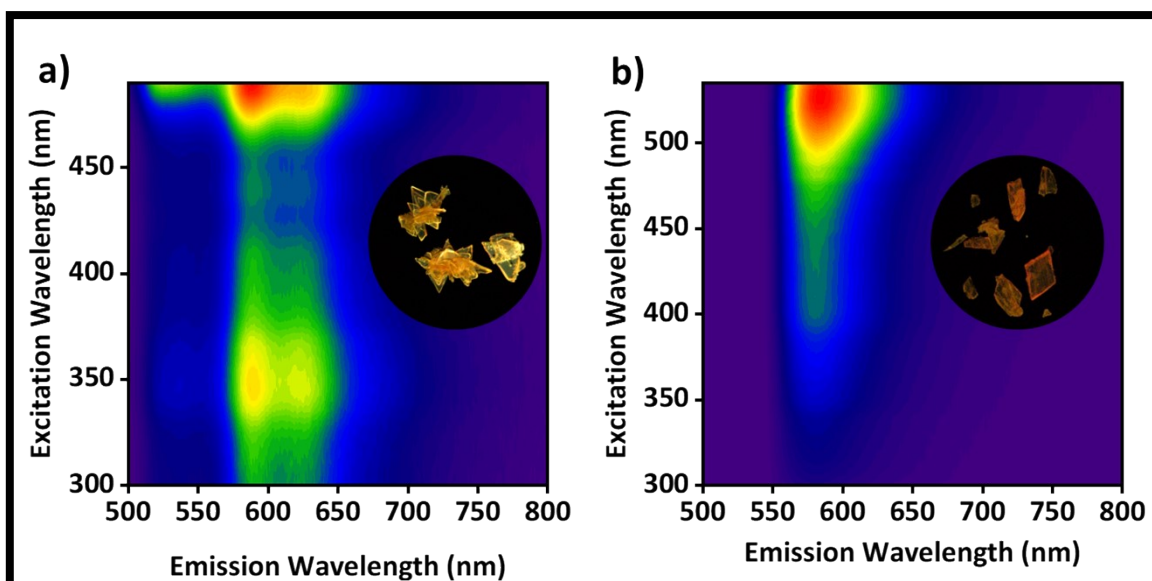
b: measured for crystals under ambient conditions

c: measured for crystals at 78K

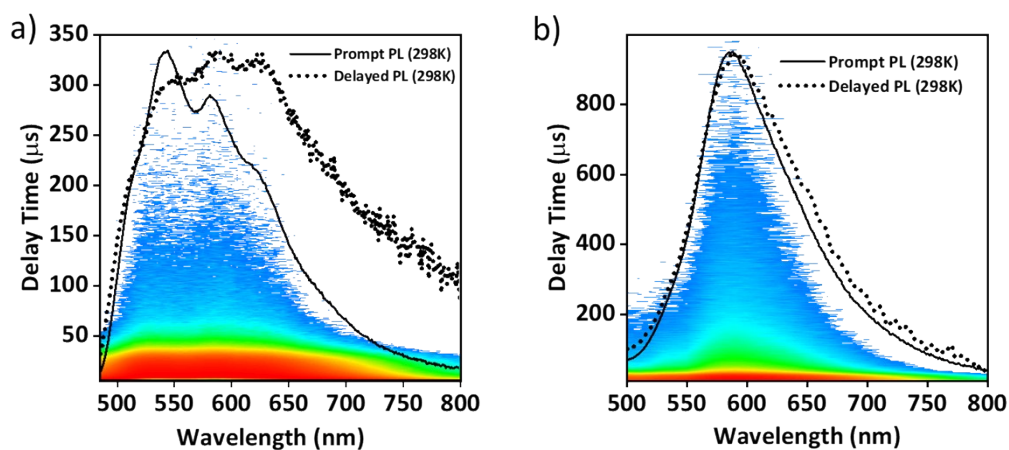
**Table S4.** Calculated energy levels and spin orbit coupling (SCO) constants for PhPyCHO and CzPyCHO using density functional theory (DFT).

