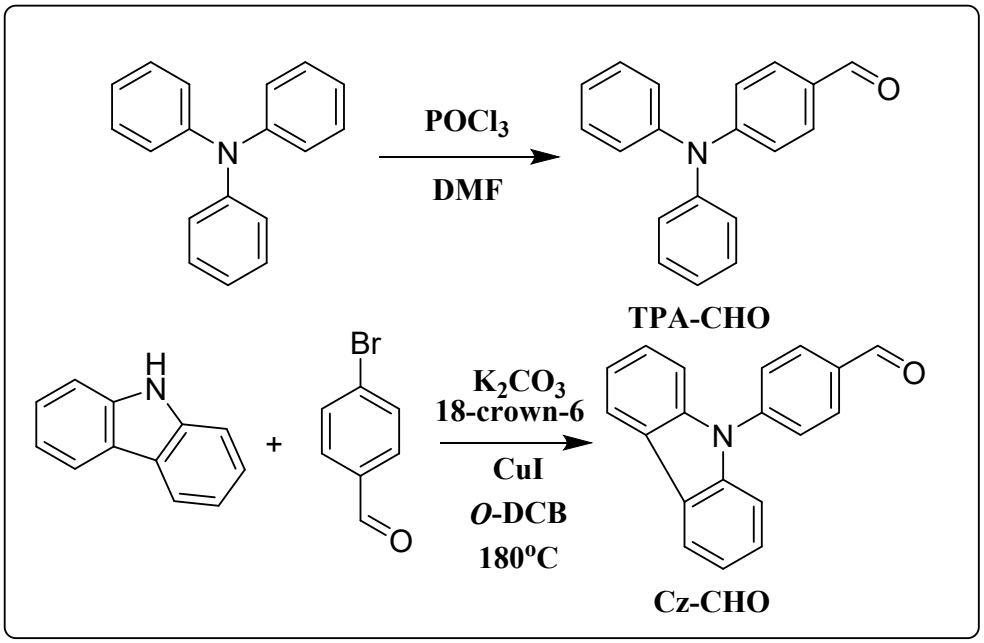
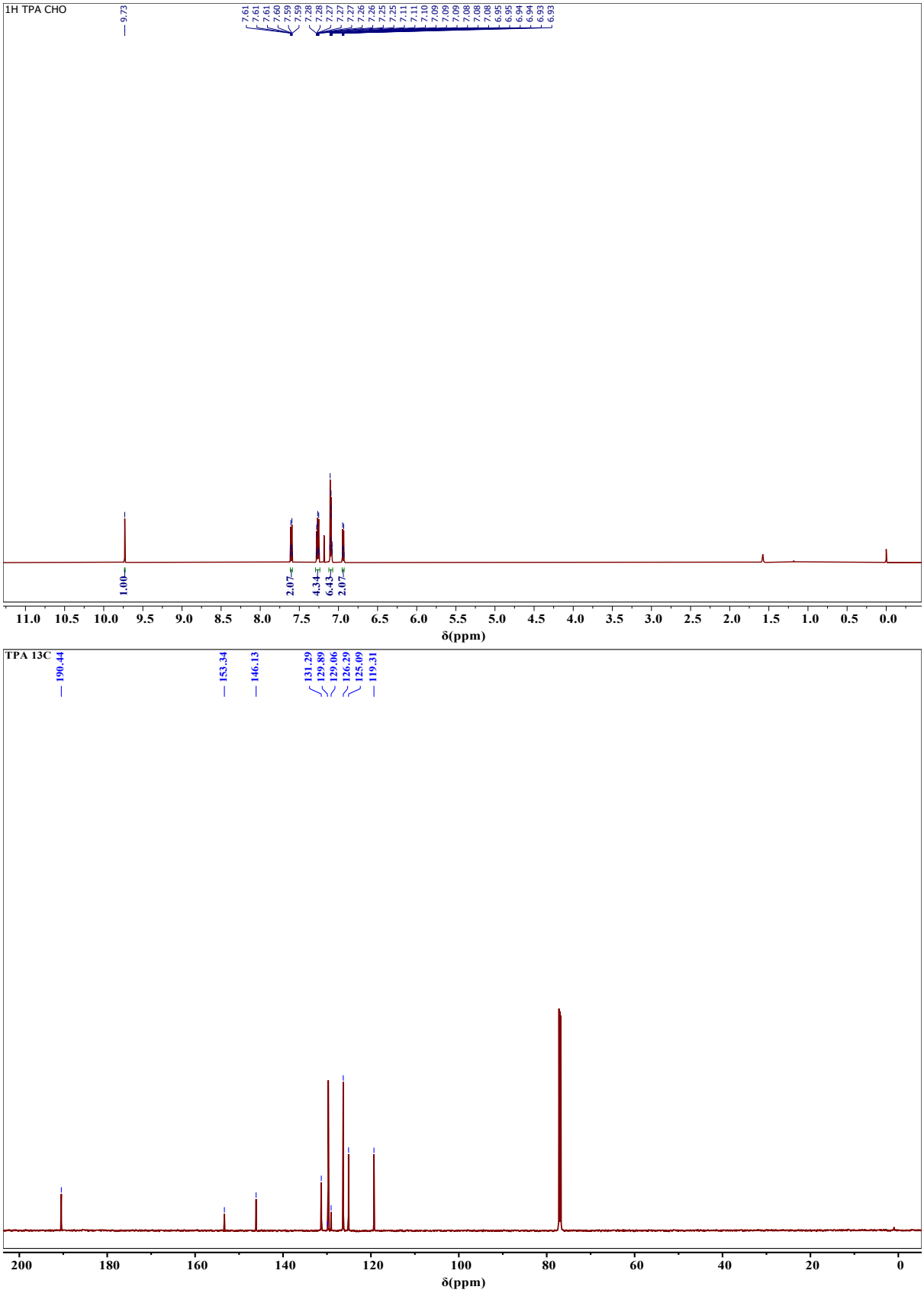
Electronic Supplementary Information (ESI)

