Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Multifunctional benzonitrile derivatives with TADF and mechanofluorochromic properties and their application in OLEDs

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1. SOLID FILMS

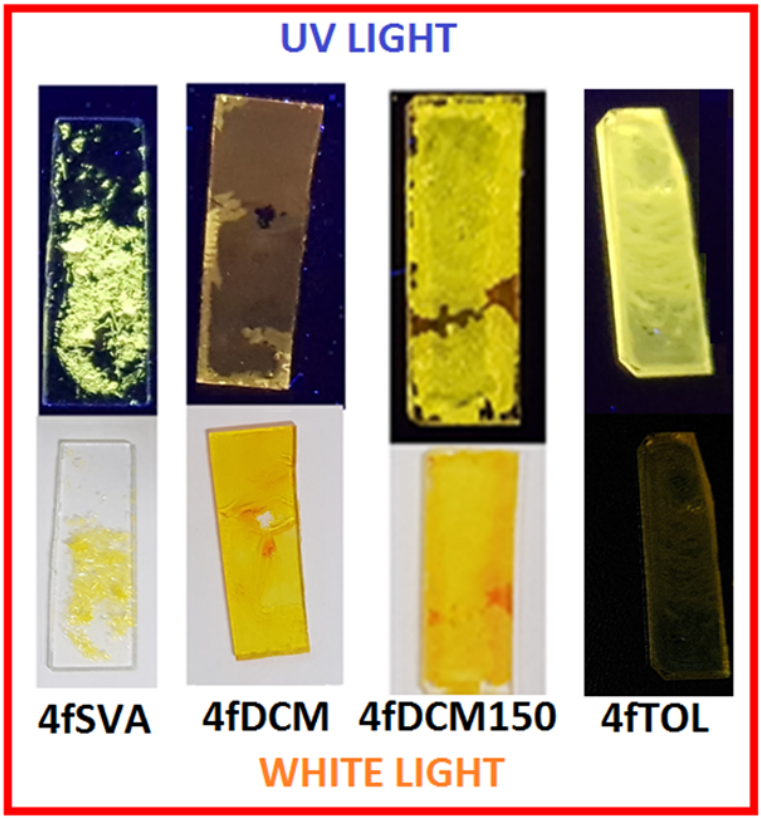


Figure S1: *Photographs of the various samples prepared with the different methods, taken under ordinary visible light and under UV lamp (360 nm) for molecule* ***4****.*

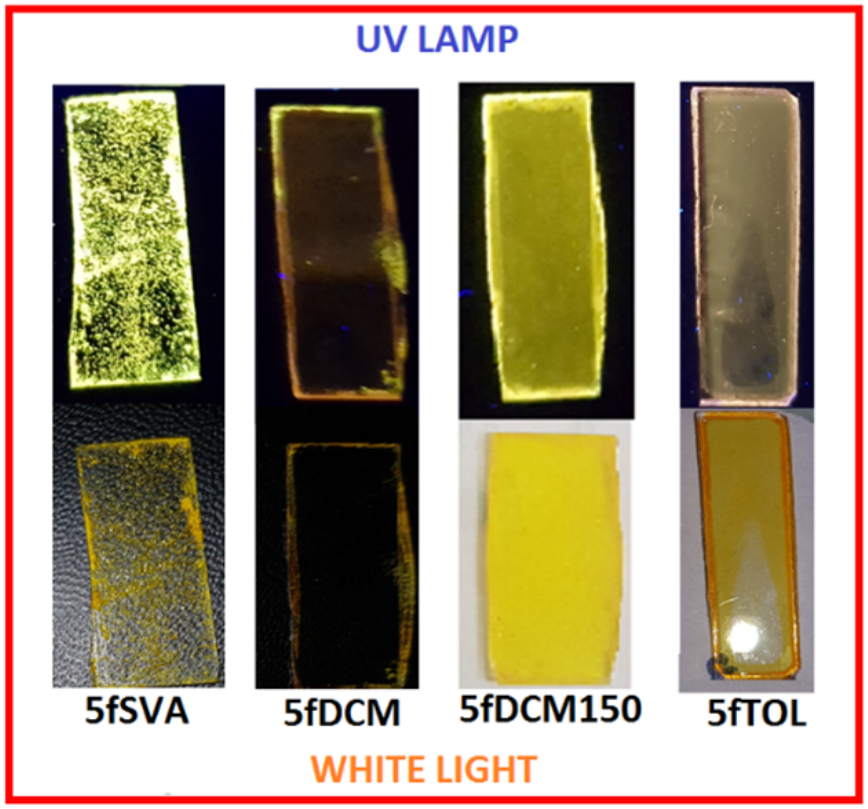


Figure S2: *Photographs of the various samples prepared with the different methods, taken under ordinary visible light and under UV lamp (360 nm) for molecule* ***5.***

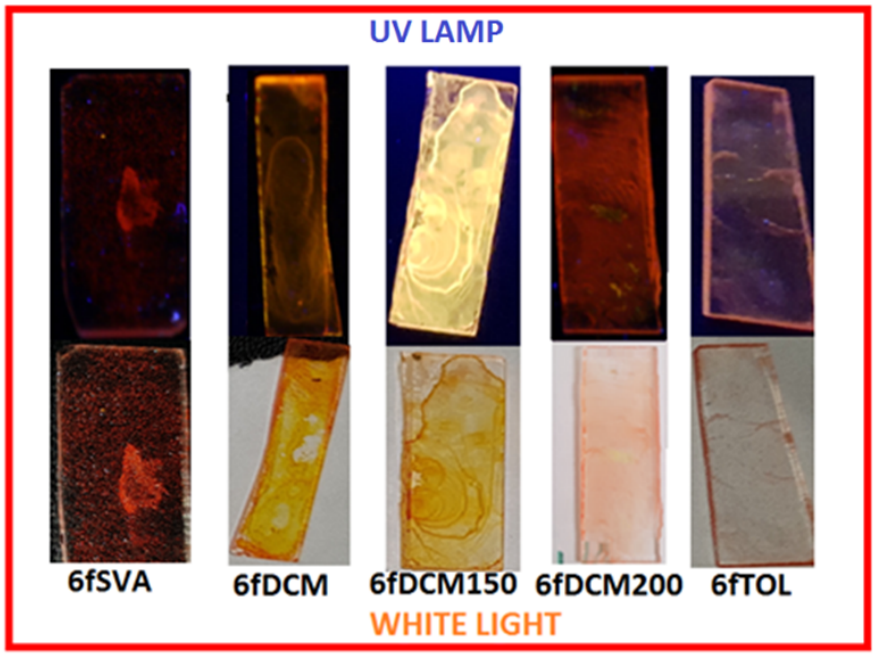


Figure S3: *Photographs of the various samples prepared with the different methods, taken under ordinary visible light and under UV lamp (360 nm) for molecule* ***6.***

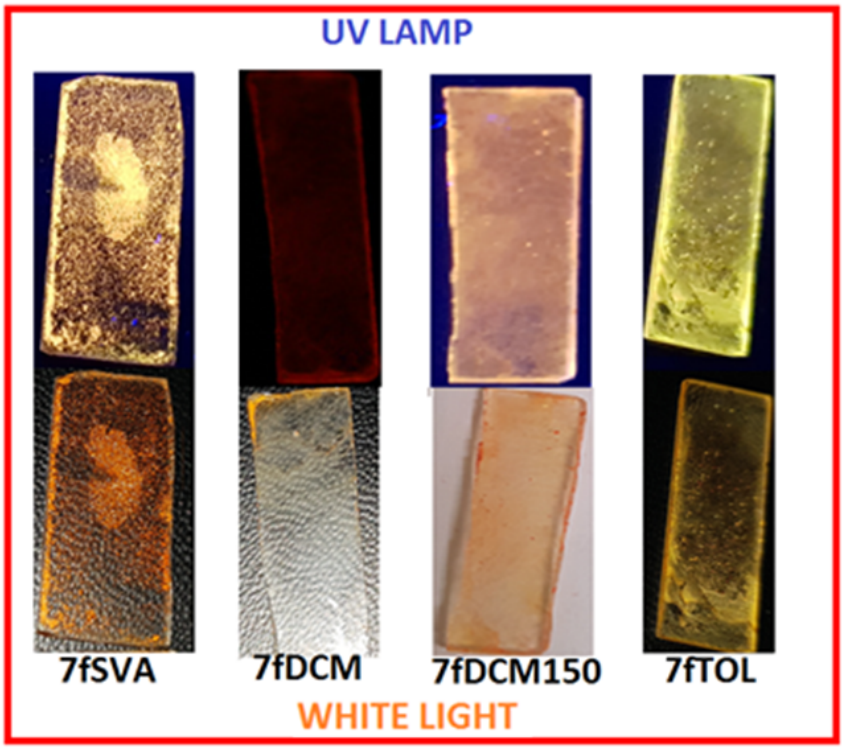
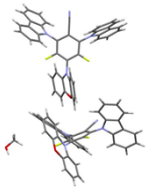
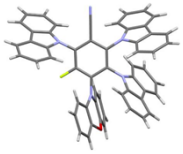
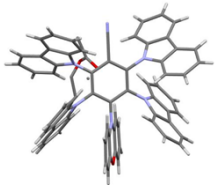


Figure S4: *Photographs of the various samples prepared with the different methods, taken under ordinary visible light and under UV lamp (360 nm) for molecule* ***7****.*

2. XRD ANALYSIS

Table S1: X-ray crystallographic structures of **1** and **4-7**, and the dihedral angles between the donor (Phx= phenoxazine, Cz= carbazole) and acceptor (BzN = benzonitrile)

	XRD structure	D-A (dihedral angle)	
4		BzN-Phx 69.37° (4) BzN-Cz 82.33° (2)	
5		**Mol 1** BzN-Phx 77.09° (4) BzN-Cz 72.36° (2) 70.29° (6)	**Mol 2** BzN-Phx 89.36° (4) BzN-Cz 73.82° (2) 58.43° (6)
6 + Solv		BzN-Phx 74.98° (4) BzN-Cz 75.43° (2) 72.98° (3) 66.50° (6)	
6		BzN-Phx 70.55° (4) BzN-Cz 76.46° (2) 71.65° (3) 76.20° (6)	
7		BzN-Phx 65.24° (4) BzN-Cz 68.54° (2) 70.21° (3) 70.21° (5) 68.54° (6)	

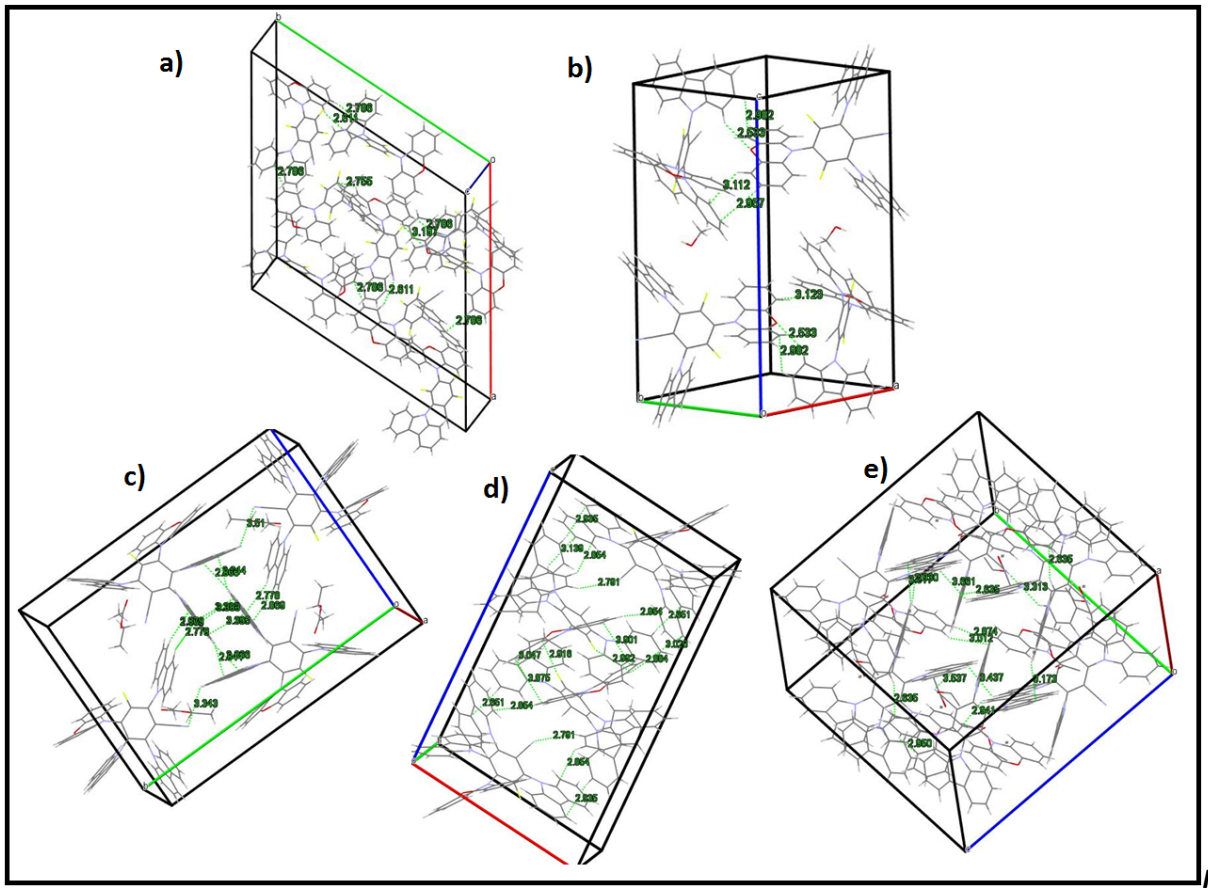


Figure S5*: *molecular packing of **4 (a)**, **5(b)**, **6+solv.(c)**, **6(d)** and **7(e)** obtained from X-ray crystallographic structures.

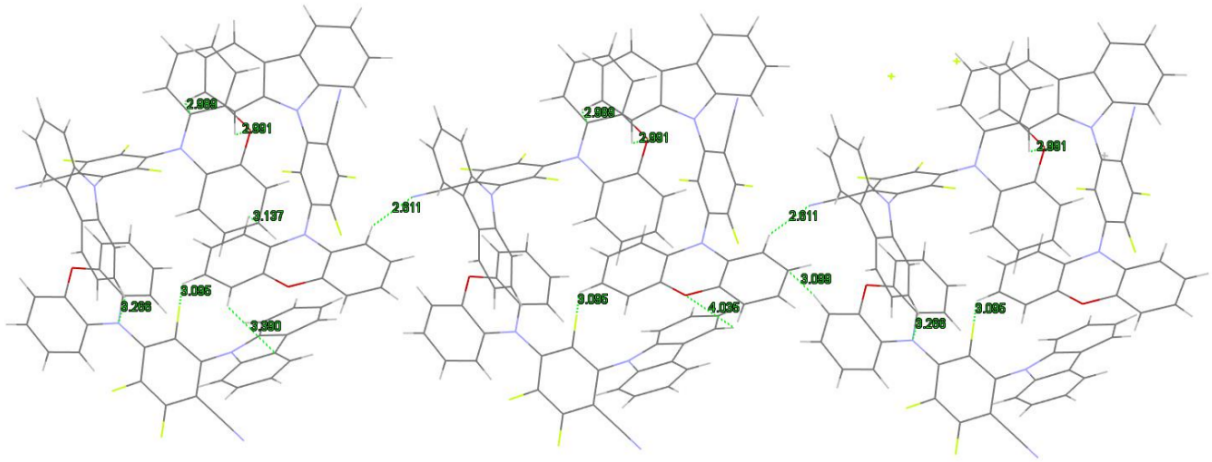


Figure S6**: molecular packing and intermolecular distances in crystal **4.

