Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Designing of Rigid Cyclic Tripyrrins: The Importance of Intermolecular Interactions on Aggregation and Luminescence

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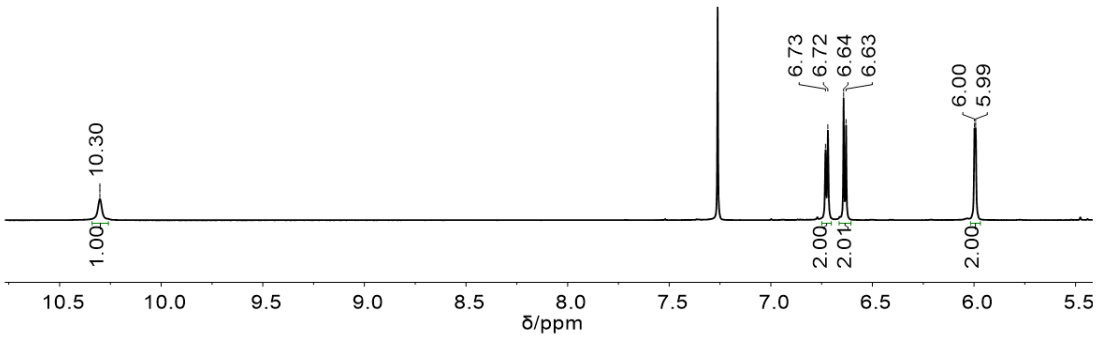

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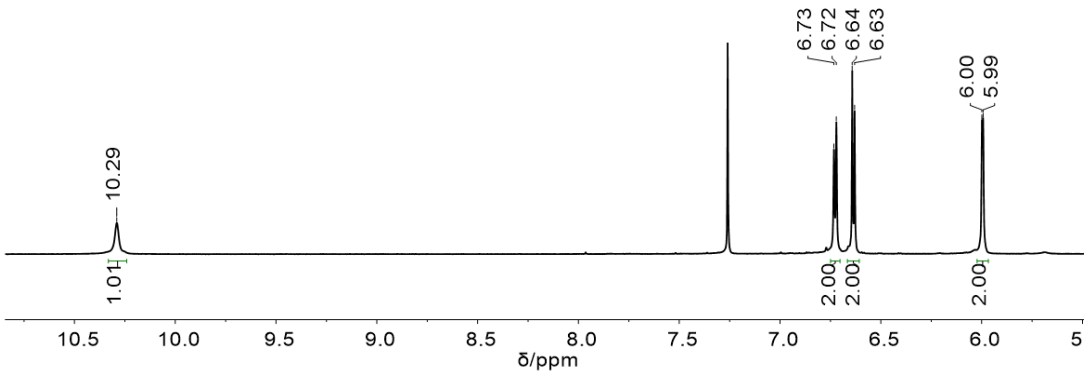

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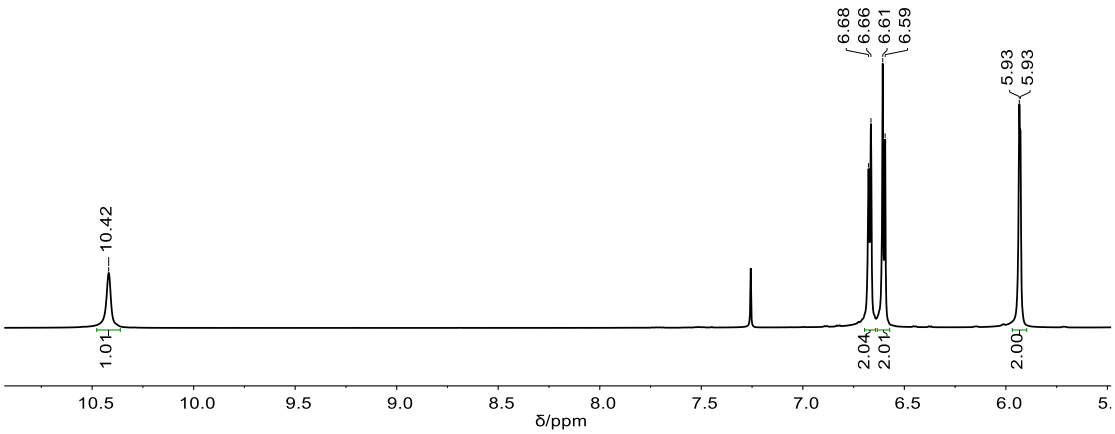