PhPyCHO monomer		CzPyCHO monomer	
	SOC ( $cm^{-1}$ )		SOC ( $cm^{-1}$ )
	$S_1 \rightarrow T_4 : 0.35$		$S_1 \rightarrow T_4 : 0.38$
	$S_1 \rightarrow T_3 : 1.47$		$S_1 \rightarrow T_3 : 0.36$
	$S_1 \rightarrow T_2 : 0.96$		$S_1 \rightarrow T_2 : 0.39$
	$S_1 \rightarrow T_1 : 0.30$		$S_1 \rightarrow T_1 : 0.44$
	$S_0 \rightarrow T_4 : 0.28$		$S_0 \rightarrow T_4 : 0.10$
	$S_0 \rightarrow T_3 : 0.30$		$S_0 \rightarrow T_3 : 0.09$
	$S_0 \rightarrow T_2 : 1.25$		$S_0 \rightarrow T_2 : 0.29$
	$S_0 \rightarrow T_1 : 0.09$		$S_0 \rightarrow T_1 : 0.30$



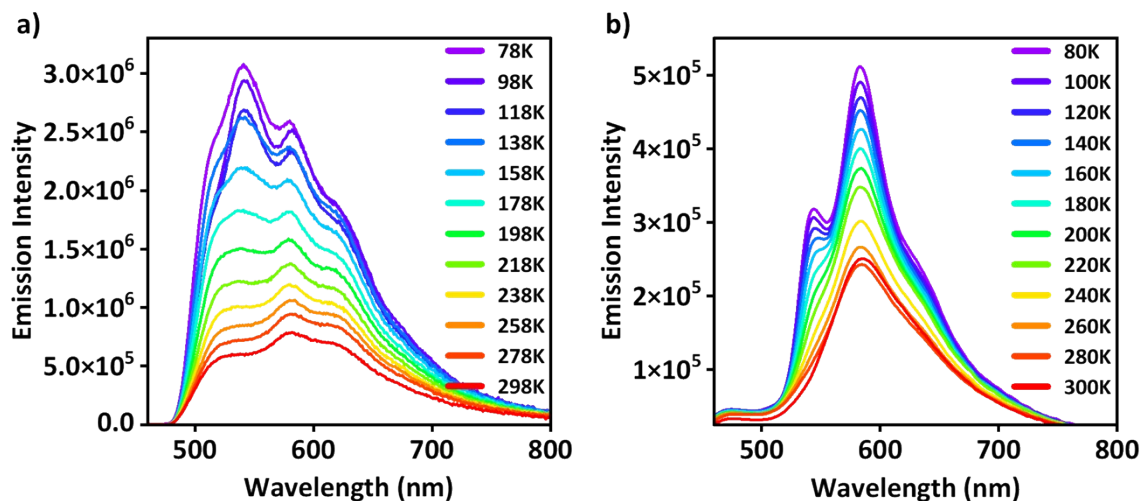


**Fig. S14.** Excitation dependence on the steady state emission of (a) PhPyCHO and (b) CzPyCHO crystals at 25°C.

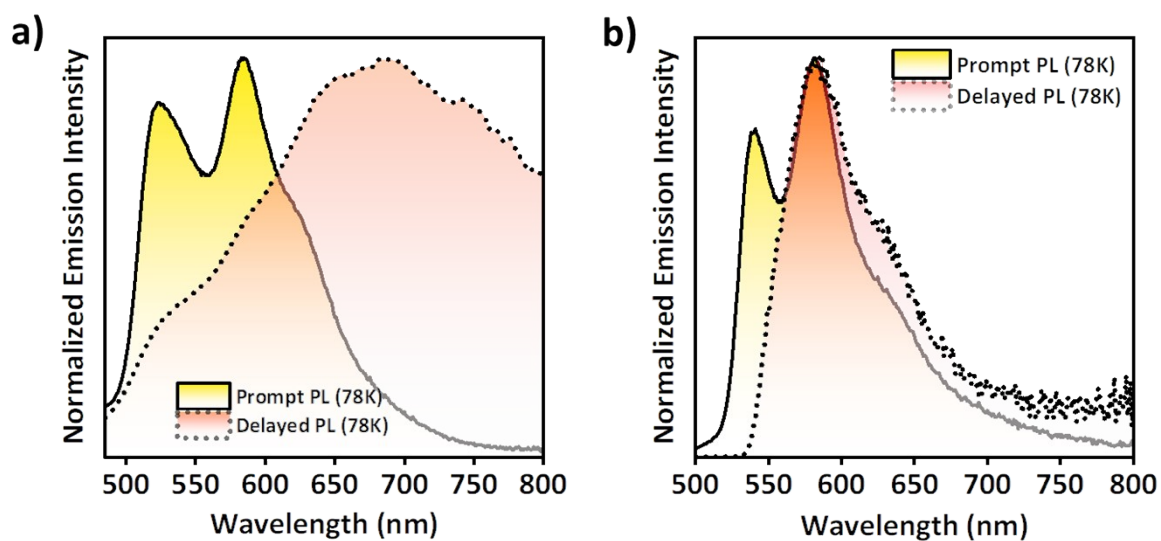


**Fig. S15.** Time resolved emission spectra (TRES) and normalized prompt and delayed spectra (100  $\mu$ s) of (a) PhPyCHO and (b) CzPyCHO crystals under ambient conditions. The prompt and delayed PL peaks overlap significantly at 298K, with some of them appearing more prominent on employing the time gate.