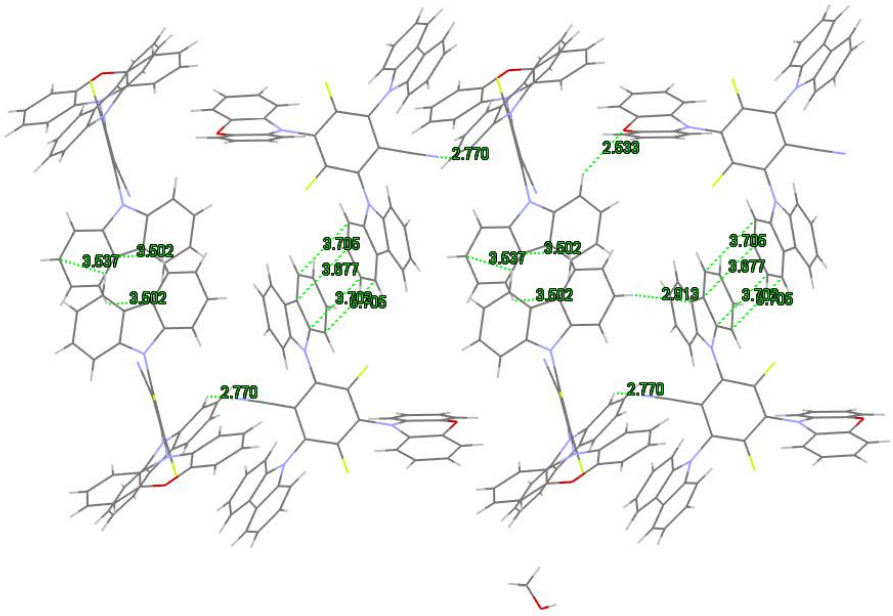


Figure S7*: molecular packing and intermolecular distances in crystal* ***5.***

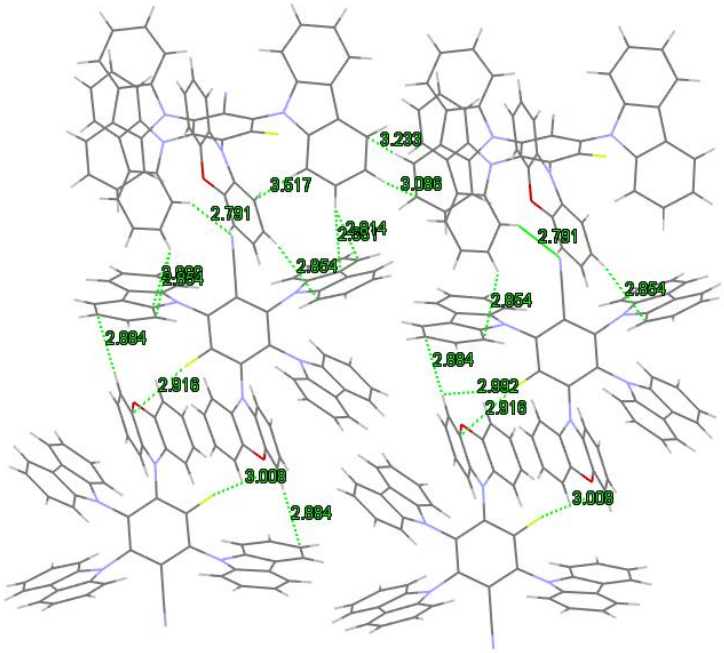


Figure S8*: molecular packing and intermolecular distances in crystal* ***6.***

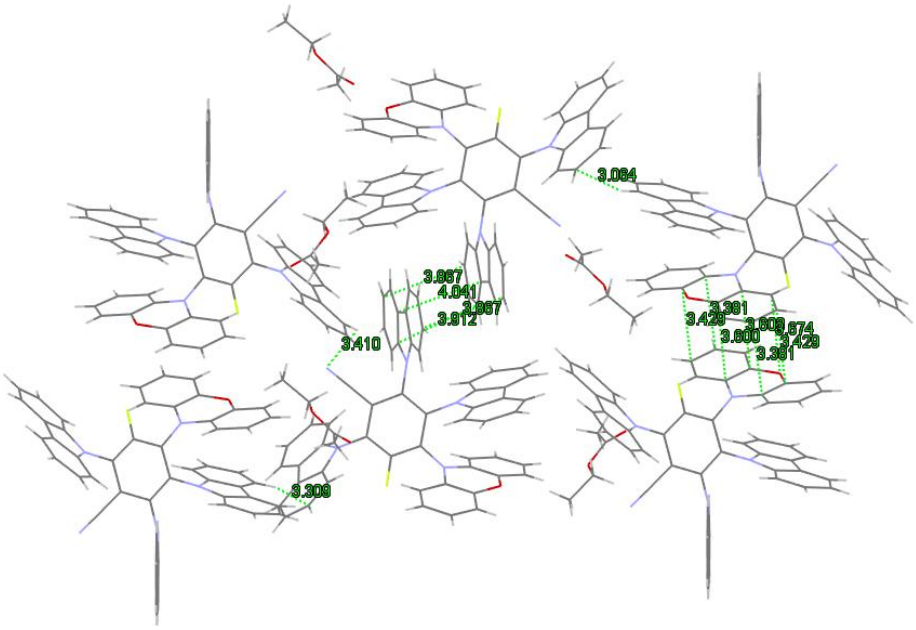


Figure S9*: molecular packing and intermolecular distances in crystal* ***6+solv.***

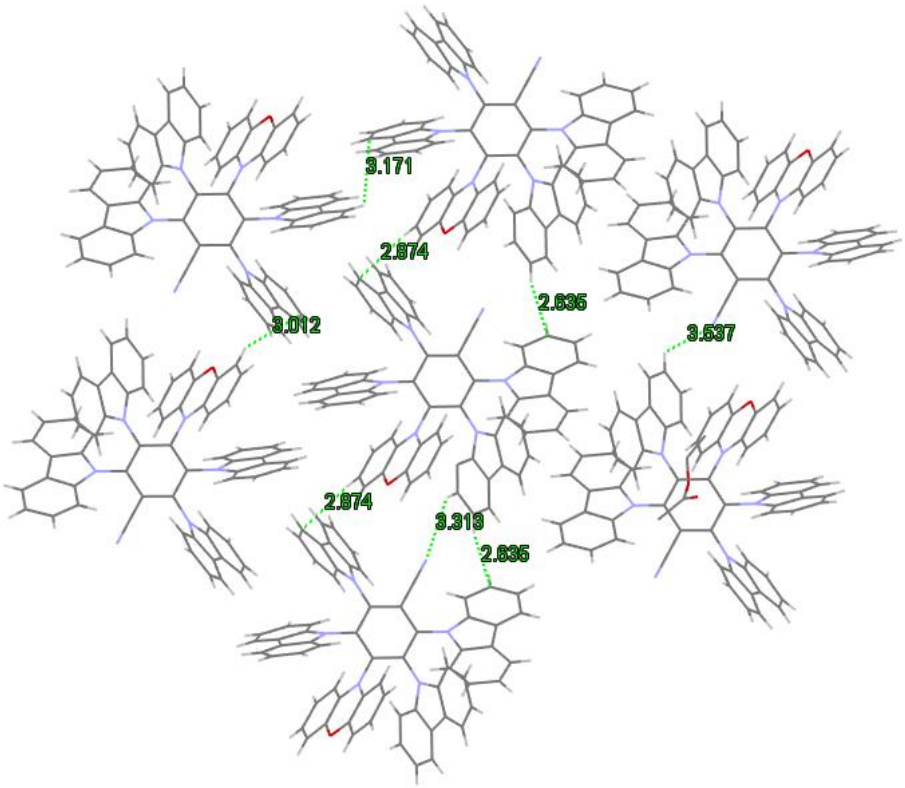


Figure S10: *molecular packing and intermolecular distances in crystal* **7**.

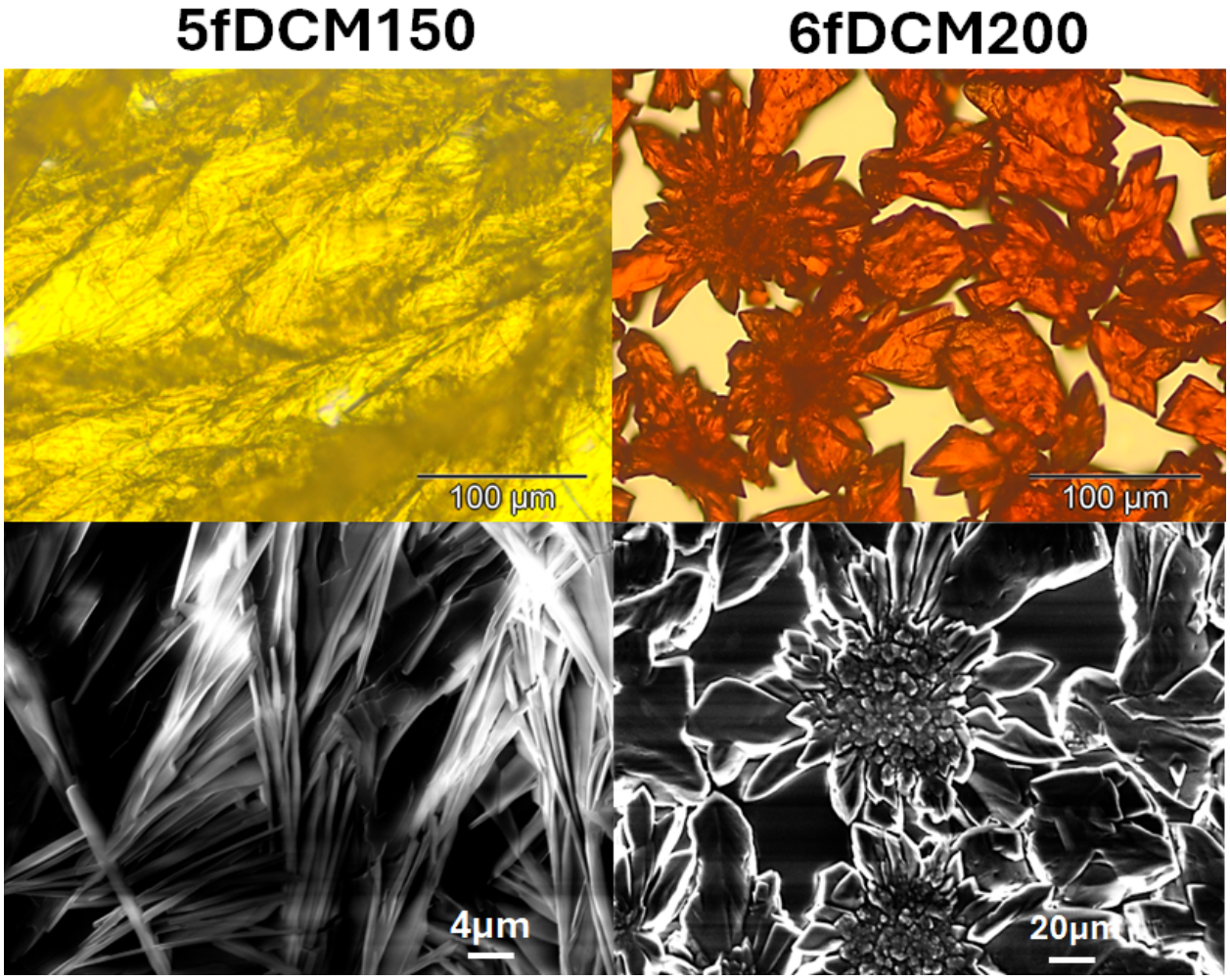


Figure S11*: Surface morphology of samples* ***5fDCM150*** *and* ***6fDCM200****.* ***Top panels*** *(colour images) show optical microscopy photographs.* ***Bottom panels*** *(black and white images) display the corresponding scanning electron microscopy (SEM) images. The images revealing microscale surface features and morphological variations induced by the preparation methods. Scale bar are included in all optical and SEM images.*

3. PHOTOPHYSICAL STUDY

3.1. STEADY STATE

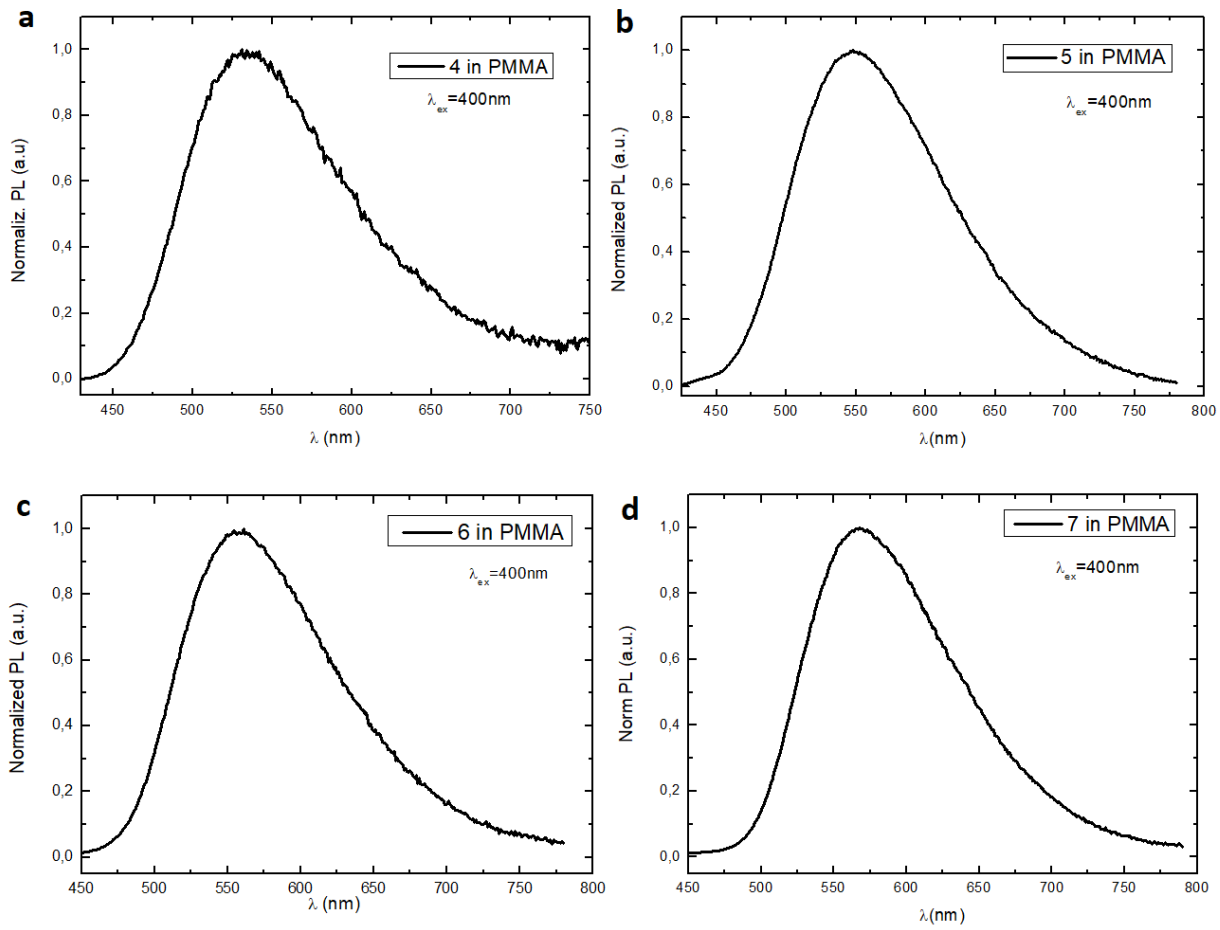


***Figure S12**: Normalized fluorescence spectra (λ_{exc}=400 nm) of molecule **4**-**7** in PMMA.*

Table S2: Summary of steady state photophysical properties in PMMA

	Abs, λ_{max} nm (CT1, CT2)	**Abs, λ_{max} nm (LE)**	**Abs, onset (eV)**	**$\lambda_{PL\ st.st.}$ (nm)**	**QY,%[a]**	**PL FWHM (nm)**	**PL onset (eV)**	**Excitation onset (eV)**
4 in PMMA	416, 369	325, 312 ,287	2.56	535	4.3 (5.2)	116	2.70	2.60
5 in PMMA	440, 387	325, 313, 287	2.48	548	4.0 (4.9)	129	2.66	2.54
6 in PMMA	453, 406	327, 316, 287	2.40	560	13.6(15.9)	122	2.58	2.44
7 in PMMA	471, 411	330, 320, 289	2.31	567	15.1(18.1)	123	2.51	2.37