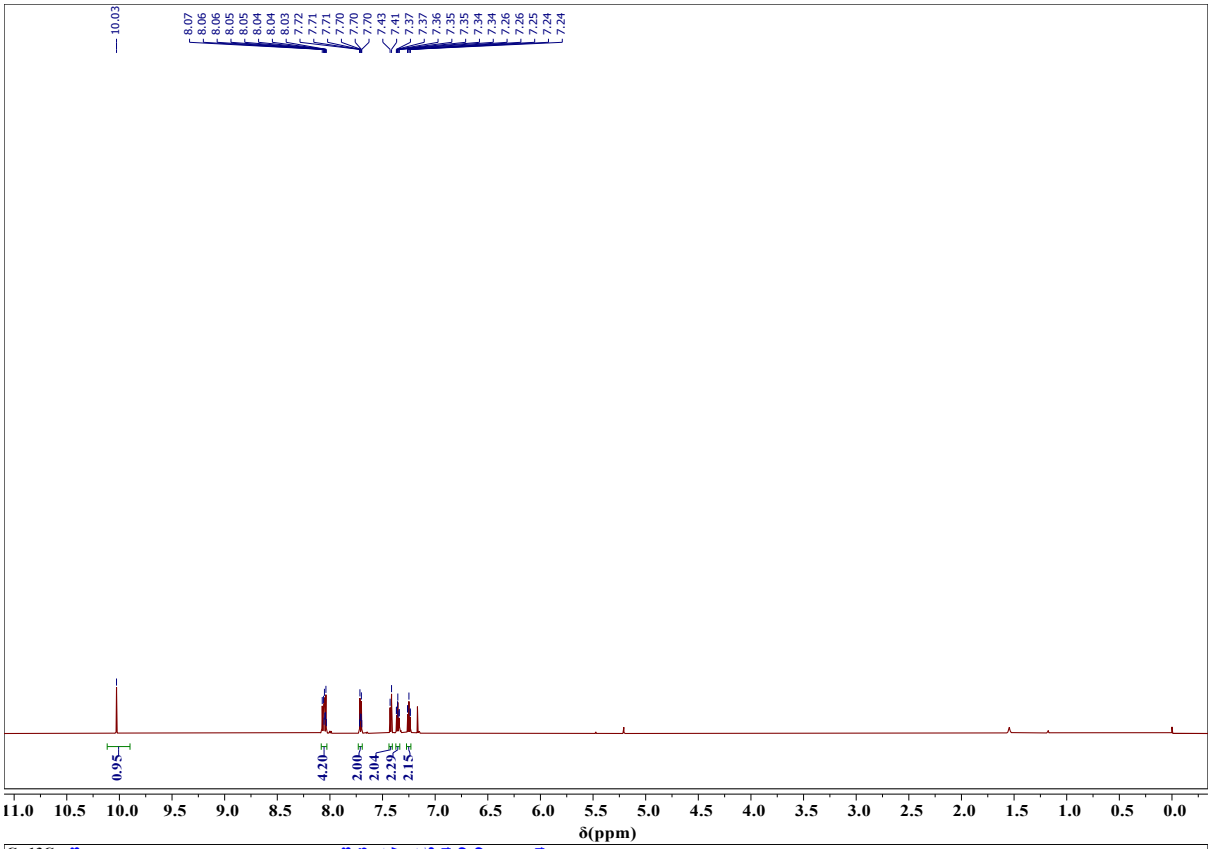
Crystallization solvent induced fluorescence tuning by subtle conformational change in a conformationally flexible fluorophore