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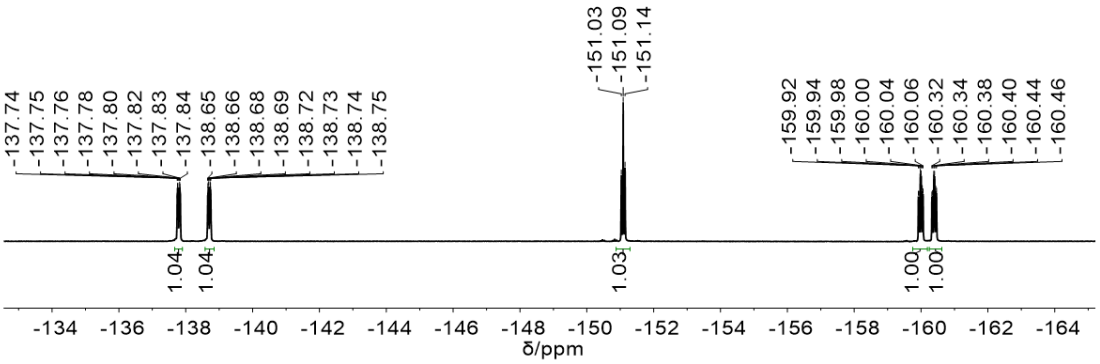

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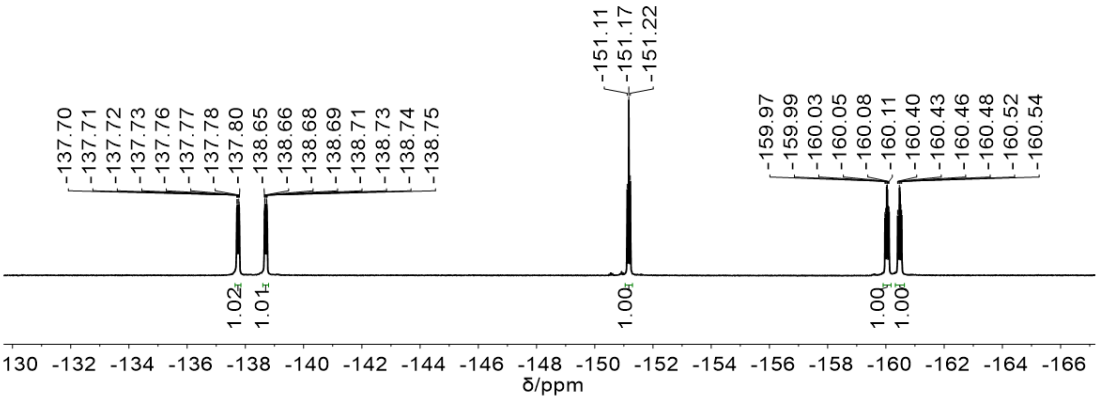