a: values in parenthesis measured in degassed conditions,

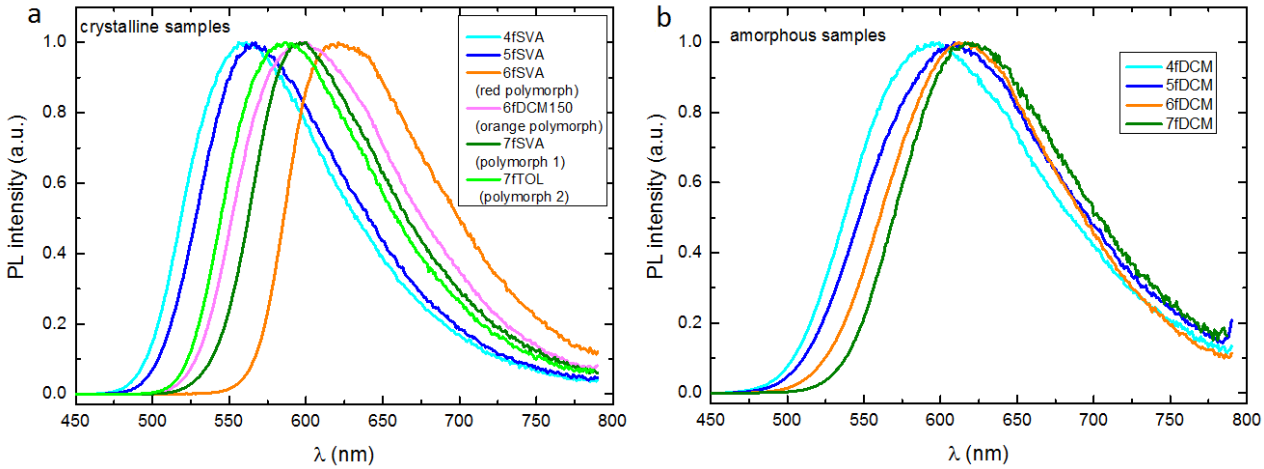


Figure S13: *Normalized fluorescence spectra (λ_{exc}=400 nm) of **a)** different crystalline phases obtained for for molecule **4**-**7**, **b)** amorphous phases obtained for molecule **4**-**7**.*

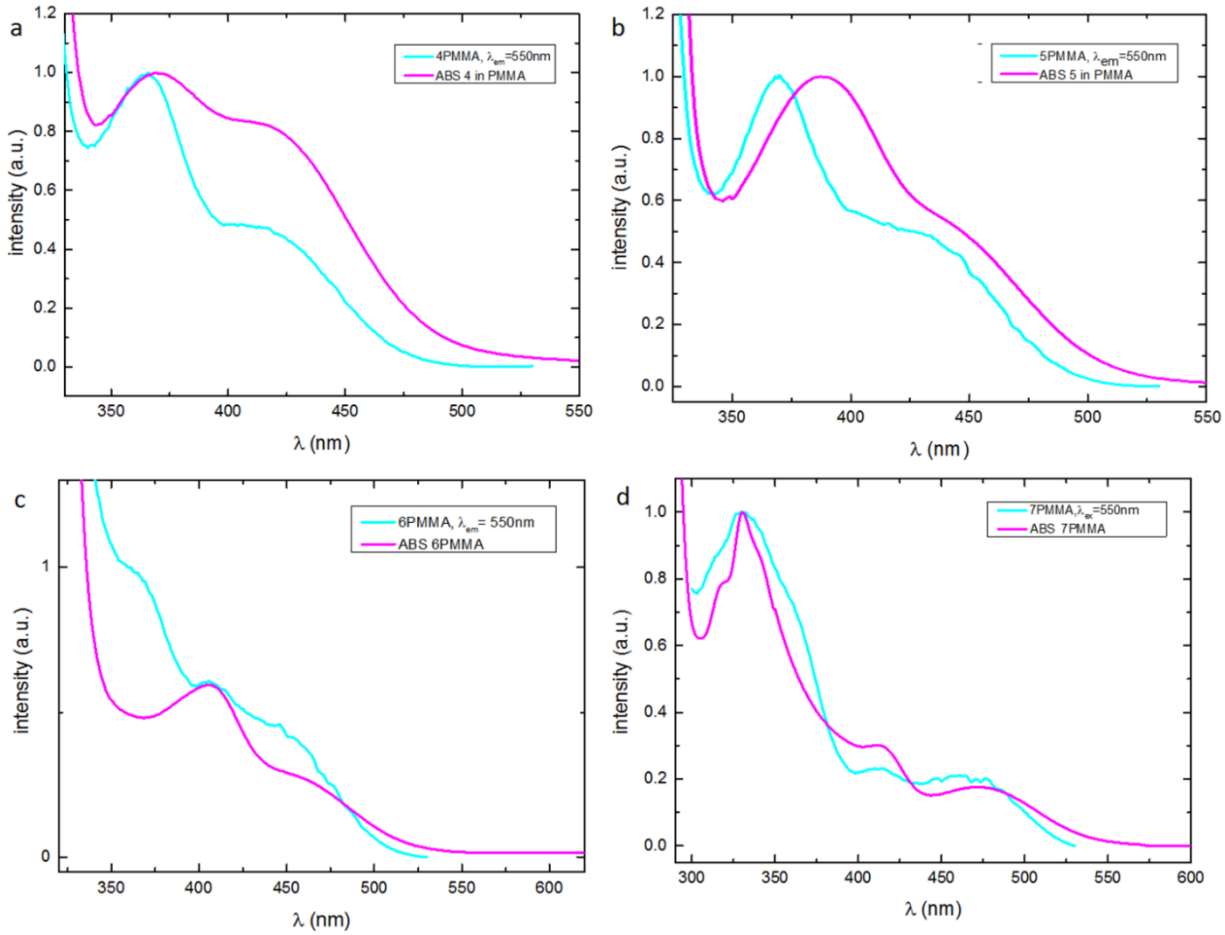


***Figure S14**: comparison between the excitation and the absorption spectra of **4**-**7** molecules in PMMA.*

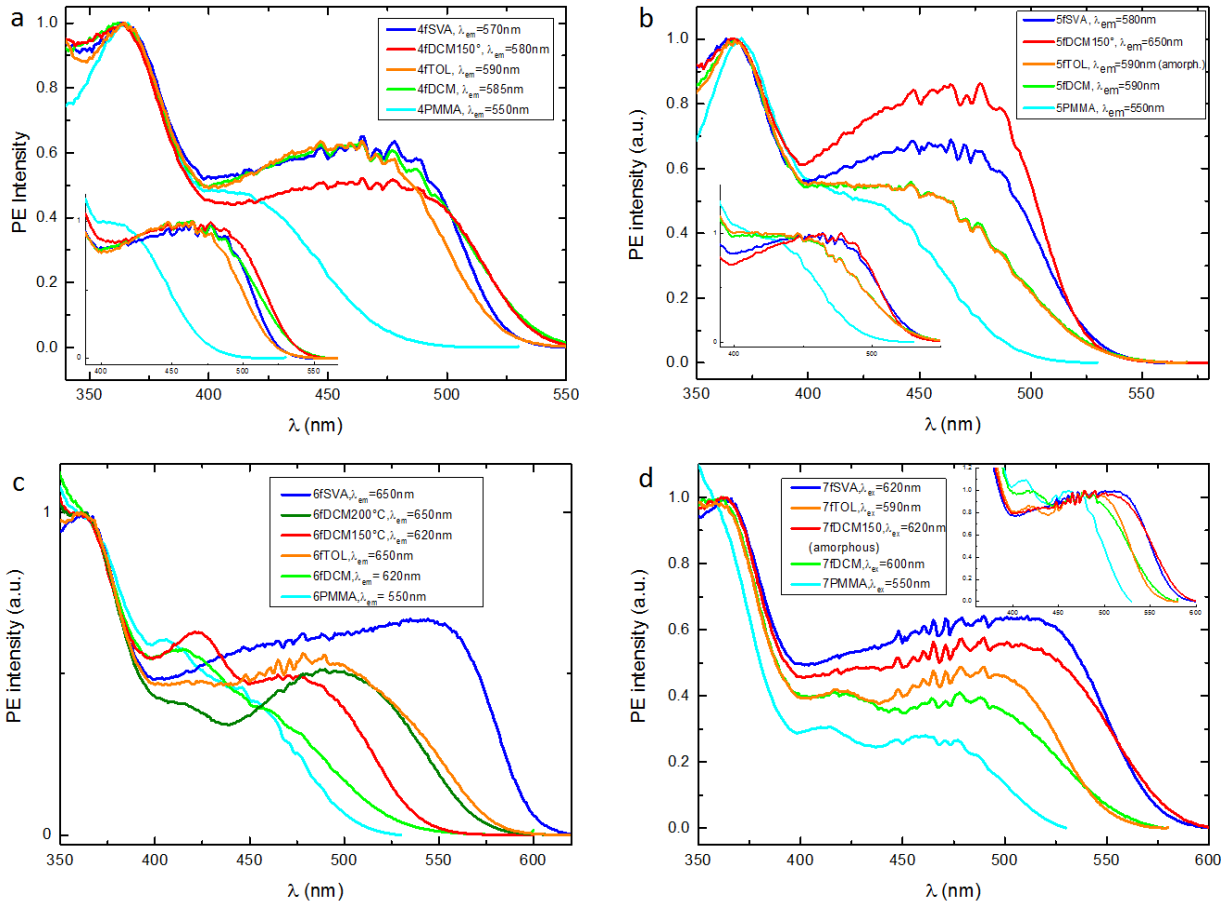


Figure S15*: Excitation spectra of the **4**-**7** solid samples compared with the corresponding excitation spectra of the isolated **4**-**7** molecules in PMMA. All spectra are normalized on the LE transition of the donors.* ***inset)*** *Excitation spectra normalized on the CT absorption band.*

Table S3: Summary of excitation photophysical properties of the different solid samples.

	PMMA, λ_{max}			fSVA, λ_{max}			fDCM150°, λ_{max}			fTOL, λ_{max}			fDCM200°, λ_{max}			fDCM, λ_{max}		
	CT1 CT2	LE	Ons. (eV)	CT1 CT2	LE	Ons (eV)	CT1 CT2	LE	Ons. (eV)	CT1 CT2	LE	Ons. (eV)	CT1 CT2	LE	Ons. (eV)	CT1 CT2	LE	Ons. (eV)
4	415 366	366	2.60	478	363	2.36	477	364	2.32	464	365	2.38	-	-	-	465	362	2.31
5	424, 400 (s)	368	2.54	464	368	2.33	477	367	2.36	454	367	2.36	-	-	-	454	367	2.36
6	446 406	361	2.44	544 460	364	2.07	476 421	361	2.31	490 418	362	2.15	498 416	363	2.16	460 (s) 415	365	2.35
7	465, 414	360 (s)	2.37	511 424	362	2.16	508 426	364	2.13	490 423	361	2.25	-	-	-	478 422	362	2.21

3.2. TIME-RESOLVED STUDY

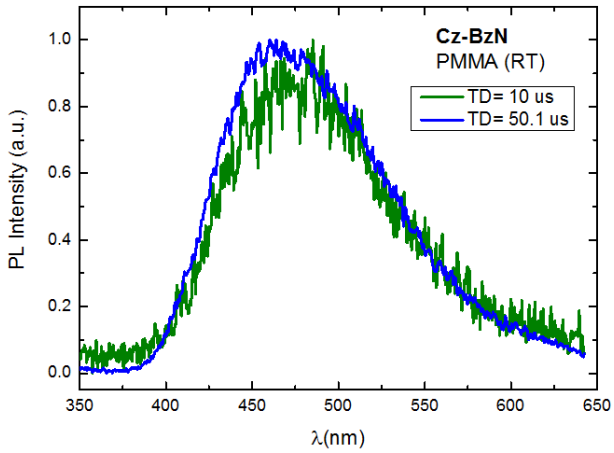


***Figure S16**: time-resolved delayed emission (TD=10 µs and 50 µs) spectra of **Cz-BzN** in PMMA (0.05wt%) at room temperature (RT)*