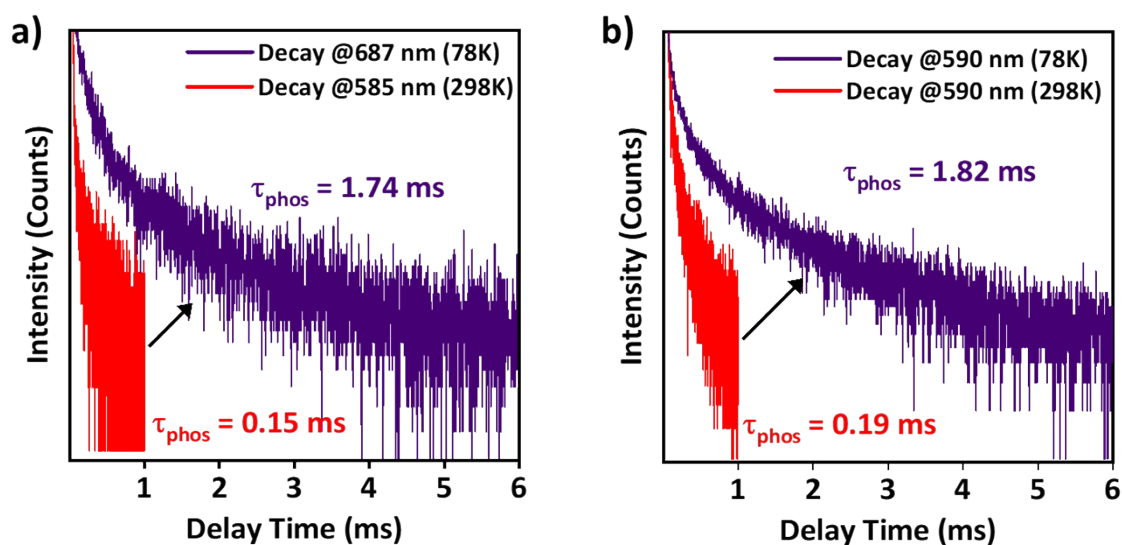




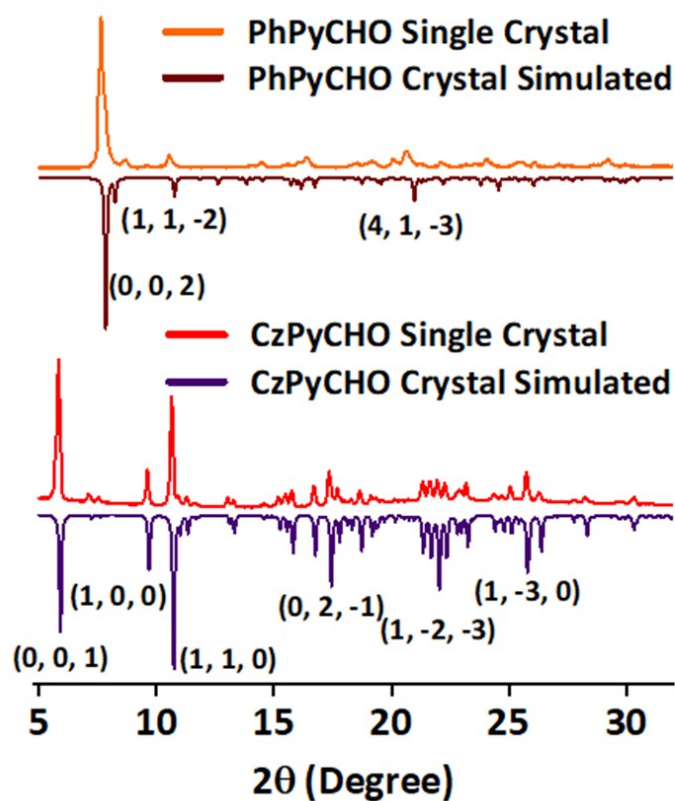
**Fig. S16.** Steady state PL spectra of (a) PhPyCHO and (b) CzPyCHO crystals at different temperatures.