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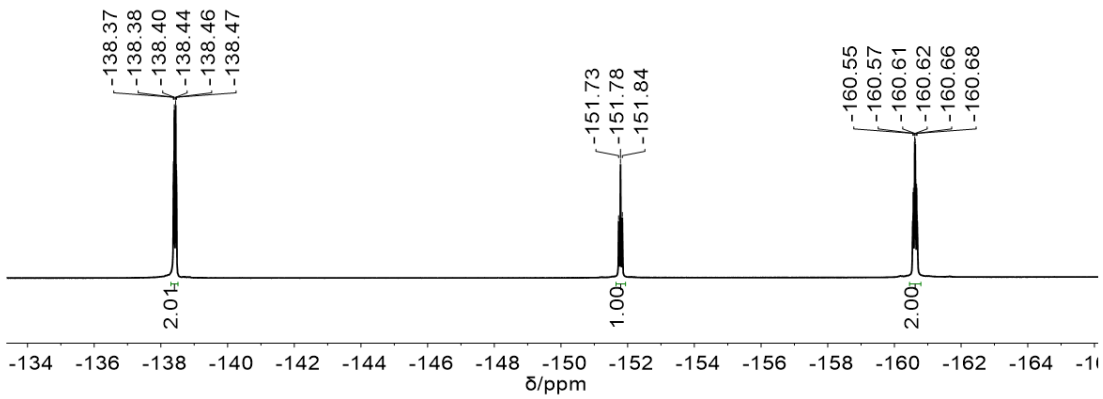

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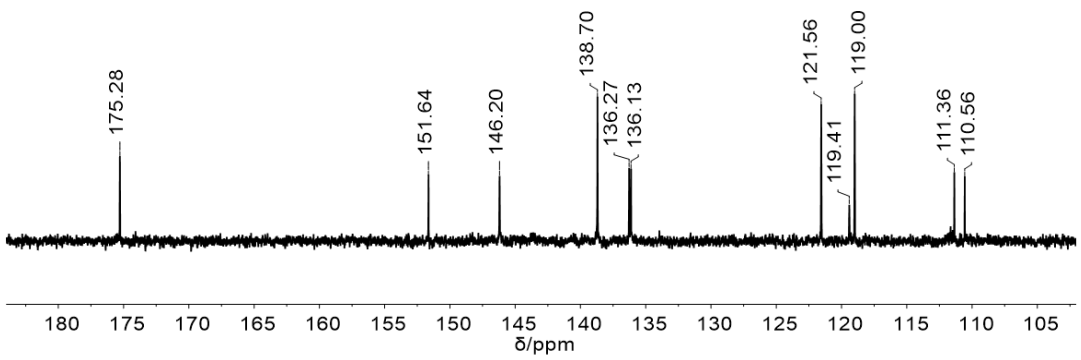

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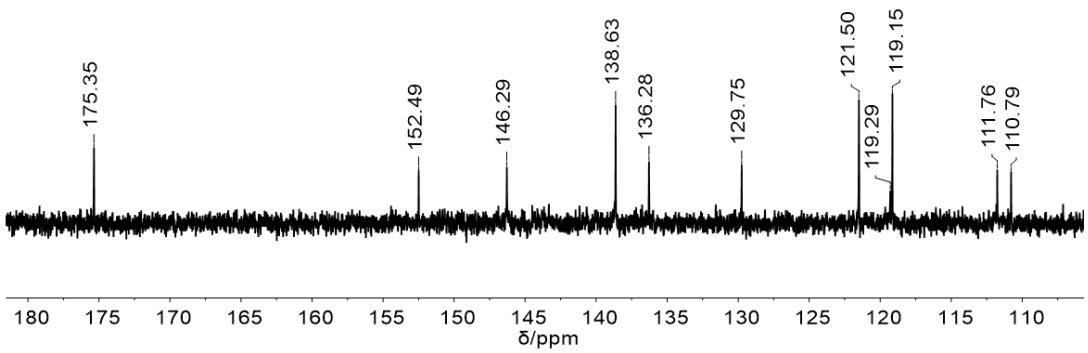