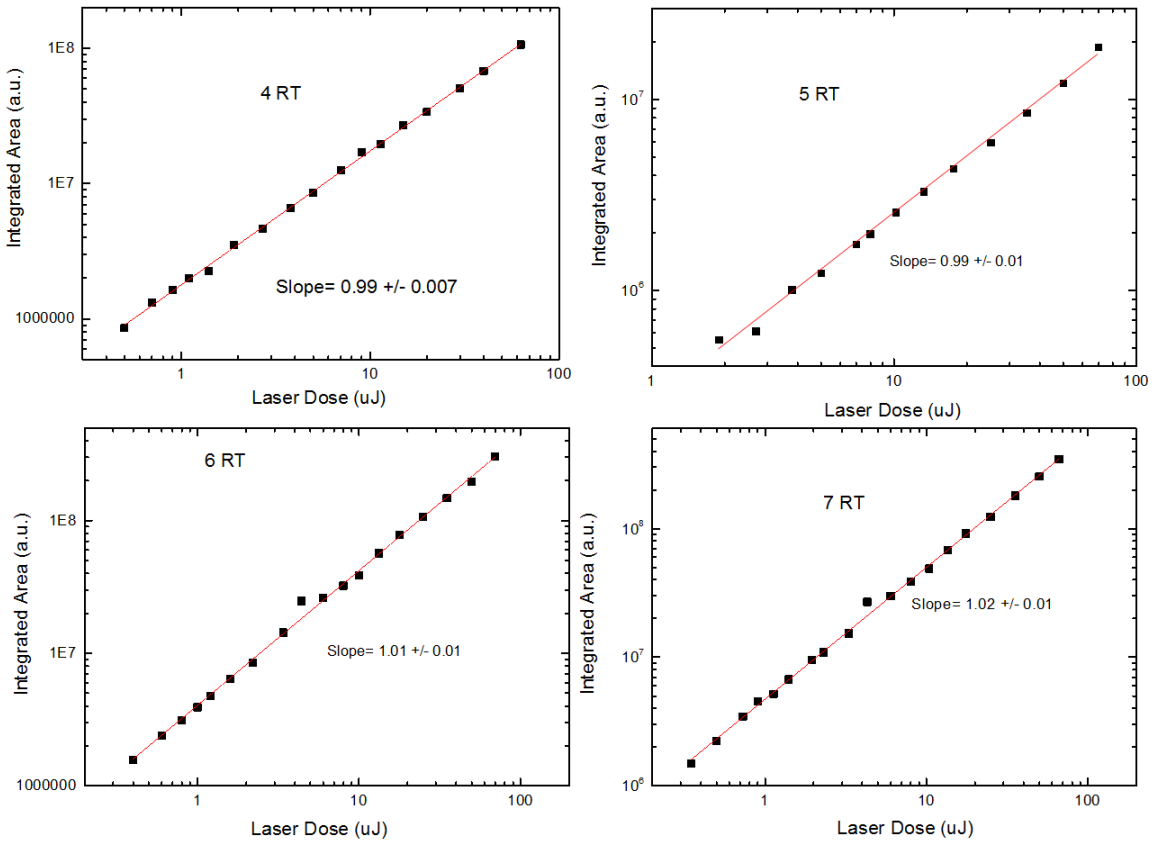


***Figure S17**: Power dependence of the integrated delayed fluorescence at room temperature for the different compounds dispersed in PMMA, from left to right: **4**,**5**,**6**,**7**. λ_{ex}= 337 nm*

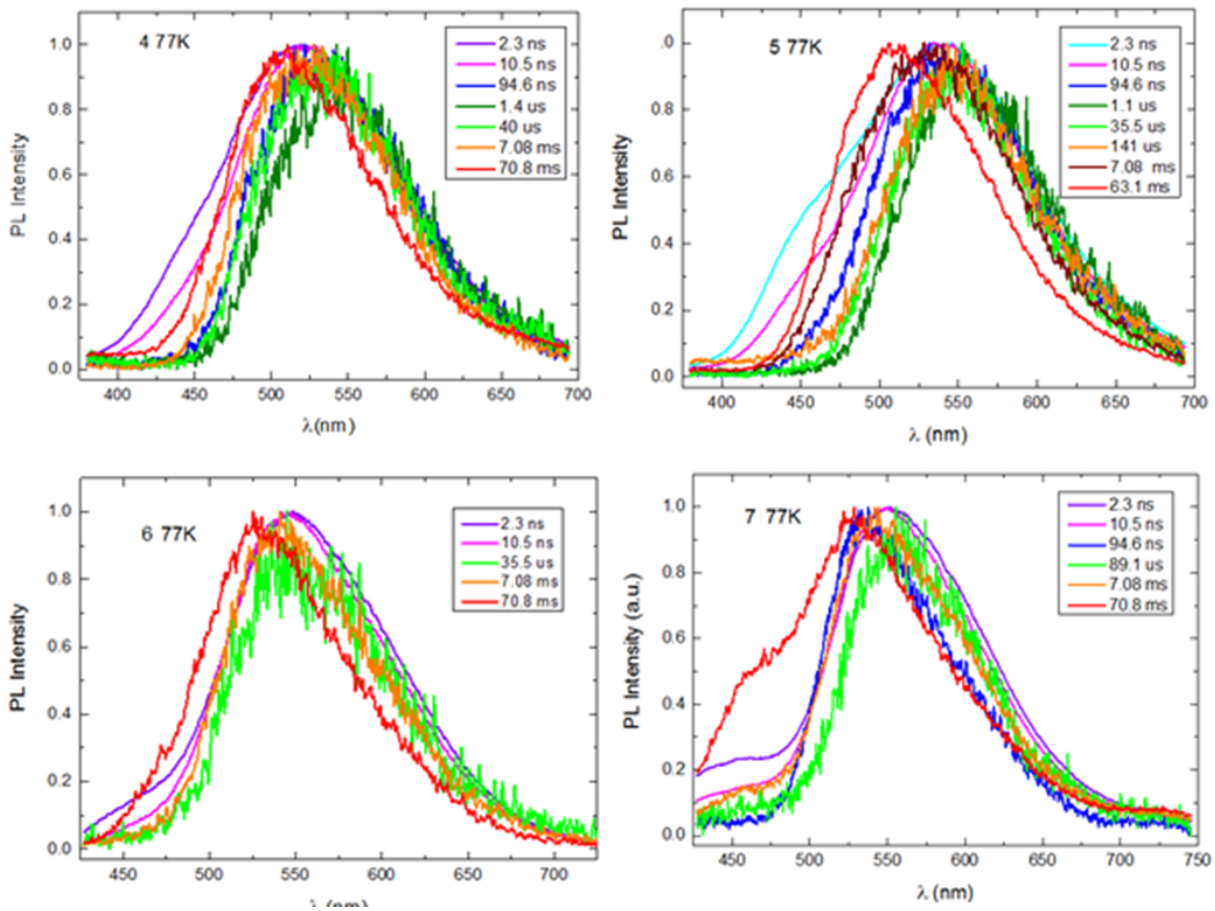


Figure S18*: show the time-resolved emission spectra of* ***4-7*** *in PMMA at 77K*

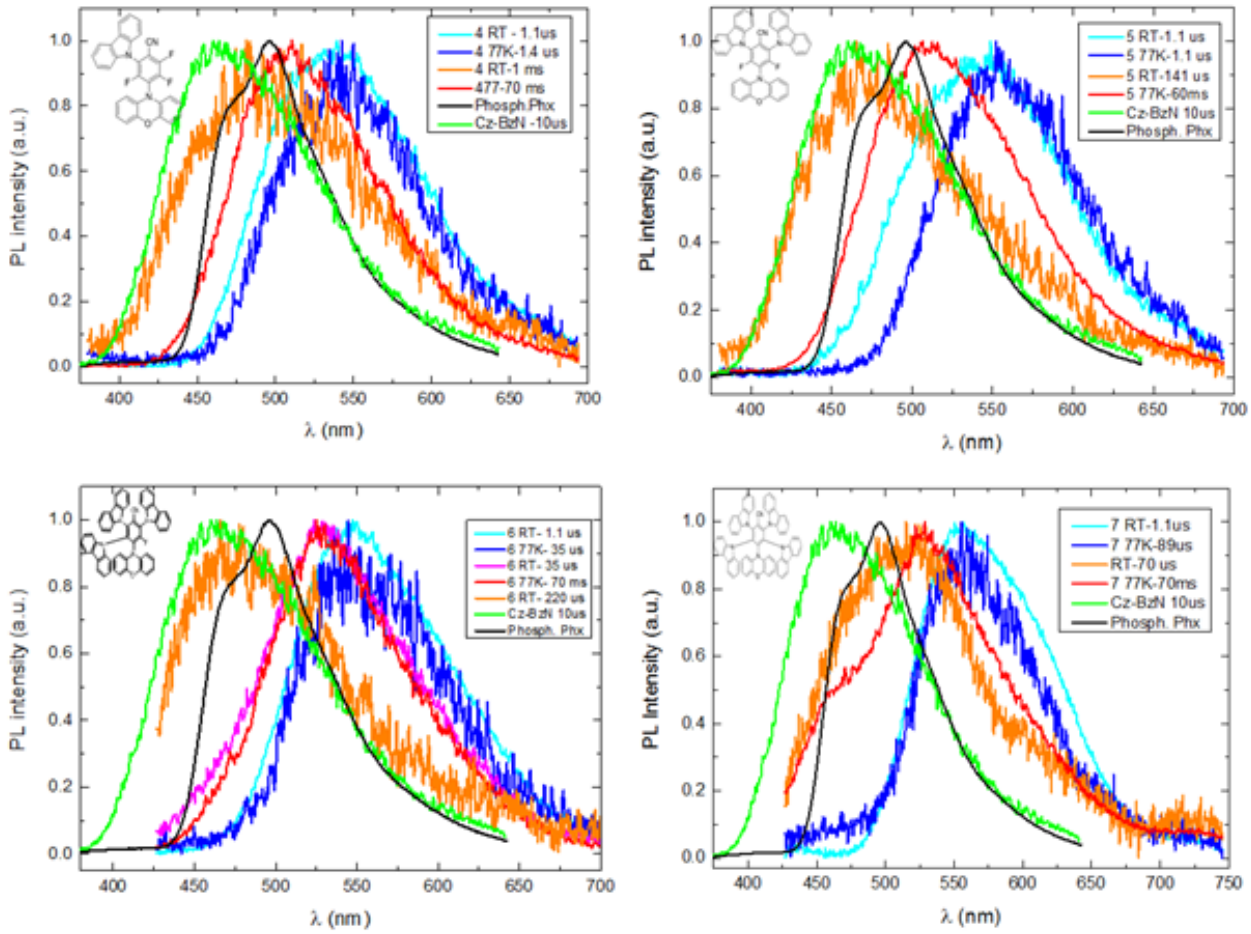


Figure S19*:* delayed emission at the longest TD and delayed emission in DF regime of **4-7**, for RT and 77 K compared with phosphorescence of phenoxazine and with the CT DF emission of Cz-BzN.

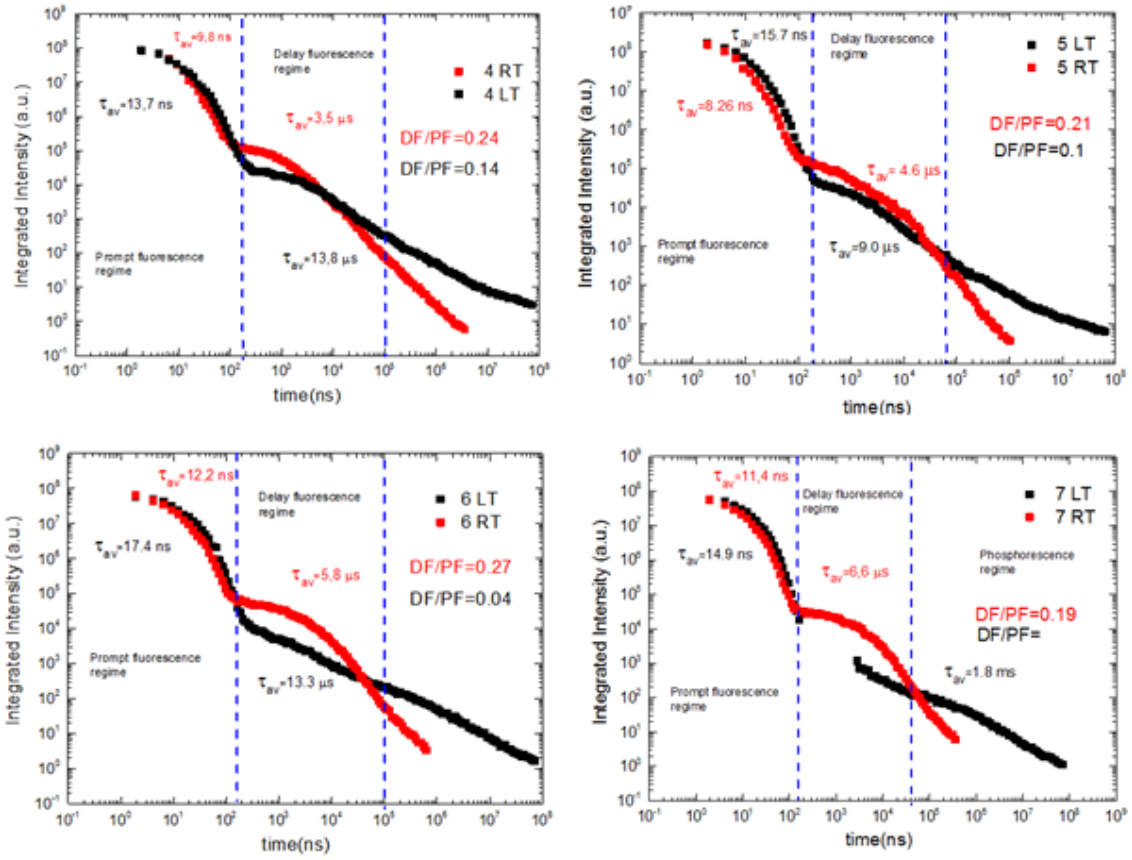


***Figure S20**: decay curve of **4-7** in PMMA at RT and 77K. All experiments were carried out at λ_{ex}= 355 nm.*

Table S4: Summary of time resolved photophysical properties in PMMA

	QY, %[a]	$\lambda_{st.State}$, nm	λ_{PF} (nm)	$S_{1,ons}$ (eV)	τ_1 (ns)	τ_2 (ns)	$\tau_{PF,av}$ (ns)	τ_3 (µs)	τ_4 (µs)	$\tau_{DF,av}$ (µs)	DF/PF
4 in PMMA	4.3 (5.2)	535	531	2.73	6.6	26.0	9.8	0.9	6.2	3.5	0.24
5 in PMMA	4.0 (4.9)	548	537	3.10	4.2	14.3	8.3	0.5	6.1	4.6	0.21
6 in PMMA	13.6 (15.9)	560	552	2.60	5.6	18.0	12.2	1.2	7.6	5.8	0.27
7 in PMMA	15.1 (18.1)	567	564	2.48	4.9	15.4	11.4	1.6	9.0	6.6	0.19

λ_{PF}= emission maximum of prompt fluorescence, $S_{1,onset}$= onset energy of singlet, $\tau_{PF,av}$= average decay time of PF, $\tau_{DF,av}$= average decay time of DF, DF/PF= ratio between DF to PF emission.