**Fig. S17.** Normalized prompt and delayed spectra (100  $\mu$ s delay) of (a) PhPyCHO and (b) CzPyCHO crystals at 78K.



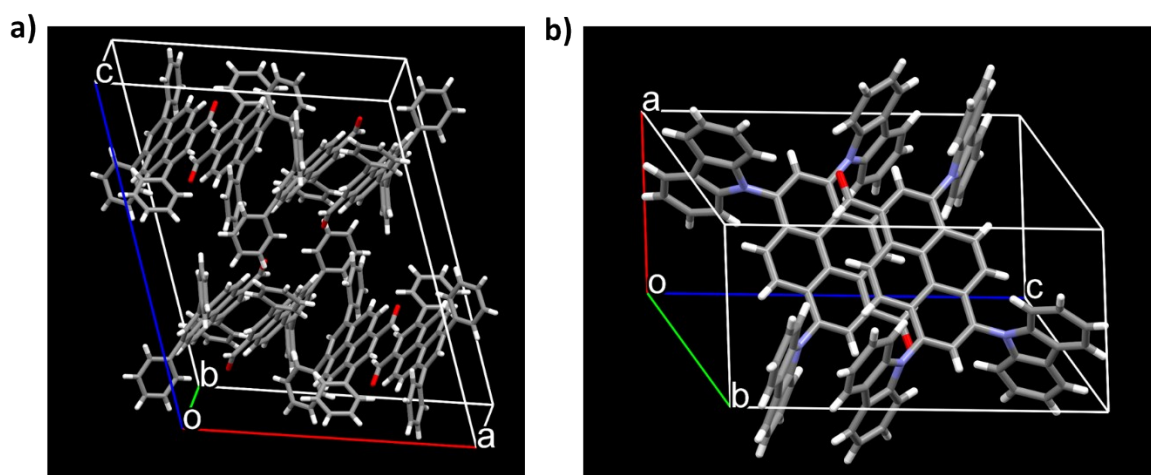
**Fig. S18.** PL decay profile at 78K and 298K of (a) PhPyCHO and (b) CzPyCHO crystals exciting the samples at 405 nm.



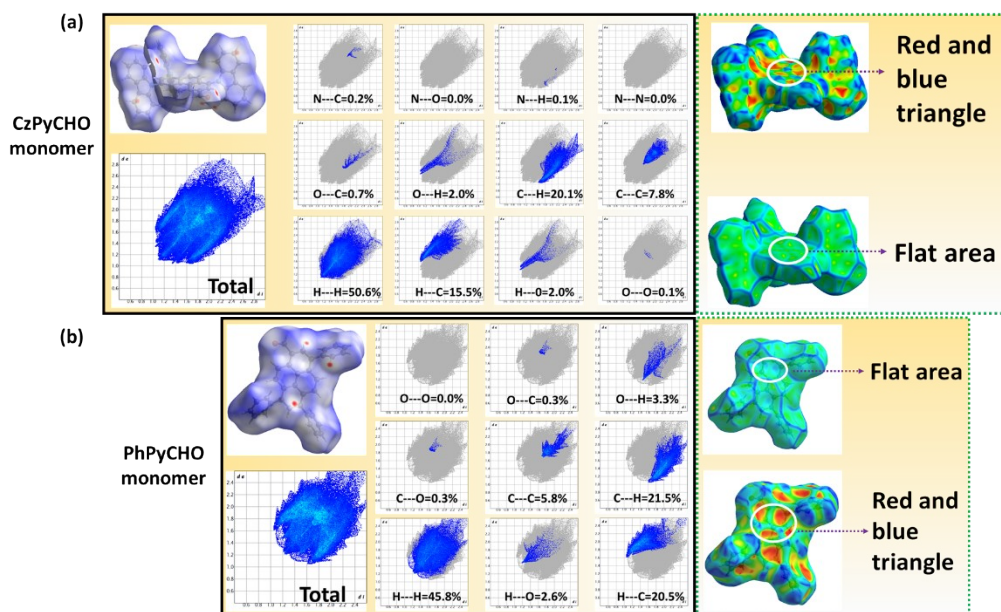
**Fig. S19.** Experimental and simulated PXRD pattern of PhPyCHO and CzPyCHO single crystals.