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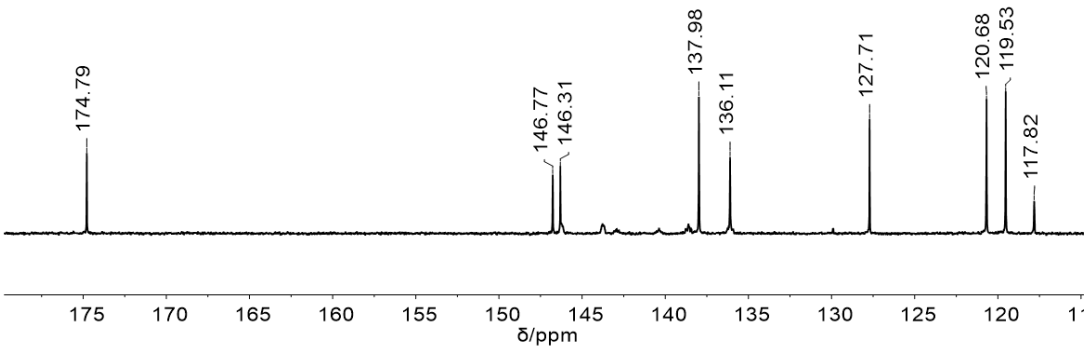

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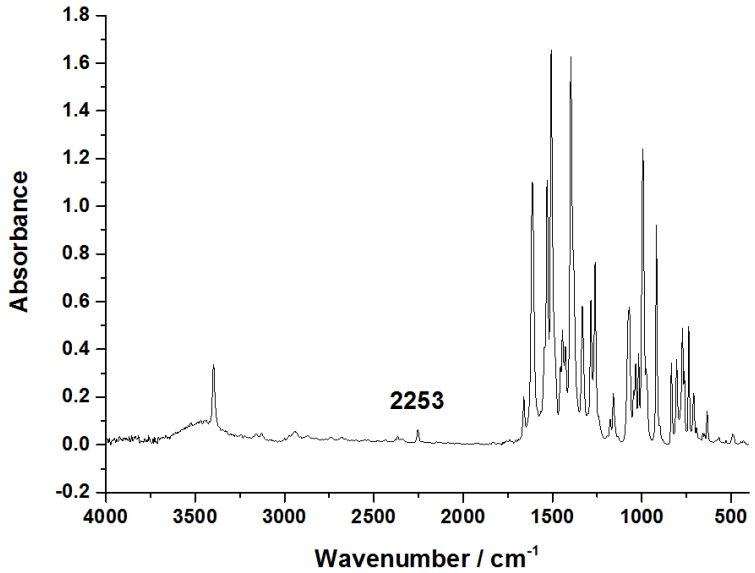

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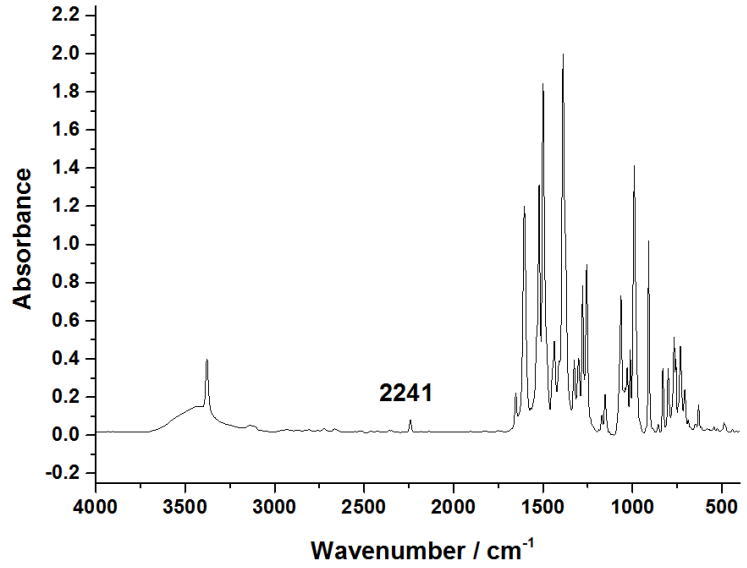