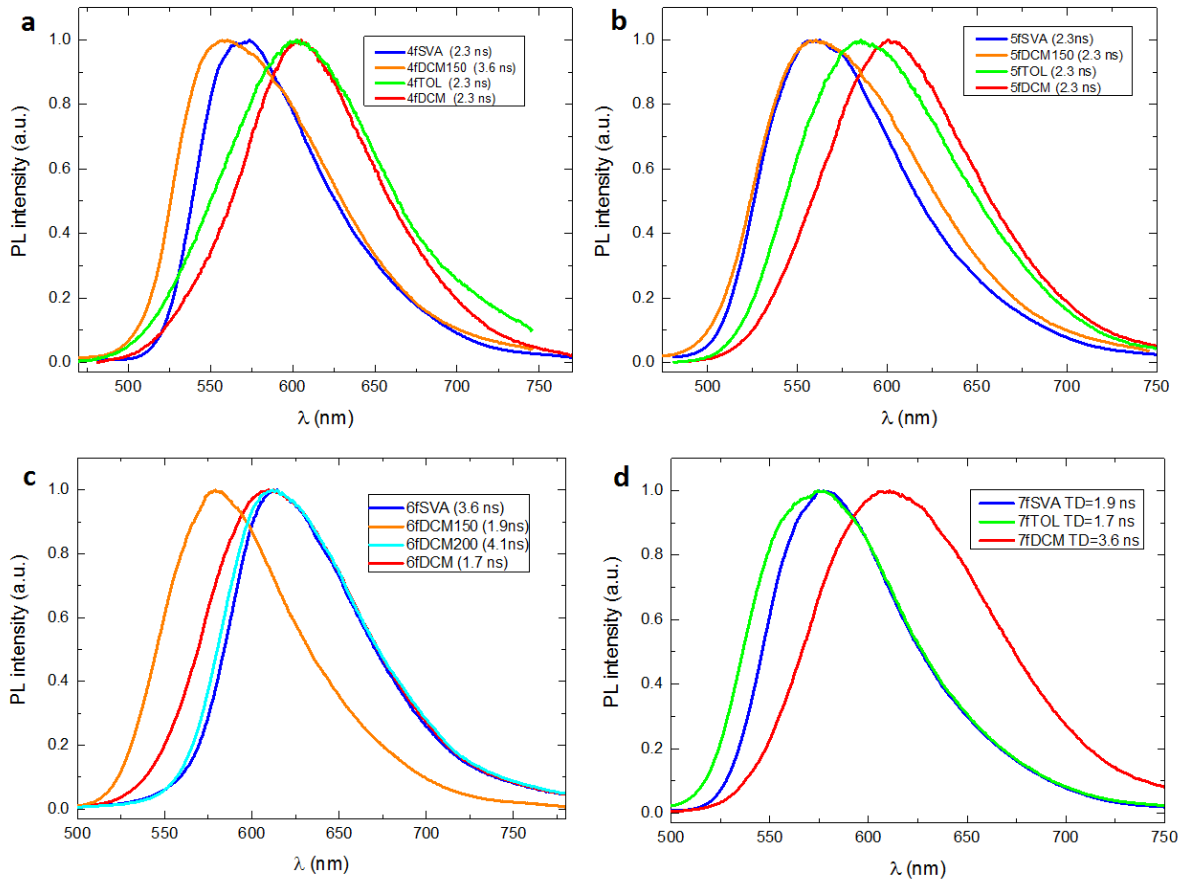


Figure S21: *time-resolved PL spectra at initial time of the various solid forms obtained from molecules:* ***a) 4, b) 5, c) 6*** *and* ***d) 7****.*

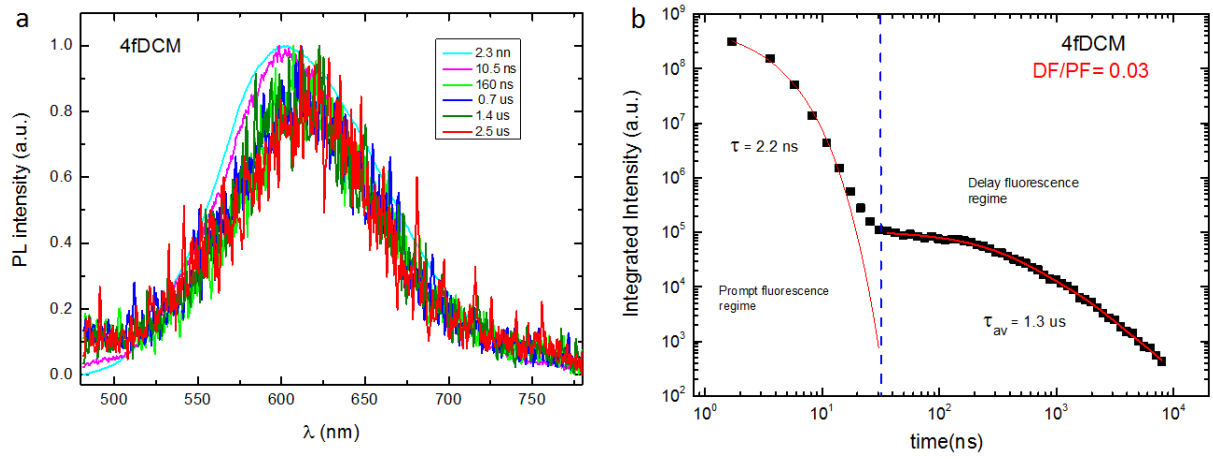


Figure S22*: **a)** time-resolved emission spectra of **4**fDCM at room temperature (RT); **b)** decay curve of **4**fDCM at RT. λ_{ex} = 355 nm.*

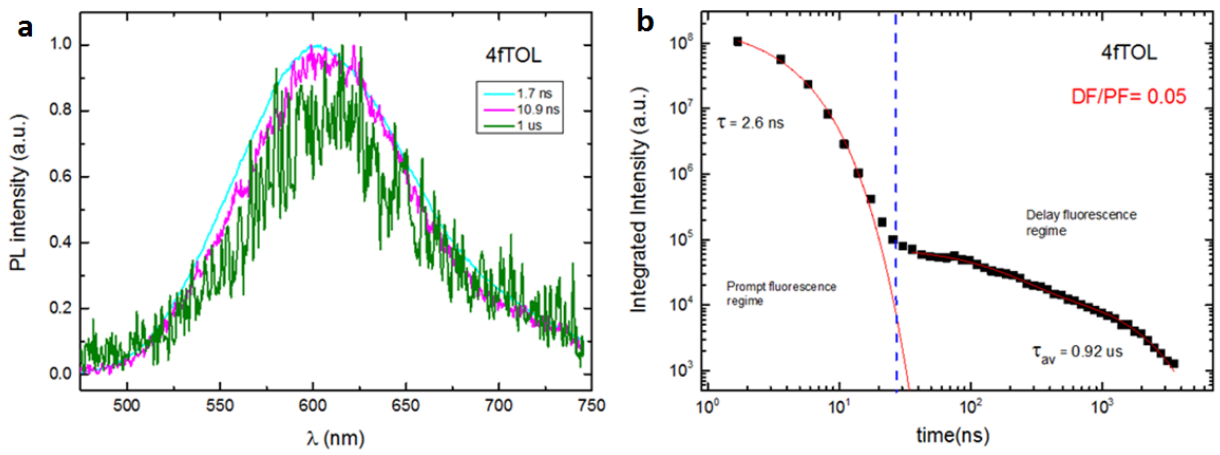


***Figure S23**: **a)** time-resolved emission spectra of **4**fTOL at room temperature (RT); **b)** decay curve of **4**fTOL at RT. λ_{ex}= 355 nm*

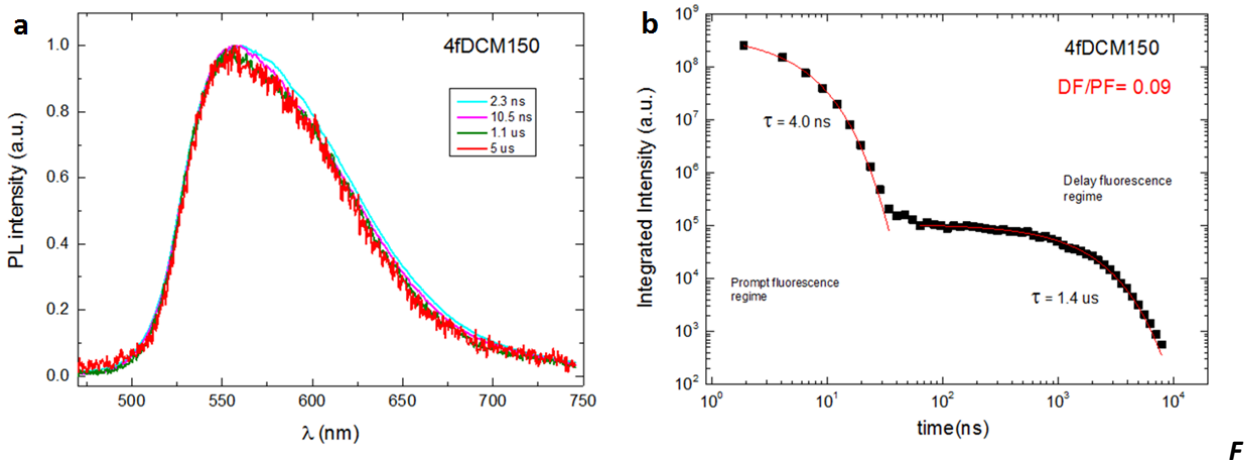


***Figure S24**: **a)** time-resolved emission spectra of **4**fDCM150 at room temperature (RT); **b)** decay curve of **4**fDCM150 at RT. λ_{ex}= 355 nm.*

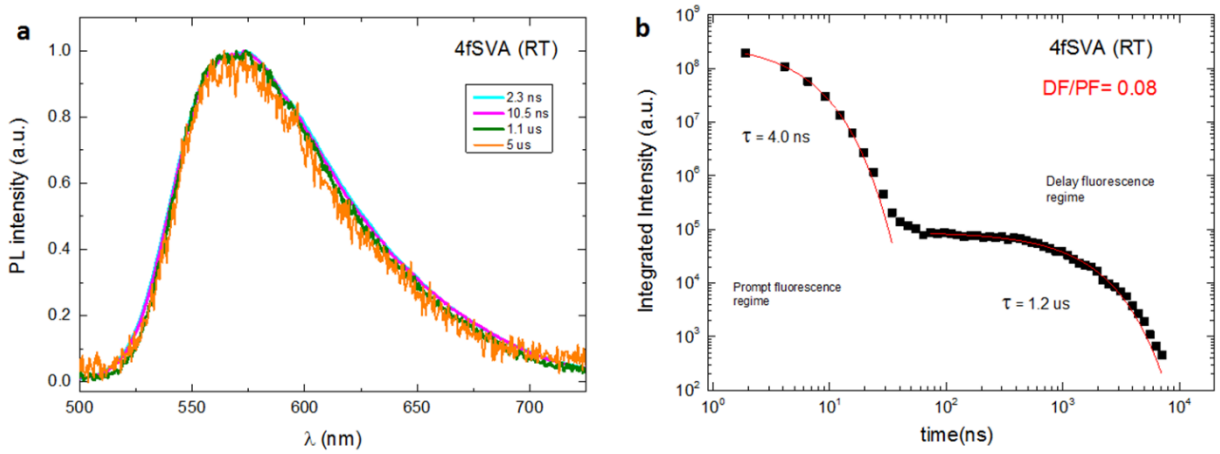


***Figure S25**: **a)** time-resolved emission spectra of **4**fSVA at room temperature (RT); **b)** decay curve of **4**fSVA at RT. λ_{ex}= 355 nm.*

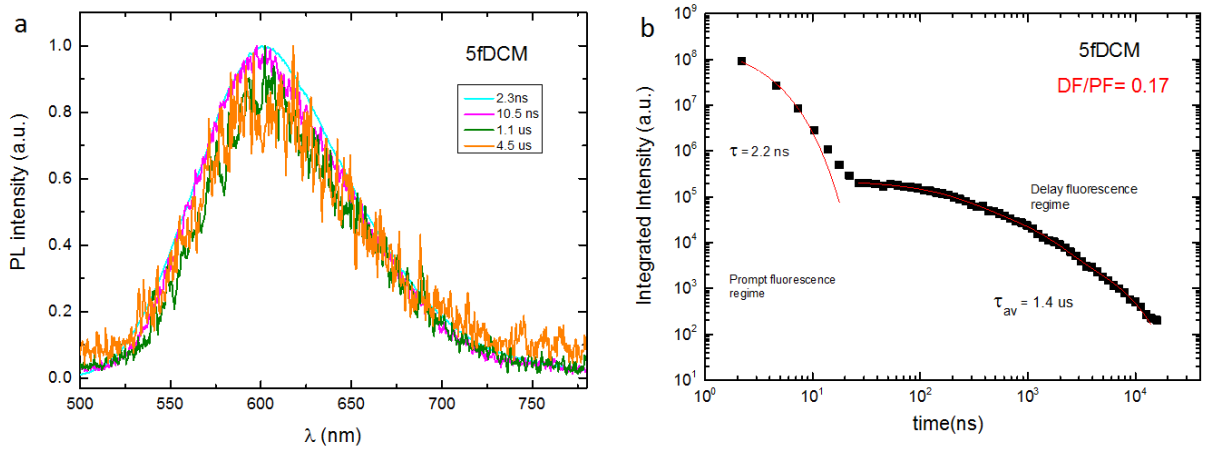


***Figure S26**: **a)** time-resolved emission spectra of **5**fDCM at room temperature (RT); **b)** decay curve of **5**fDCM at RT. λ_{ex}= 355 nm.*

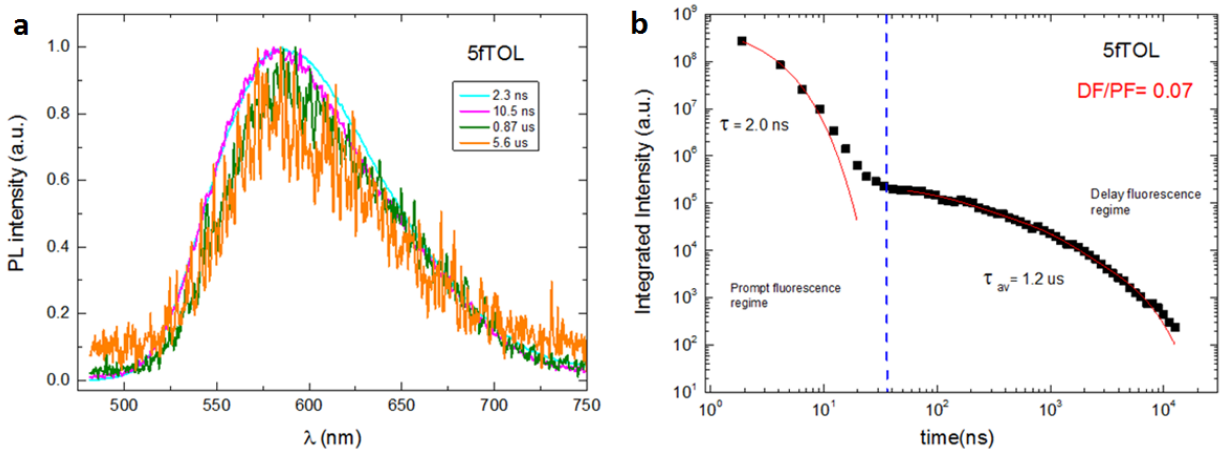


***Figure S27**: **a)** time-resolved emission spectra of **5**fTOL at room temperature (RT); **b)** decay curve of **5**fTOL at RT. λ_{ex}= 355 nm.*