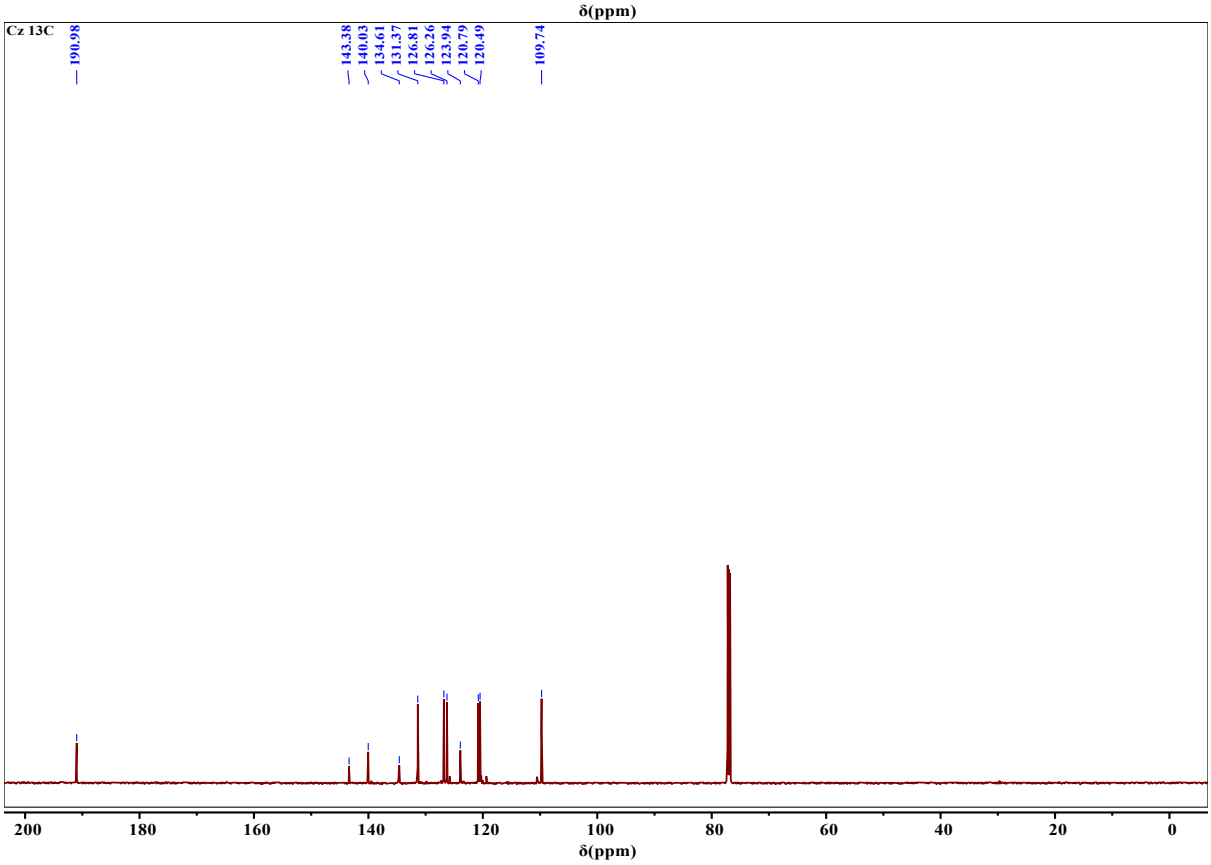


Scheme S1. Synthesis of **TPA-CHO** and **Cz-CHO**.