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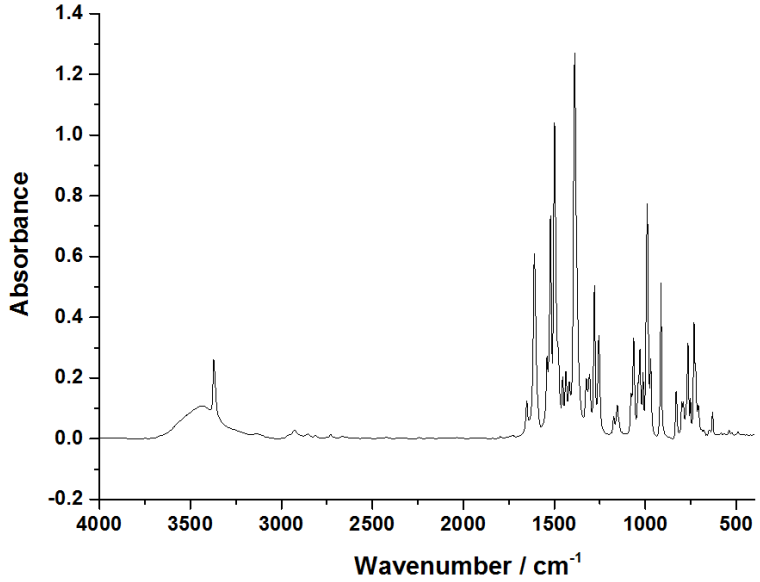

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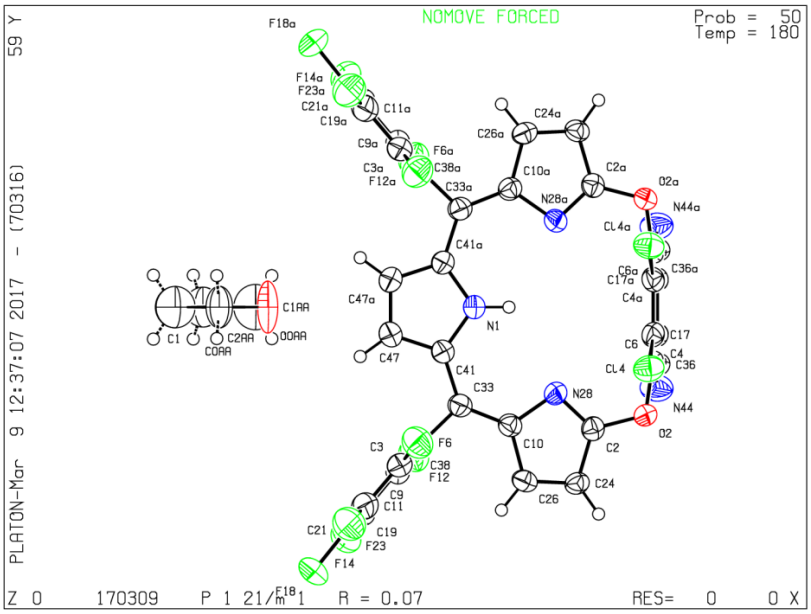

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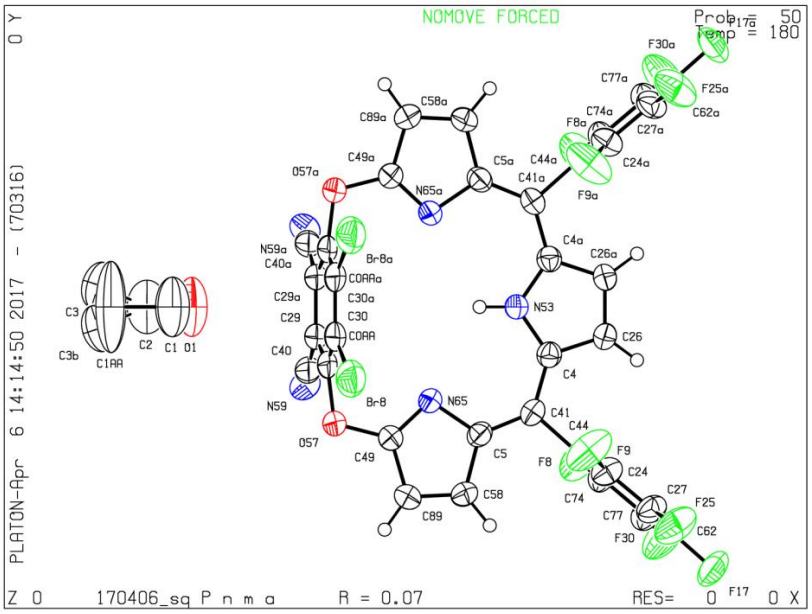