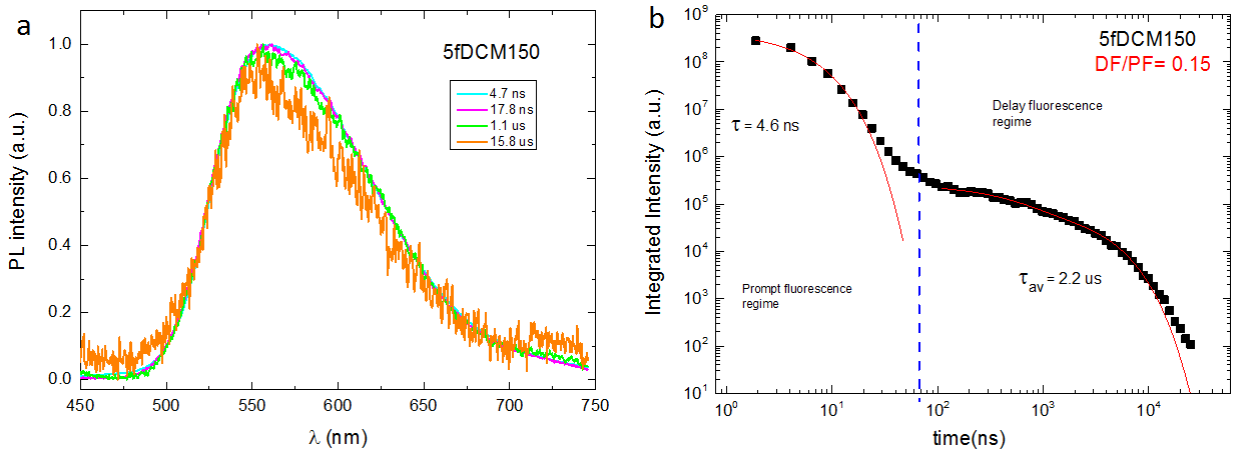


***Figure S28**: **a)** time-resolved emission spectra of **5**fDCM150 at room temperature (RT); **b)** decay curve of **5**fDCM150 at RT. λ_{ex}= 355 nm.*

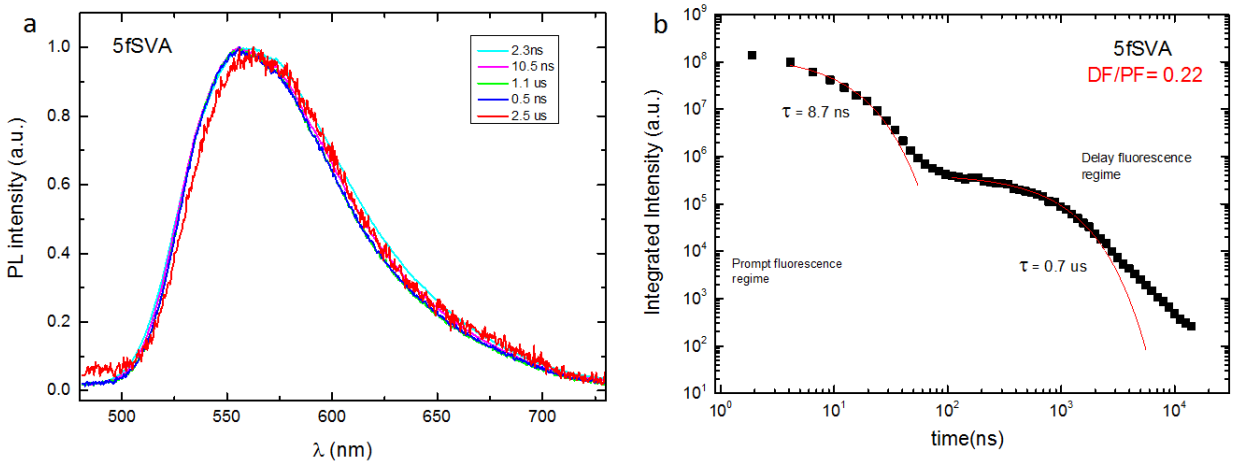


***Figure S29**: **a)** time-resolved emission spectra of **5**fSVA at room temperature (RT); **b)** decay curve of **5**fSVA at RT. λ_{ex}= 355 nm.*

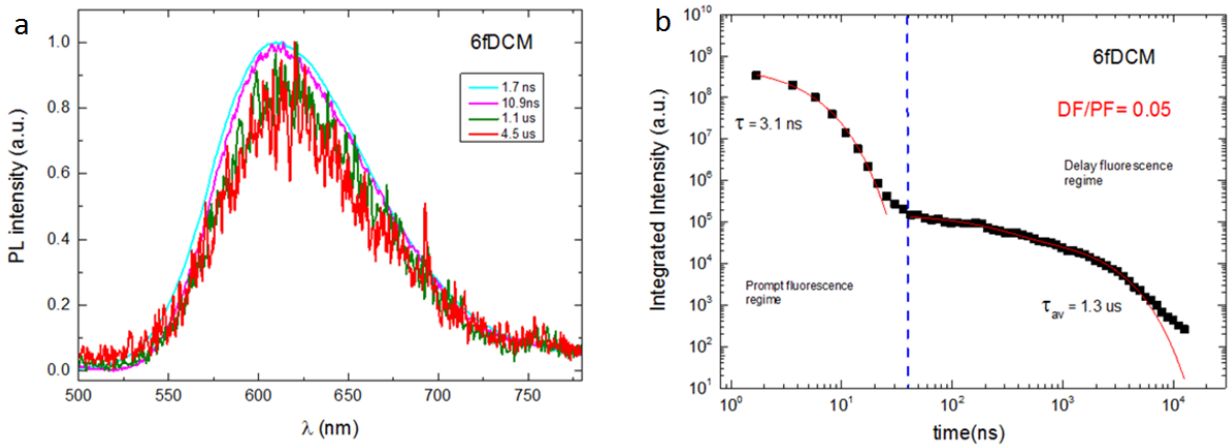


***Figure S30**: **a)** time-resolved emission spectra of **6**fDCM at room temperature (RT); **b)** decay curve of **6**fDCM at RT. λ_{ex}= 355 nm.*

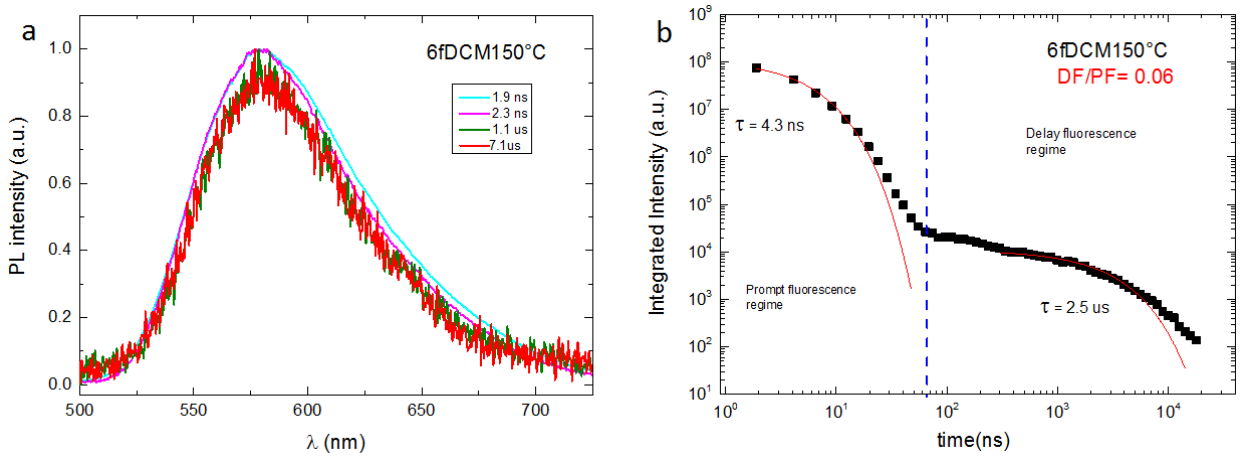


***Figure S31**: **a)** time-resolved emission spectra of **6**fDCM150° at room temperature (RT); **b)** decay curve of **6**fDCM150° at RT. λ_{ex}= 355 nm.*

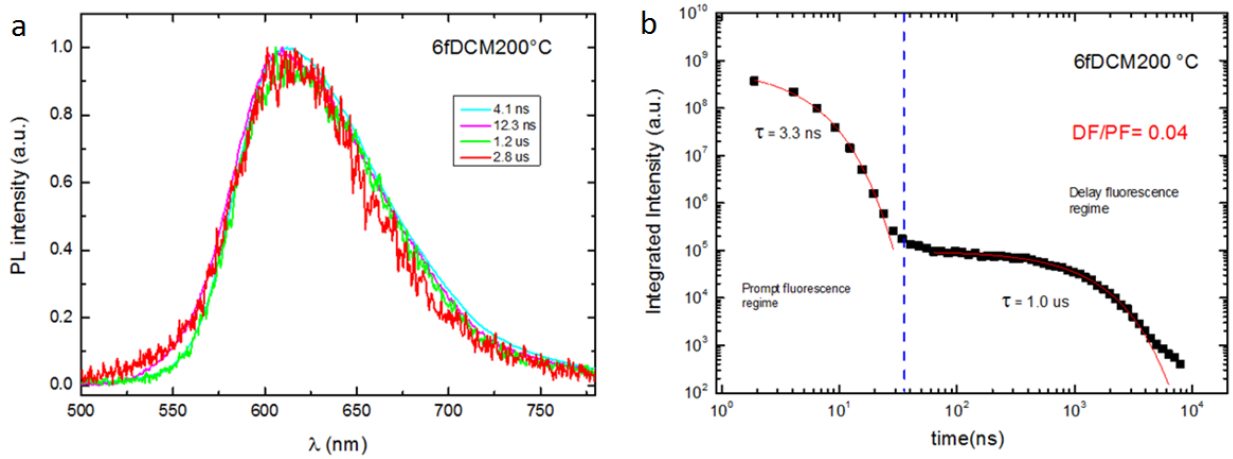


***Figure S32**: **a)** time-resolved emission spectra of **6**fDCM200 at room temperature (RT); **b)** decay curve of **6**fDCM200 at RT. λ_{ex}= 355 nm.*

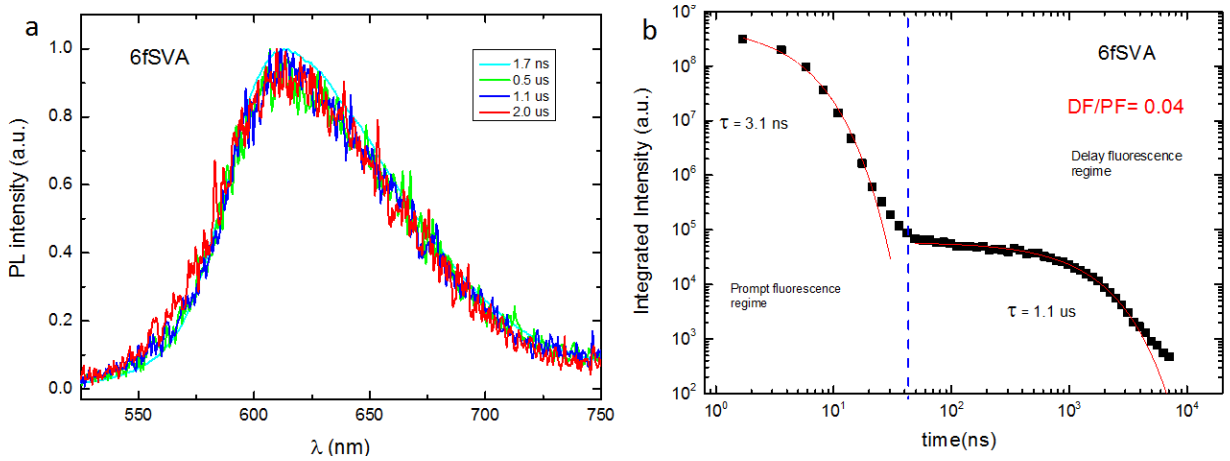


***Figure S33**: **a)** time-resolved emission spectra of **6**fSVA at room temperature (RT); **b)** decay curve of **6**fSVA at RT. λ_{ex}= 355 nm.*

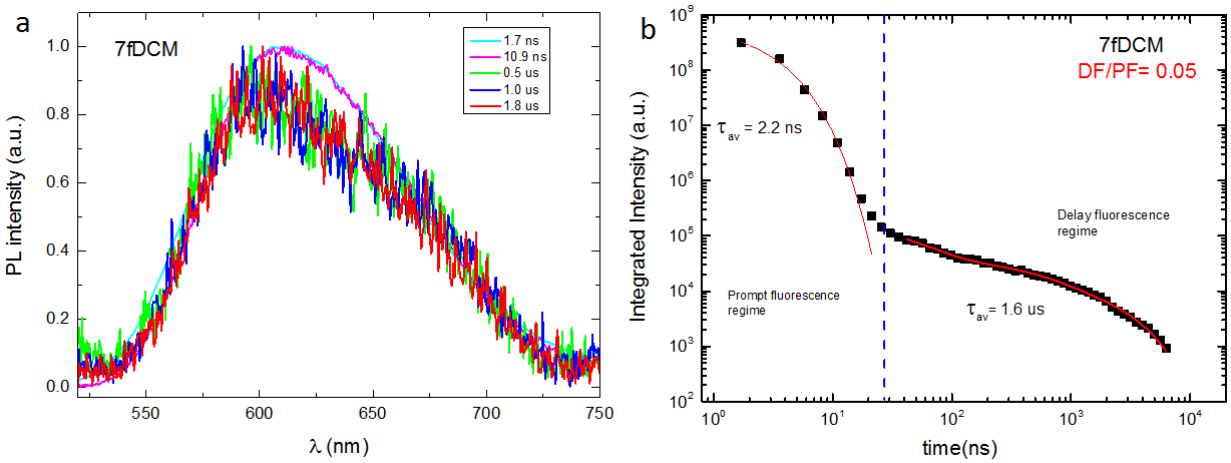


***Figure S34**: **a)** time-resolved emission spectra of **7**fDCM at room temperature (RT); **b)** decay curve of **7**fDCM at RT. λ_{ex}= 355 nm.*