^{1}H and ^{13}C NMR of **TPA-CHO** in $CDCl_3$.





^{1}H and ^{13}C NMR of **Cz-CHO** in $CDCl_3$.

Time-resolved fluorescence measurement

Fluorescence lifetimes were measured from time-resolved intensity decay by the method of time-correlated single-photon counting (TCSPC) technique by FluoroCube-01-NL spectrometer (Horiba Jobin Yovon IBH Ltd.) using a nano LED light source at 340 nm, and the signals were collected at the magic angle (54.7◦) polarization. The IRF of the detector is (fwhm) =750 ps. DAS6 software was used to deconvolute the fluorescence decays. The relative contribution of each component was obtained from the bi-exponential fitting and finally expressed by the following equation.

$a_n = B_n / \sum B_i$

B_i is the pre-exponential factor. The mean fluorescence lifetimes for the decay curves were calculated from the decay times and the relative contribution of the components using the following equation.

$\langle \tau \rangle = \sum a_i \tau_i^2 / \sum a_i \tau_i$

τ_i and a_i are the fluorescence lifetime and its coefficient of the i^{th} component, respectively.

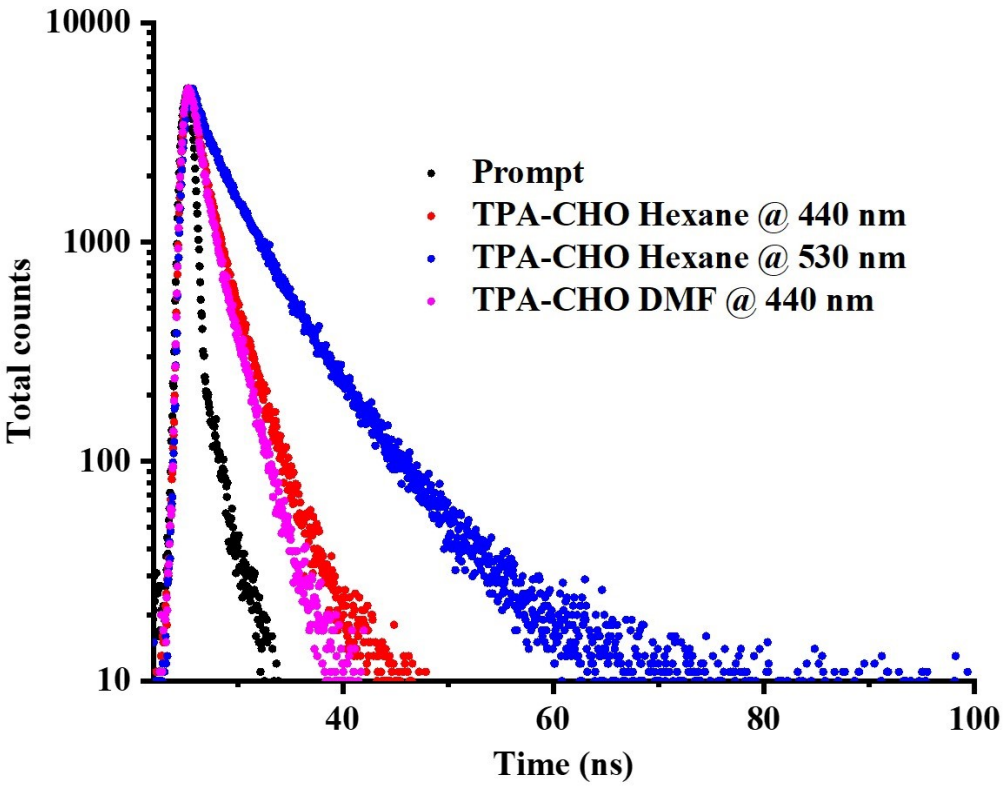


Figure S1. Excited state decay profiles of TPA-CHO crystals grown from hexane and DMF.