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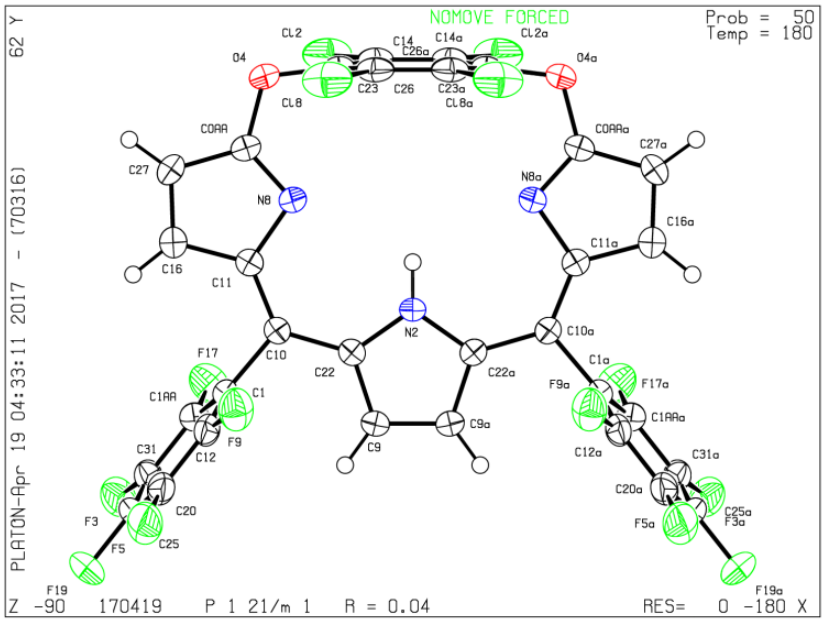

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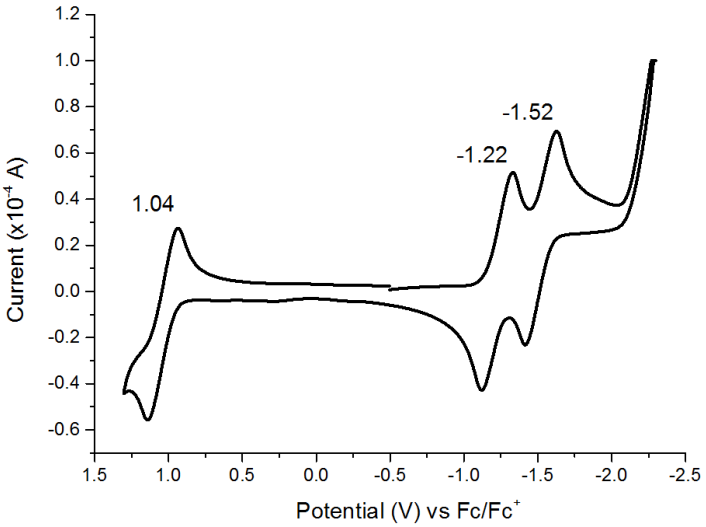