**Table S5.** SCXRD data of PhPyCHO and CzPyCHO at 279K.

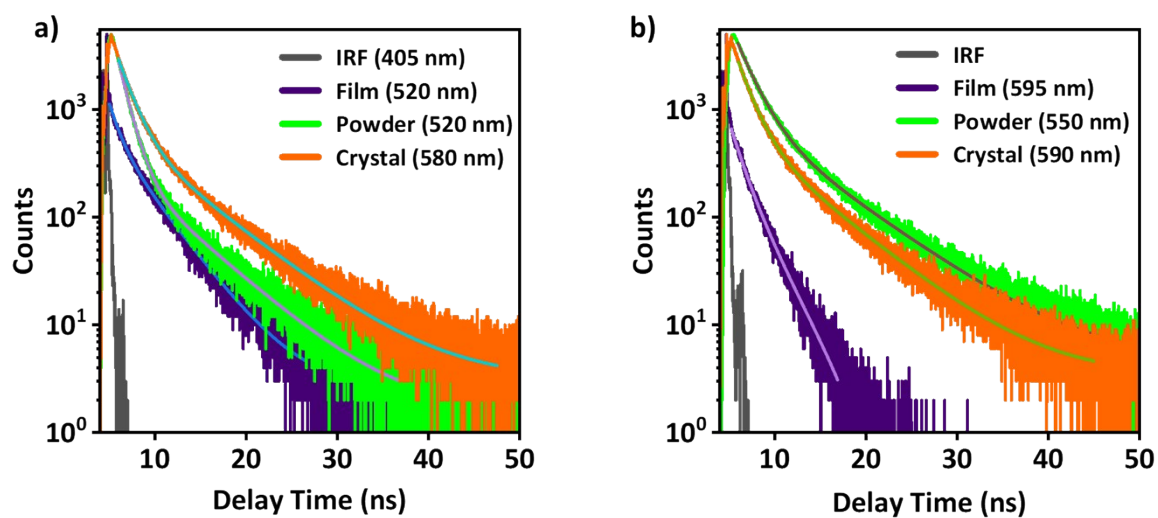
Name	PhPyCHO	CzPyCHO
Space group	I 2/a	P -1
Cell lengths	a=19.0544(5), b=12.1894(3), c=23.5040(6)	a=9.3559(2), b=13.3006(2), c=15.9009(2)
Cell angles	$\alpha=90$ , $\beta=106.505(3)$ , $\gamma=90$	$\alpha=70.3560(10)$ , $\beta=89.4980(10)$ , $\gamma=77.8020(10)$
Cell volume	5234.14	1817.29
Z,Z'	Z:8 Z':0	Z:2 Z':0
R-Factor	4.9	4.23



**Fig. S20.** Unit cells of (a) PhPyCHO and (b) CzPyCHO crystals.



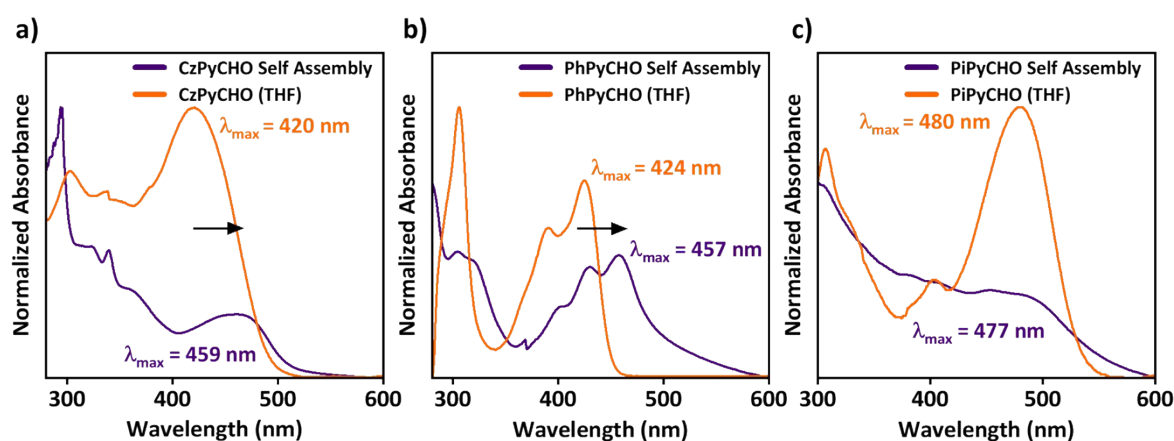
**Fig. S21.** 2D fingerprint plots of (a) CzPyCHO and (b) PhPyCHO monomers to obtain the quantitative non-covalent interactions outlined from Hirshfeld surface analysis along with the Hirshfeld surface mapped over shape index and curvedness for the two compounds.



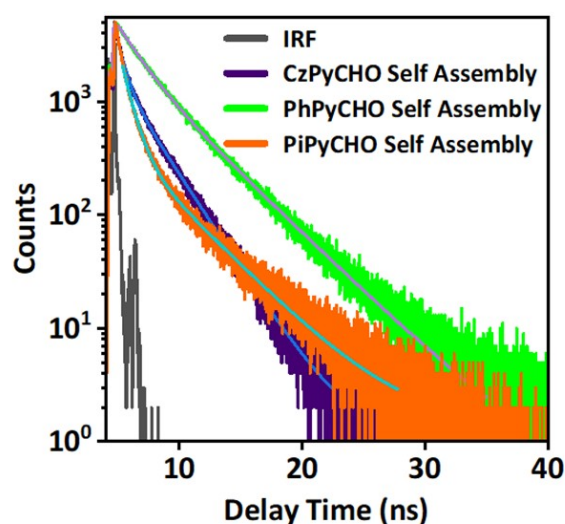
**Fig. S22.** Transient PL decay profiles in neat film, powder and crystals of (a) PhPyCHO and (b) CzPyCHO.