Table S1. Fluorescence life time decay of TPA-CHO crystals. a_1, a_2 are relative individual component contributions to τ_1, τ_2 $< \tau >$ (ns) is the average lifetime from multiple decay profiles.

Crystals	τ_1 (ns)	τ_2 (ns)	Relative Intensity		$<\tau>$ (ns)	χ^2
			a1	a2		
DMF (@ 440nm)	0.25	2.01	44.02	55.98	0.49	1.01
Hexane (@440nm)	0.60	2.91	49.83	50.17	0.99	1.05
Hexane (@530nm)	3.24	7.81	58.45	41.55	4.28	1.30

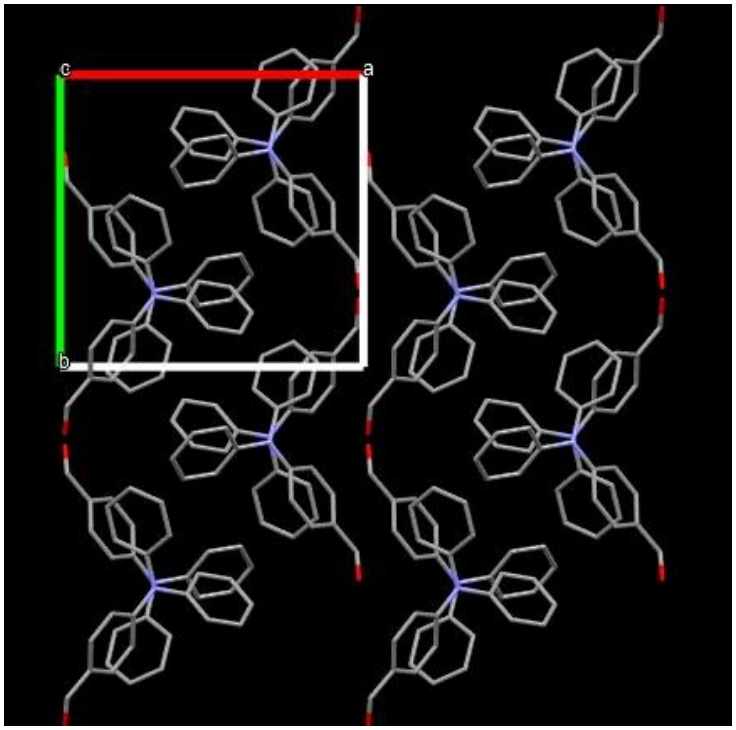


Figure S2. Molecular packing in the crystal lattice of TPA-CHO crystallized from MeOH. H-atoms are omitted for clarity. C (grey), N (blue) and O (red).

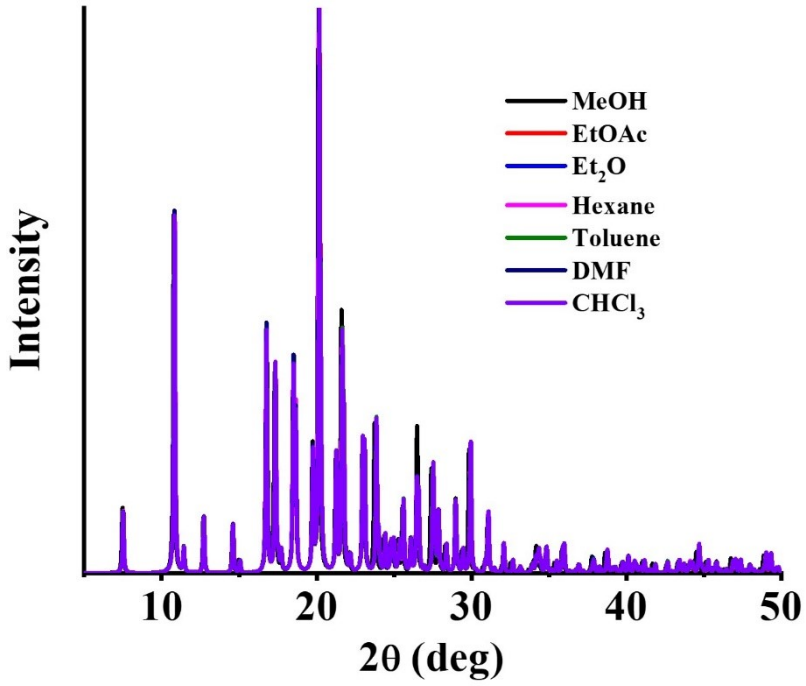


Figure S3. Simulated PXRD pattern of TPA-CHO crystals obtained form different solvents.