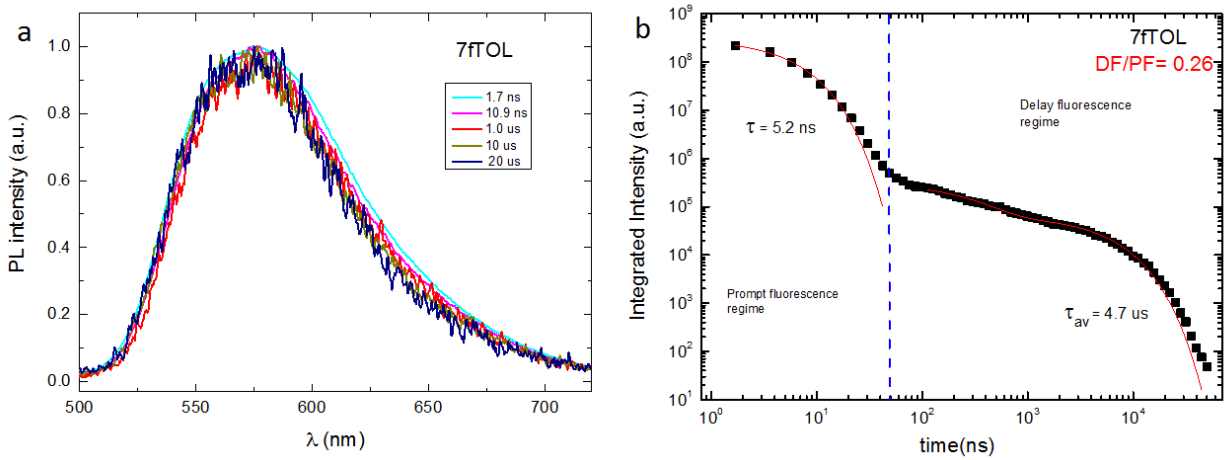


***Figure S35**: **a)** time-resolved emission spectra of **7**fTOL at room temperature (RT); **b)** decay curve of **7**fTOL at RT. λ_{ex}= 355 nm.*

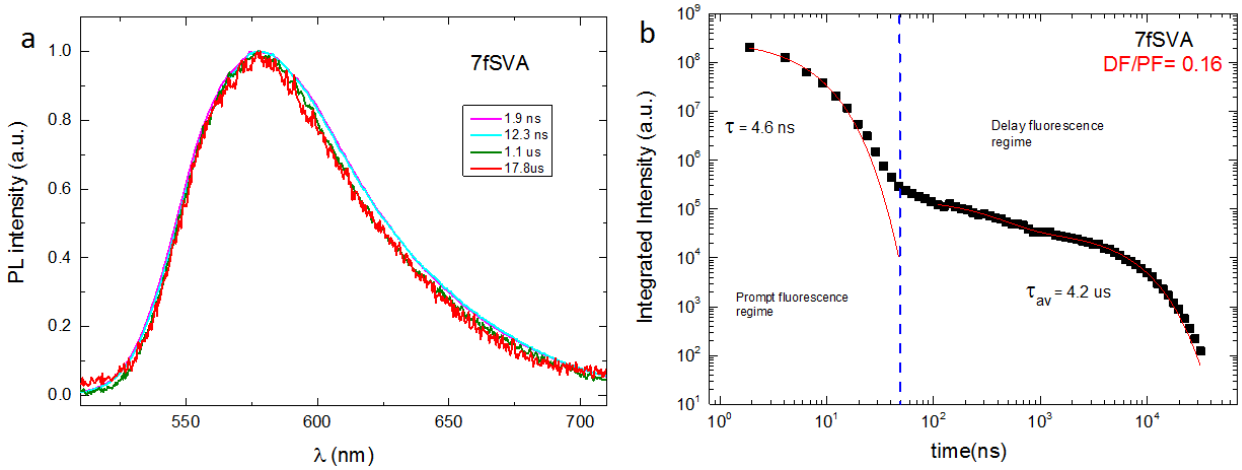


***Figure S36**: **a)** time-resolved emission spectra of **7**fSVA at room temperature (RT); **b)** decay curve of **7**fSVA at RT. λ_{ex}= 355 nm.*

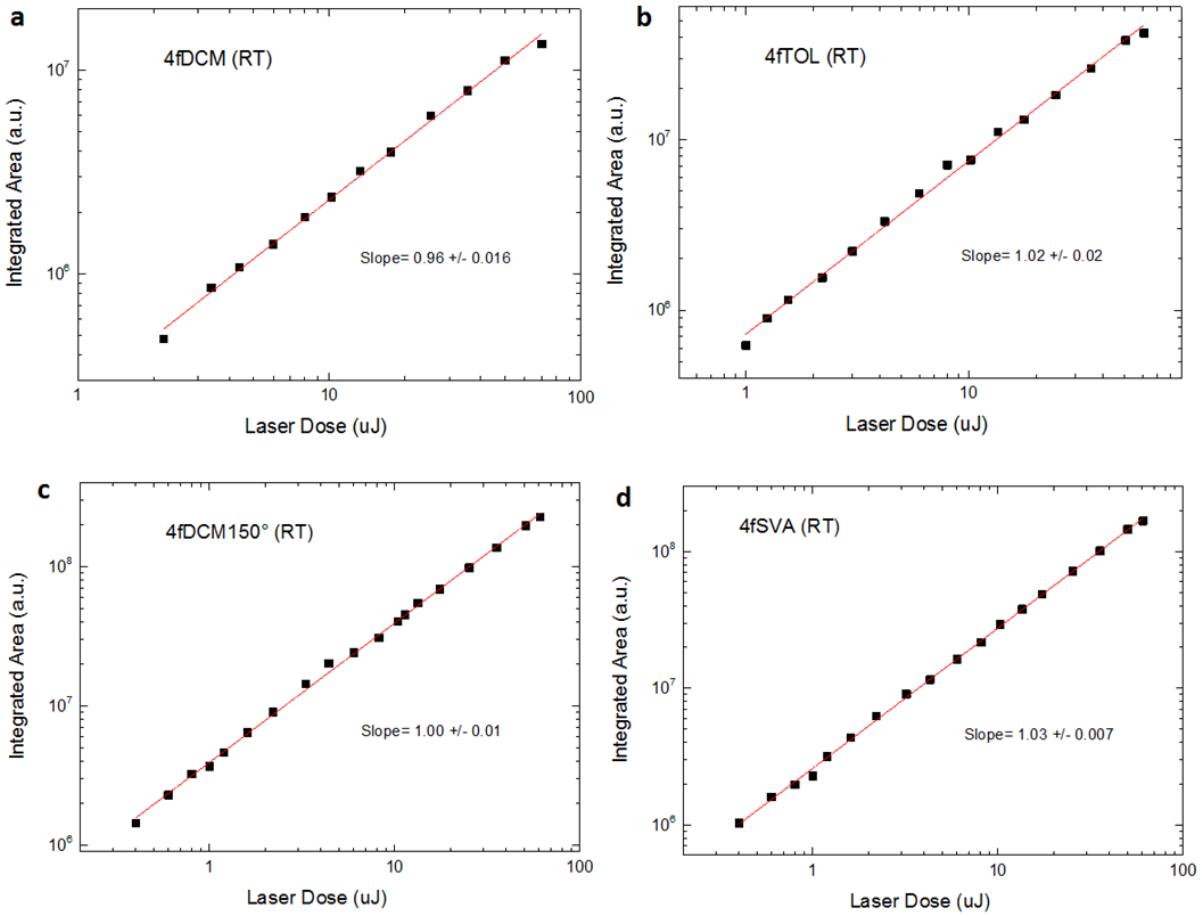


***Figure S37**: Power dependence of the integrated delayed fluorescence at room temperature for the different samples: **a) 4**fDCM, **b) 4**fTOL, **c) 4**fDCM150, **d) 4**fSVA**.** λ_{ex}= 337 nm.*

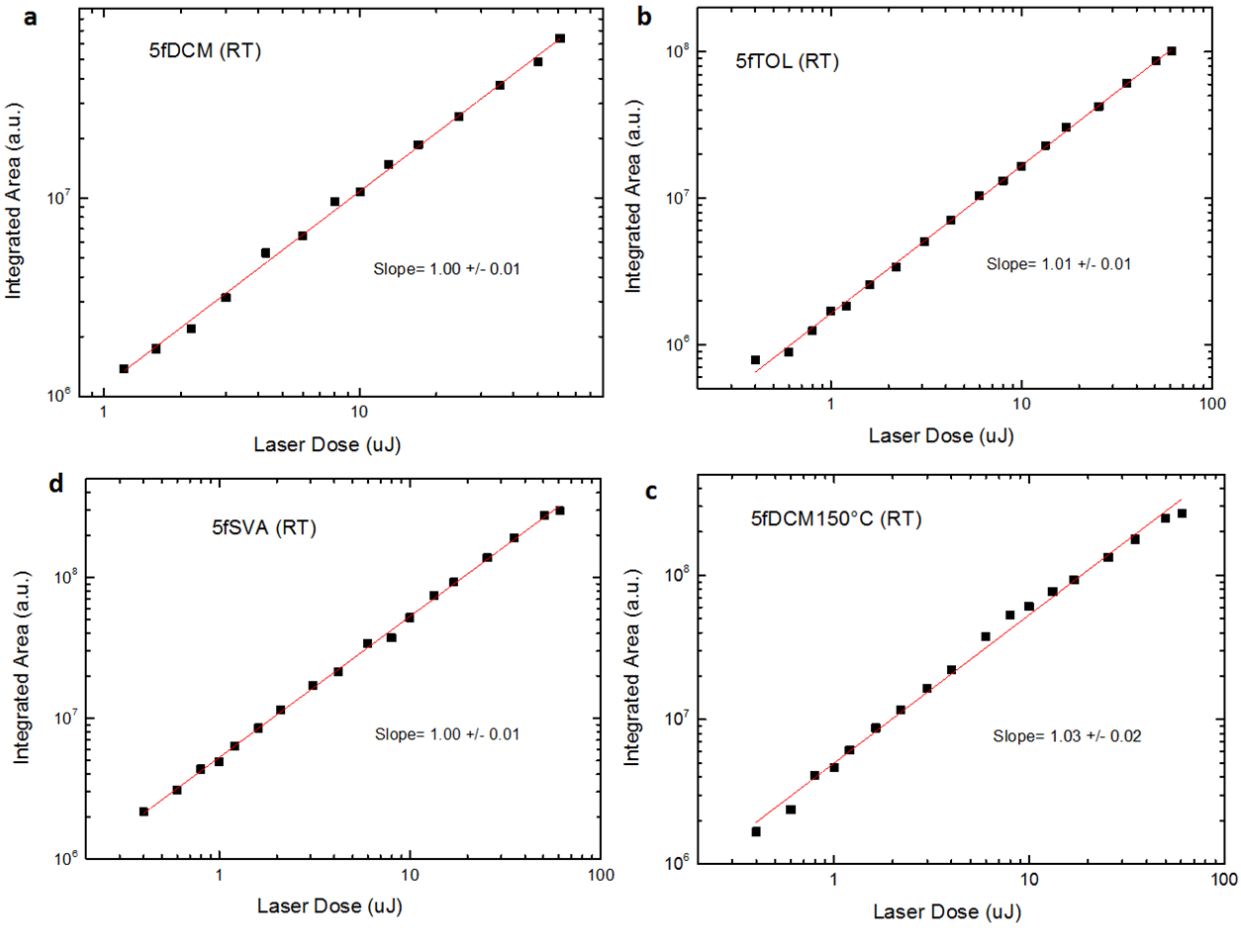


***Figure S38**: Power dependence of the integrated delayed fluorescence at room temperature for the different samples: **a) 5**fDCM, **b) 5**fTOL, **c) 5**fDCM150, **d) 5**fSVA. λ_{ex}= 337 nm.*

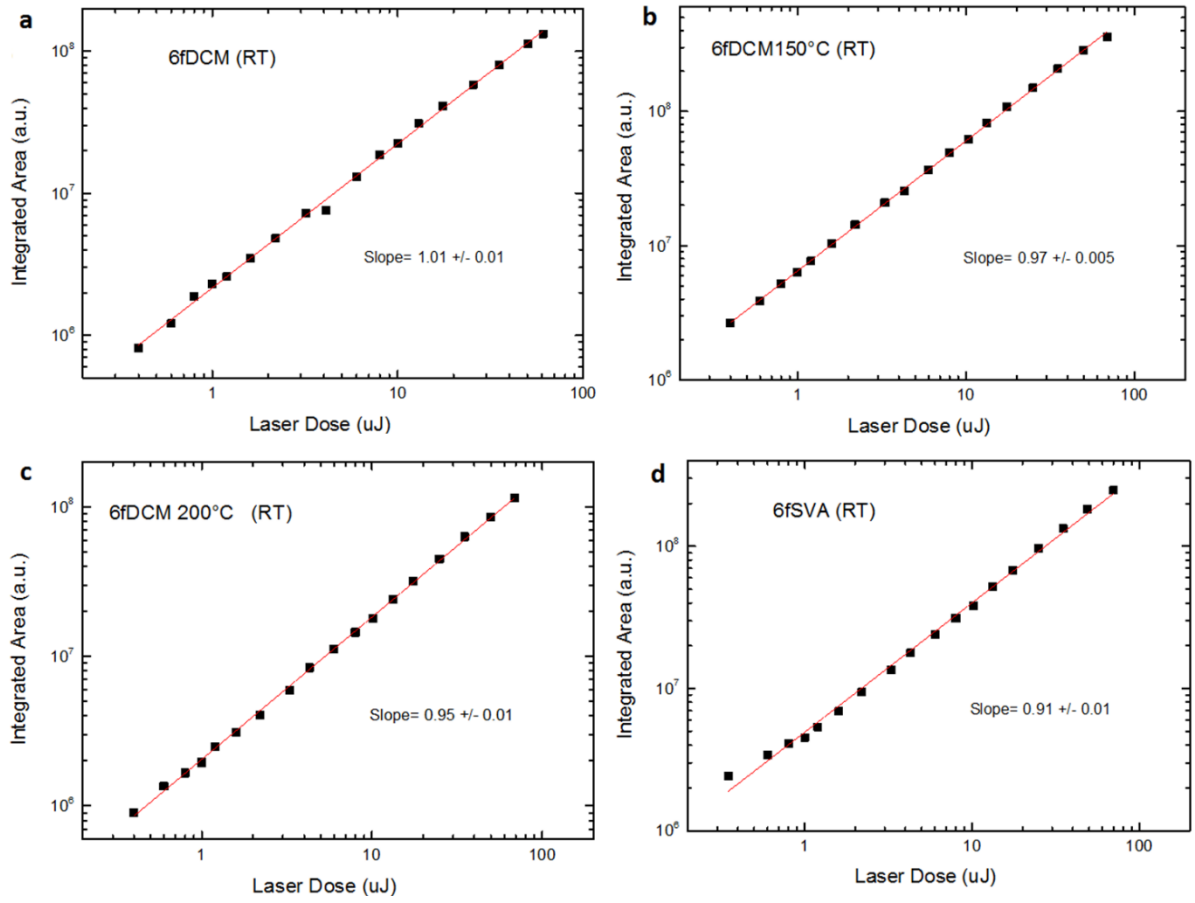


Figure S39*: Power dependence of the integrated delayed fluorescence at room temperature for the different samples:* ***a) 6****fDCM,* ***b) 6****fDCM150,* ***c) 6****fDCM200,* ***d) 6****fSVA.* λ_{ex}*= 337 nm.*