## 8. Additional Information in Self-assemblies

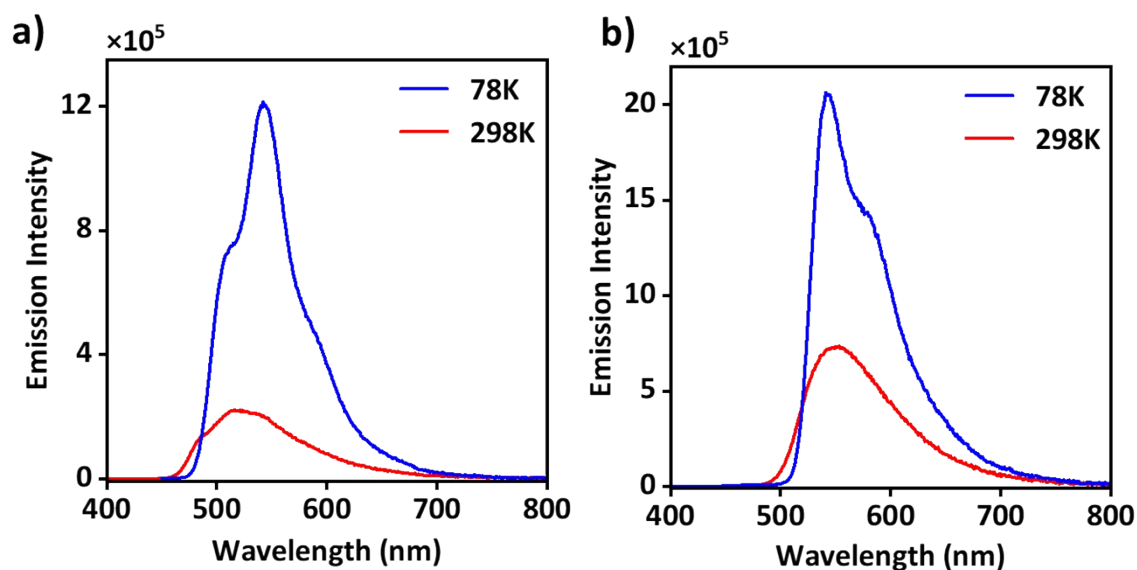
The stock solutions of CzPyCHO, PhPyCHO, and PiPyCHO in THF (1 mM each) were injected rapidly into a 5 mL aqueous solution of sodium dodecyl sulfate (SDS) (2 mg/mL) under vigorous agitation. After sonication for 5 min, the mixture was left undisturbed and sealed for 24 hours for micro crystallization.



**Fig. S23.** The absorption spectra of (a) CzPyCHO, (b) PhPyCHO and (c) PiPyCHO self-assemblies at 298 K.



**Fig. S24.** Fluorescence decay profile of PiPyCHO, PhPyCHO and CzPyCHO self-assemblies at 298 K in THF.



**Fig. S25.** Steady-state PL spectra of (a) PhPyCHO and (b) CzPyCHO self-assemblies at 78 K and 298 K. Consequent increase in the PL intensity with lowering of temperature rules out TADF behaviour from the luminogens of self assemblies of PhPyCHO and CzPyCHO.

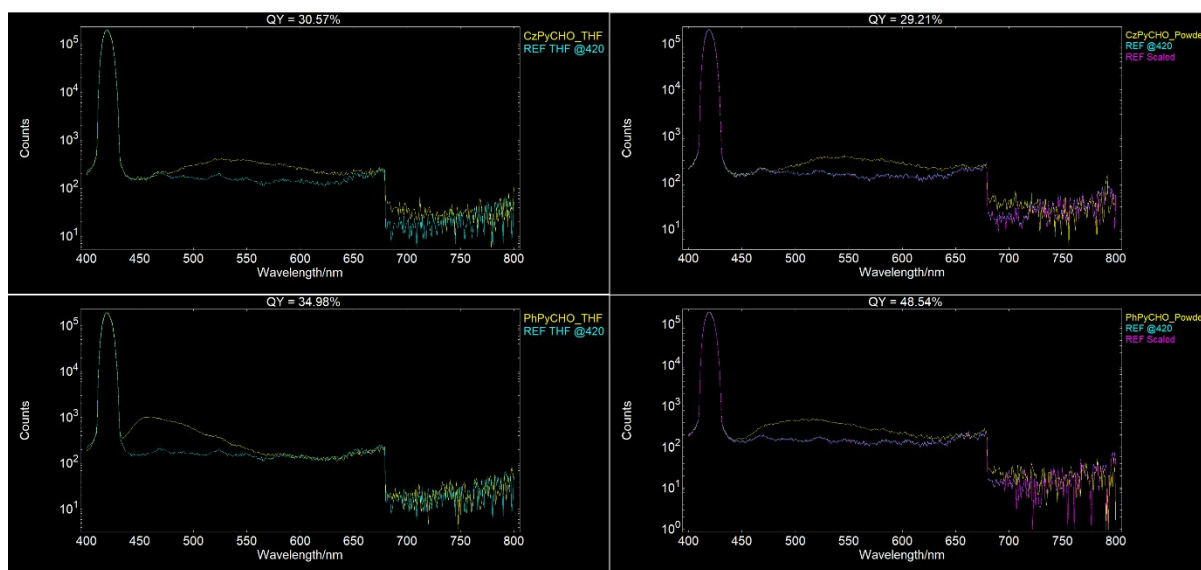
**Table S6.** The photophysical parameters for CzPyCHO, PhPyCHO and PiPyCHO self-assemblies obtained by exciting at 405 nm and monitoring the respective long-wavelength emission maxima at 25°C. The phosphorescence measurements were done at 78K obtained by using liquid nitrogen.