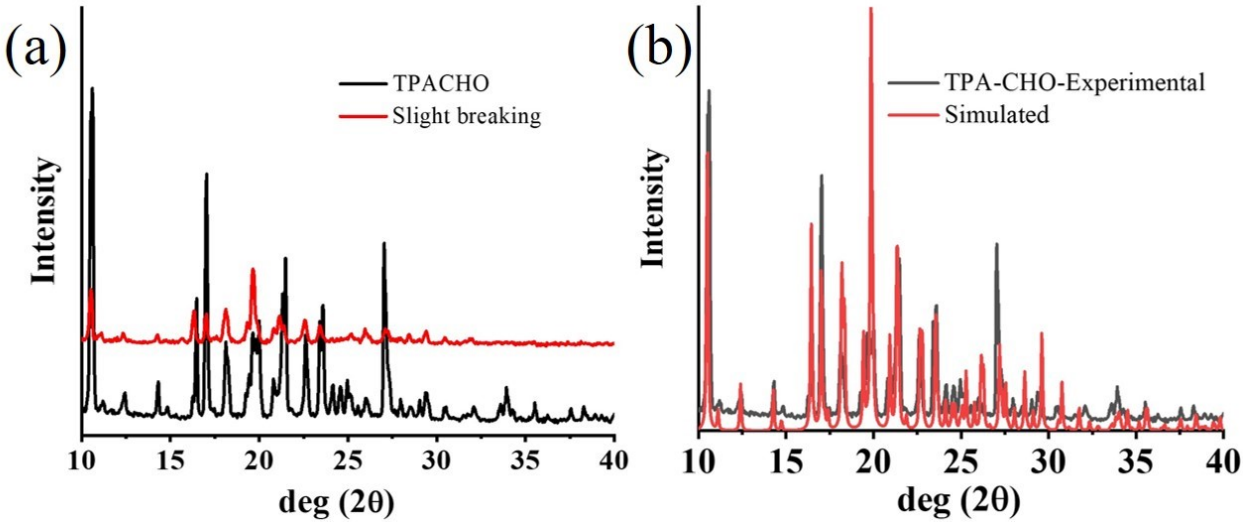
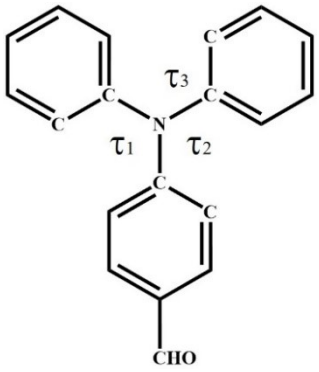


Figure S4. PXRD TPA-CHO (b) before and after slight breaking and (b) comparison with the simulated pattern.

Table S2. Crystallographic details of TPA-CHO grown from different solvents.