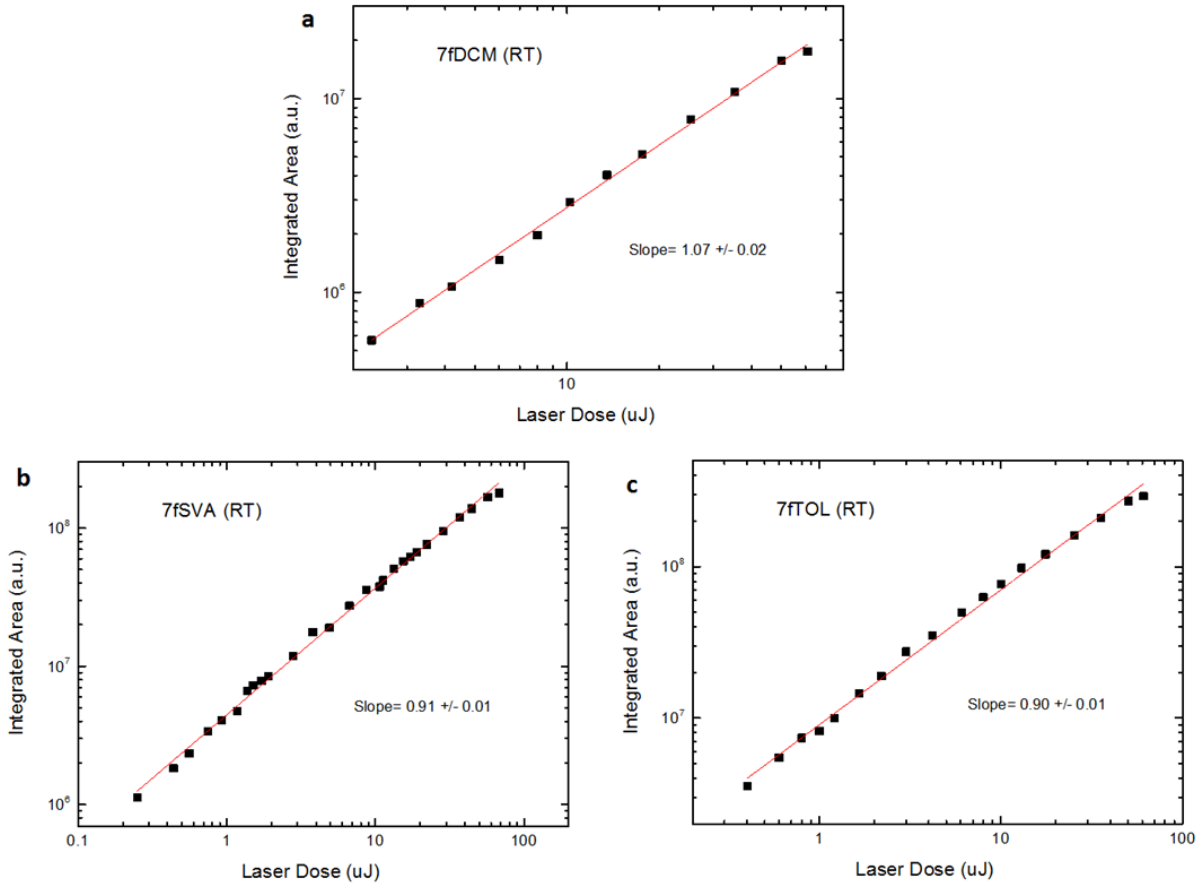


***Figure S40**: Power dependence of the integrated delayed fluorescence at room temperature for the different samples: **a) 7**fSVA, **b) 7**fDCM, **c) 7**fTOL. λ_{ex}= 337 nm.*

4. OLEDs CHARACTERIZATION

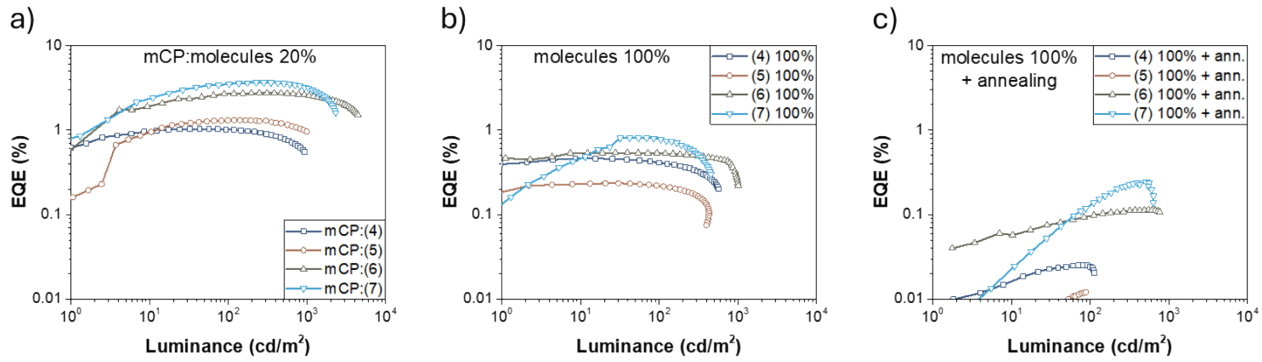


Figure S41*: External Quantum Efficiency (EQE) as a function of luminance for OLEDs with different emitting layers: a) mCP:molecules 20 w%; b) neat films (molecules 100%); c) annealed neat films.*

5. MECHANOCHROMIC LUMINESCENCE STUDY

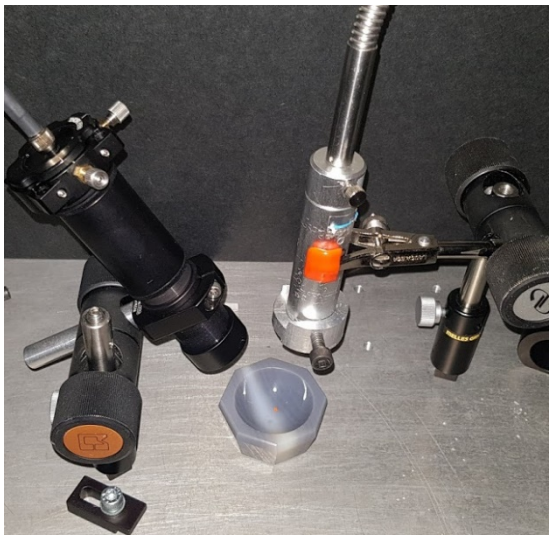


Figure S42*: Setup used for the mechanochromic luminescence study.*

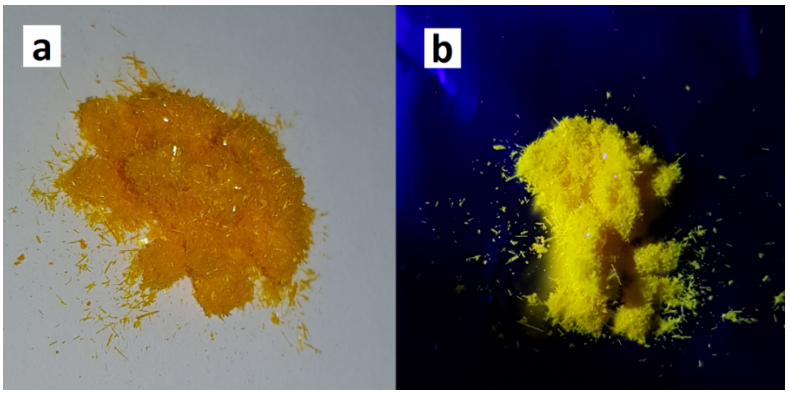


***Figure S43**: **a)** Photographs of **4** initial crystalline powder under natural lamp **b)** Photographs of **4** initial crystalline powder under UV lamp.*

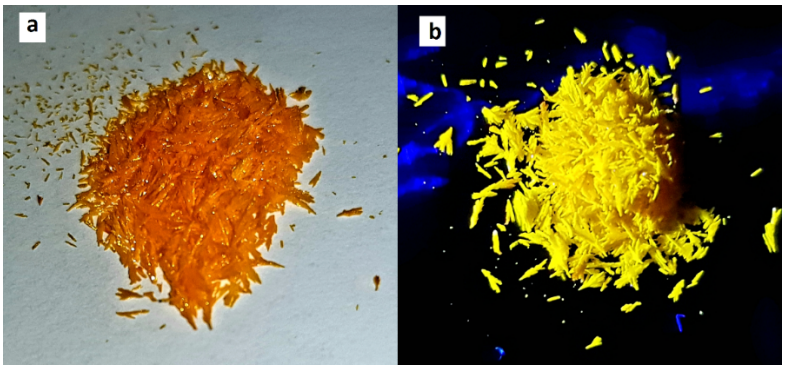


***Figure S44**: **a)** Photographs of **5** initial crystalline powder under natural lamp **b)** Photographs of **5** initial crystalline powder under UV lamp.*

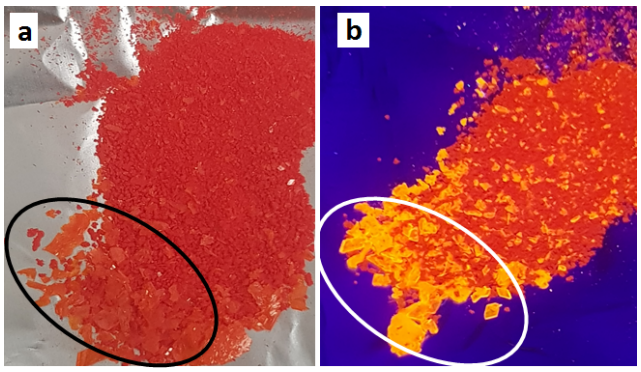


***Figure S45**: **a)** Photographs of **6** initial red crystalline powder and **6** initial orange crystals (circle) under natural lamp **b)** Photographs of **6** initial red crystalline powder and **6** initial orange crystals (circle) under UV lamp.*

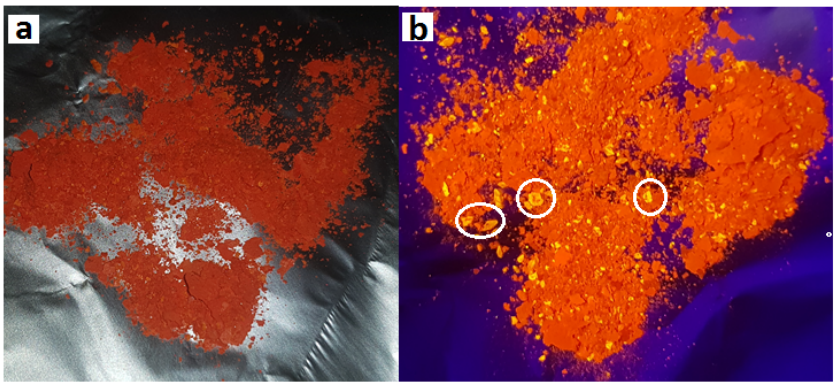


***Figure S46**: **a)** Photographs of **7** initial red powder and **7** initial orange crystalline powder under natural lamp **b)** Photographs of **7** initial red powder and orange **7** initial crystalline powder (circle) under UV lamp.*

Table S5: emission maxima of the samples deposited on Quartz detected with MCL setup and fluorimeter.

	MCL setup λ_{PL},nm	**Fluorimeter λ_{PL},nm**
4fSVA	577	561
6fSVA	626*	626
6fDCM150	600	598
6fDCM200	618	621
6fDCM	608*	612
7fSVA	607	600
7fTOL	585	585
7fDCM	622	620

* noisy spectra (extimated, λ_{PL})

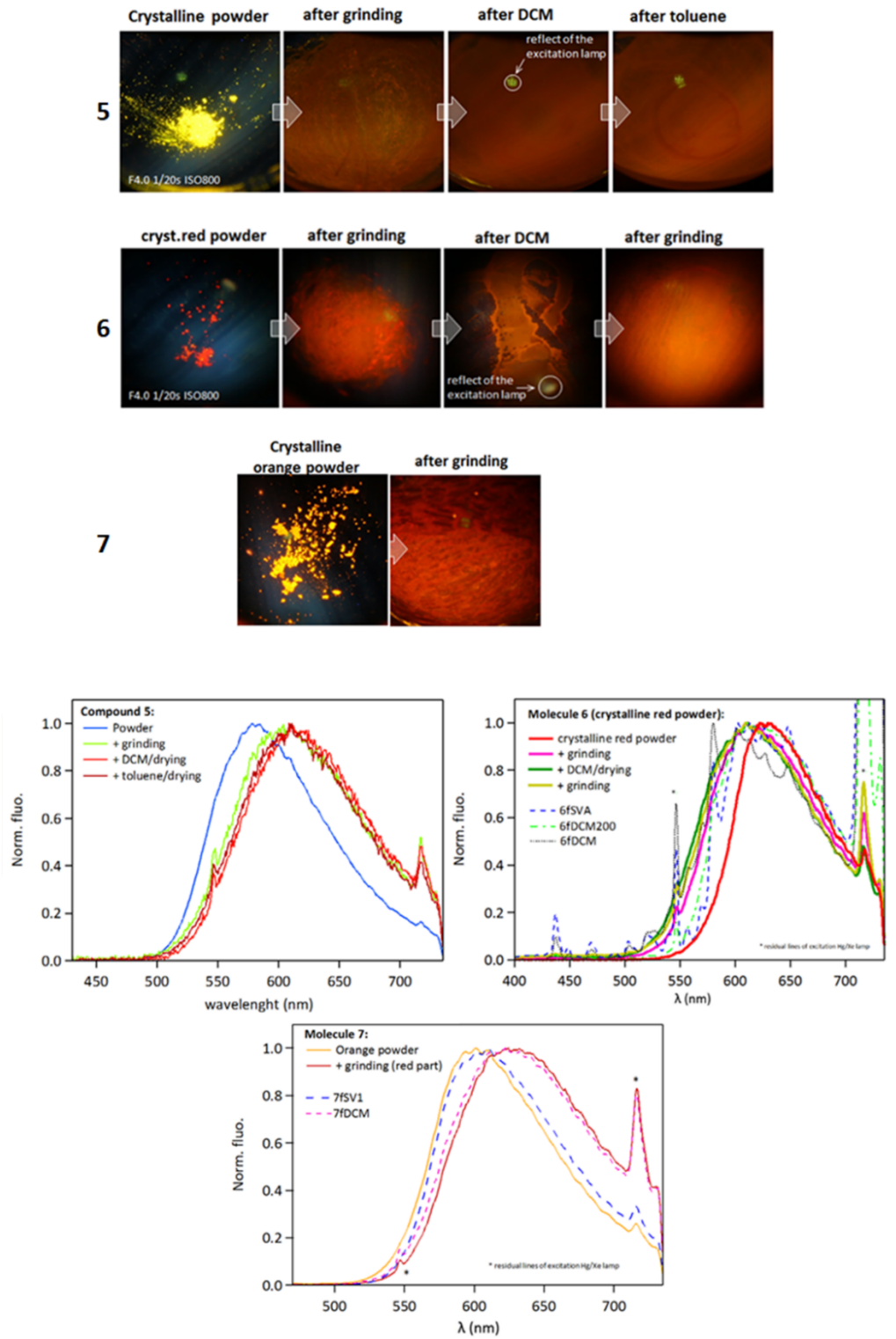


Figure S47*: MLC study for molecule* ***5****,* ***6*** *(red crystalline powder), and* ***7*** *(orange crystalline powder):* ***top)*** *photographs of various forms obtained during the MCL study (the photographs were taken at 365 nm excitation);* ***bottom)*** *PL spectra of the various forms studied in MCL study, and PL spectra of corresponding neat films obtained with the MCL setup.*