Self Assembly	$\lambda_{\text{abs}}^{\text{a}}$ (nm)	$\lambda_{\text{fl}}^{\text{a}}$ (nm)	$\tau_{\text{Fl}}^{\text{a}}$ (ns)	$\lambda_{\text{phos}}^{\text{a}}$ (nm)	$\tau_{\text{phos}}^{\text{a}}$ ( $\mu\text{s}$ )	$\lambda_{\text{phos}}^{\text{b}}$ (nm)	$\tau_{\text{phos}}^{\text{b}}$ (ms)	$\Phi_{\text{self}}^{\text{a}}$ (%)
CzPyCHO	460	545	2.48	591	173.4	582	1.36	61
PhPyCHO	459	513	3.80	539	161.2	545	1.76	83
PiPyCHO	478	604	4.00	----	----	----	----	2

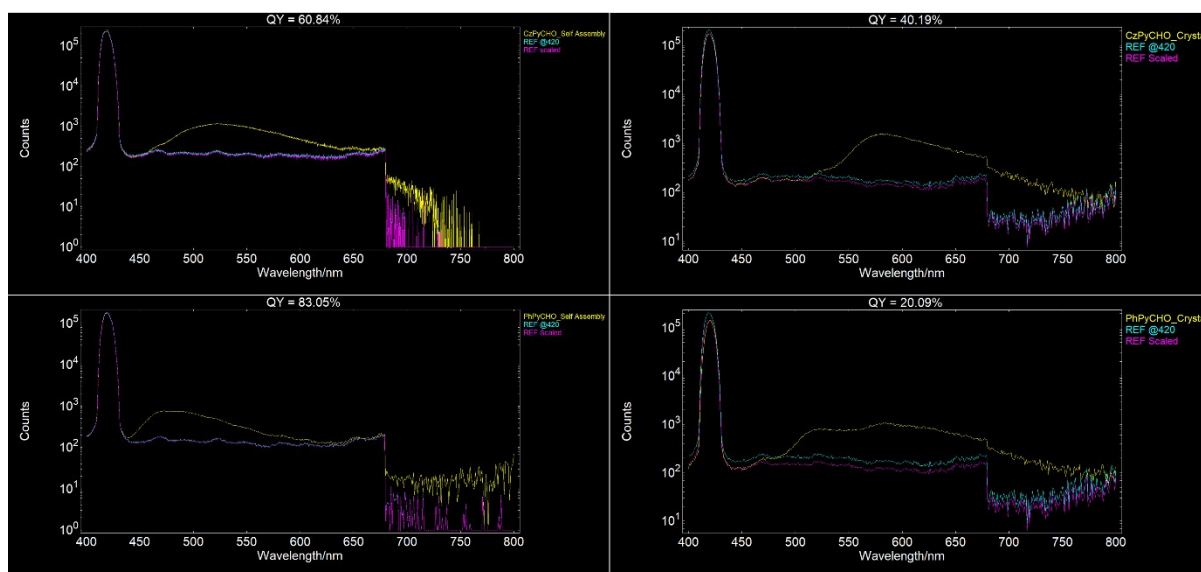
a: measured in ambient conditions

b: measured at 78K

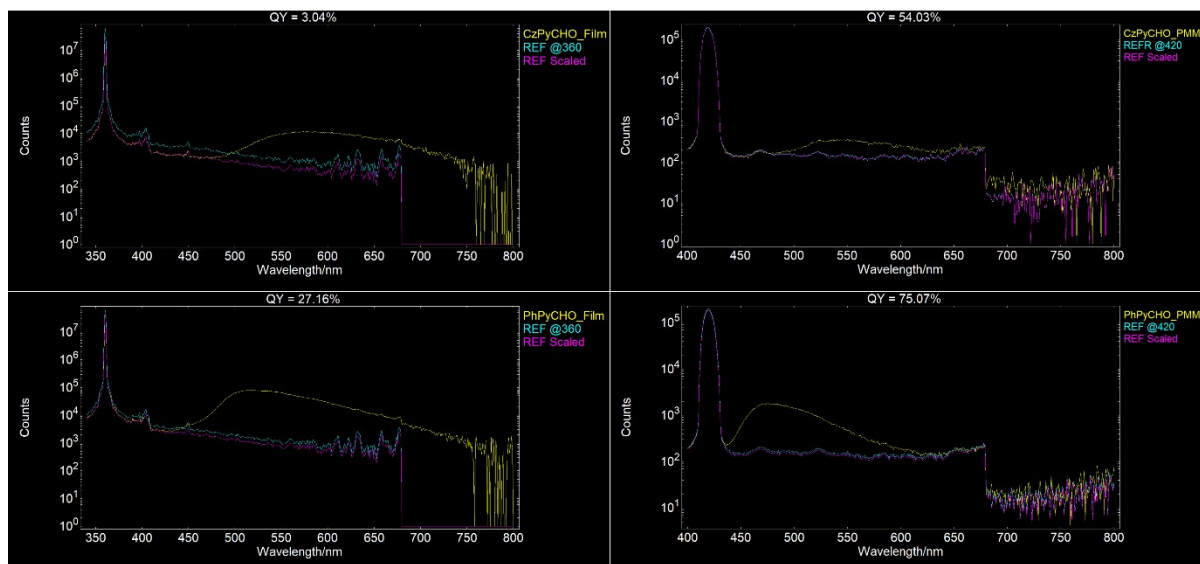