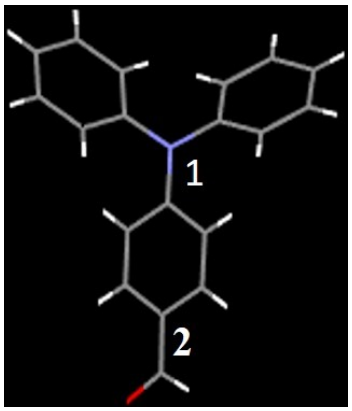
	Hexane CCDC No: 2406006	Toluene CCDC No: 2406007	Et_2O CCDC No: 2406008	$CHCl_3$ CCDC No: 2406009	EtOAc CCDC No: 2406010	MeOH CCDC No: 2406011	DMF CCDC No: 2406012
Empirical formula	C19 H15 N O	C19 H15 N O	C19 H15 N O	C19 H15 N O	C19 H15 N O	C19 H15 N O	C19 H15 N O
Formula weight	273.32	273.32	273.32	273.32	273.32	273.32	273.32
Wavelength	0.630 Å	0.630 Å	0.630 Å	0.630 Å	0.630 Å	0.630 Å	0.630 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	P21/c	P21/c	P21/c	P21/c	P21/c	P21/c
a (Å)	12.003(2)	12.008(2)	12.012(2)	12.005(2)	12.006(2)	12.075(2)	12.004(2)
b (Å)	11.347(2)	11.352(2)	11.349(2)	11.349(2)	11.351(2)	11.371(2)	11.352(2)
c (Å)	10.802(2)	10.791(2)	10.792(2)	10.792(2)	10.793(2)	10.787(2)	10.797(2)
α	90°	90°	90°	90°	90°	90°	90°
β	101.75(3)°	101.70(3)°	101.68(3)°	101.71(3)°	101.67(3)°	101.73(3)°	101.70(3)°
γ	90°	90°	90°	90°	90°	90°	90°
Volume $Å^3$	1440.4(5)	1440.4(5)	1440.8(5)	1439.7(5)	1440.5(5)	1450.2(5)	1440.7(5)
Z	4	4	4	4	4	4	4
Density (calculated) Mg/m^3	1.260	1.260	1.260	1.261	1.260	1.252	1.260
F(000)	576	576	576	576	576	576	576
Independent reflections	4081 [R(int) = 0.0806]	4059 [R(int) = 0.0694]	4060 [R(int) = 0.0648]	3639 [R(int) = 0.0804]	3441 [R(int) = 0.0384]	3618 [R(int) = 0.0647]	3948 [R(int) = 0.0461]
Goodness-of-fit on F^2	1.058	1.083	1.071	1.047	1.066	1.048	1.048
R indices (all data)	R1 = 0.0831, wR2 = 0.1841	R1 = 0.0750, wR2 = 0.1496	R1 = 0.0624, wR2 = 0.1370	R1 = 0.0800, wR2 = 0.1503	R1 = 0.0540, wR2 = 0.1215	R1 = 0.0592, wR2 = 0.1303	R1 = 0.0518, wR2 = 0.1243

Table S3. Conformational changes of TPA-CHO in the crystal lattices.



	Torsion angle (τ)		
	τ_1	τ_2	τ_3
Hexane	42.56	22.92	47.72
Toluene	58.37	34.78	50.87
Et_2O	58.15	34.57	50.88
EtOAc	43.05	23.10	47.60
$CHCl_3$	58.31	34.63	50.89
MeOH	57.07	34.19	50.40
DMF	58.39	34.76	50.93

Table S4. Bond distances between diphenylamine nitrogen and phenyl carond and aldehyde and phenyl carbon in the crystal lattice of TPA-CHO.



	Bond distance (Å)	
	1	2
Hexane	1.393	1.452
Toluene	1.395	1.459
Et_2O	1.394	1.455
EtOAc	1.394	1.457
$CHCl_3$	1.393	1.450
MeOH	1.393	1.466
DMF	1.397	1.453

Table S5. Calculated HOMO-LUMO and optical band gap.

	HOMO	LUMO	Band gap (eV)
Hexane	-5.67	-1.72	3.95
Toluene	-5.66	-1.70	3.96
Et_2O	-5.66	-1.72	3.94
$CHCl_3$	-5.66	-1.71	3.95
EtOAc	-5.67	-1.72	3.95
MeOH	-5.65	-1.68	3.97
DMF	-5.66	-1.68	3.98

Table S6. Crystallographic details of Cz-CHO grown from hexane and DMF.

	Hexane	DMF
Empirical formula	C19 H13 N O	C19 H13 N O
Formula weight	271.30	271.30
Wavelength	0.630 Å	0.630 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.3230(17)	8.3230(17)
b (Å)	20.735(4)	20.735(4)
c (Å)	8.2530(16)	8.2530(16)
α	90°	90°
β	105.94(3)°	105.91(3)°
γ	90°	90°
Volume $Å^3$	1369.5(5)	1371.4(5)
Z	4	4
Density (calculated) Mg/m^3	1.316	1.314
F(000)	568	568
Reflections collected	14181	20056
Independent reflections	3840 [R(int) = 0.0559]	5191 [R(int) = 0.0388]
Goodness-of-fit on F^2	1.054	1.107
R indices (all data)	R1 = 0.0557, wR2 = 0.1368	R1 = 0.0722, wR2 = 0.1754