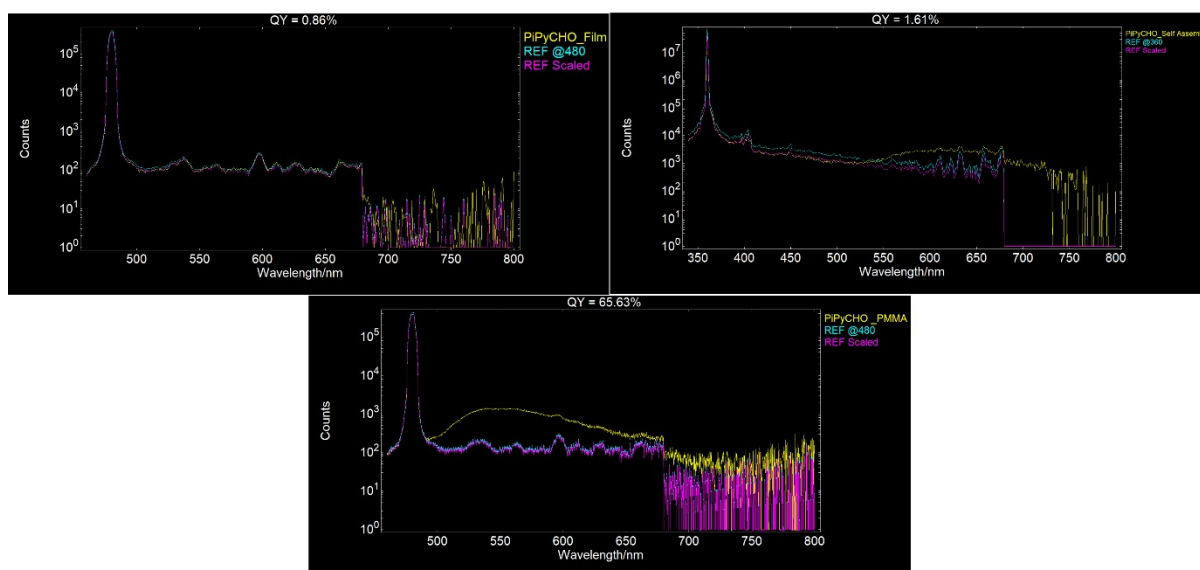
Absolute PLQY of CzPyCHO in THF and powder state (upper panel) and PhPyCHO in THF and powder state (lower panel).



Absolute PLQY of CzPyCHO self-assemblies and crystal (upper panel) and PhPyCHO in self-assemblies and crystal (lower panel).



Absolute PLQY of CzPyCHO in neat film and PMMA matrix (upper panel) and PhPyCHO in neat film and PMMA matrix (lower panel).



Absolute PLQY of PiPyCHO in neat film, self assemblies and PMMA matrix.



## References

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