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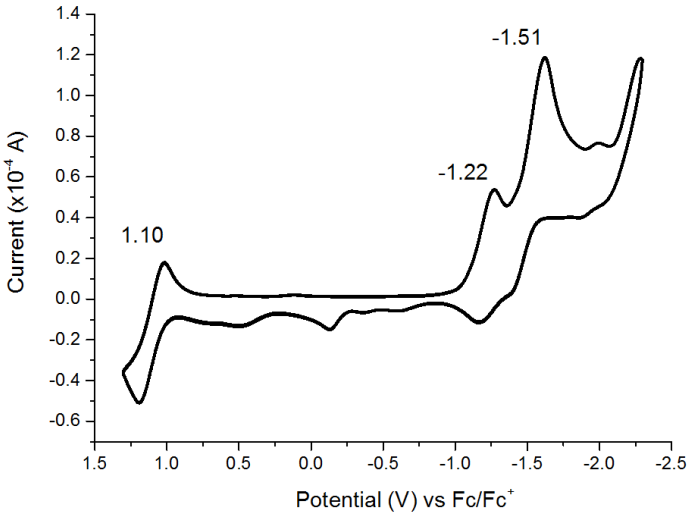

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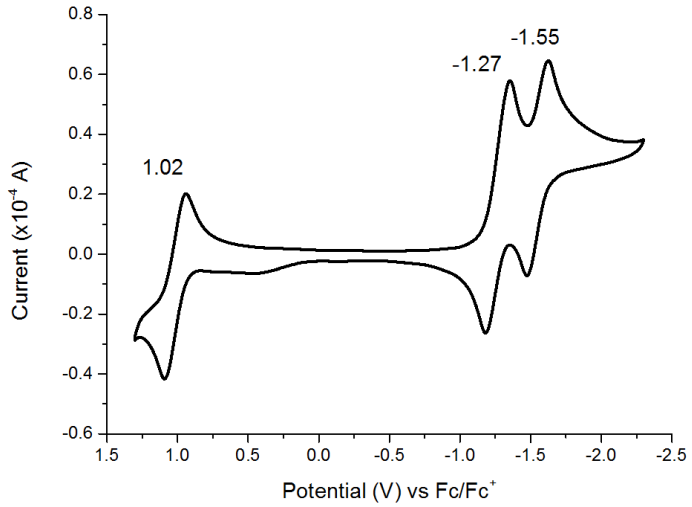

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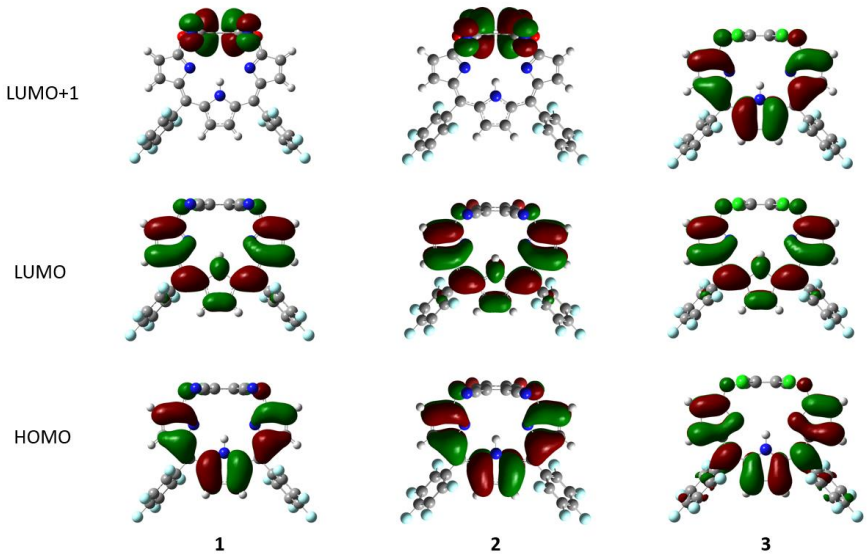

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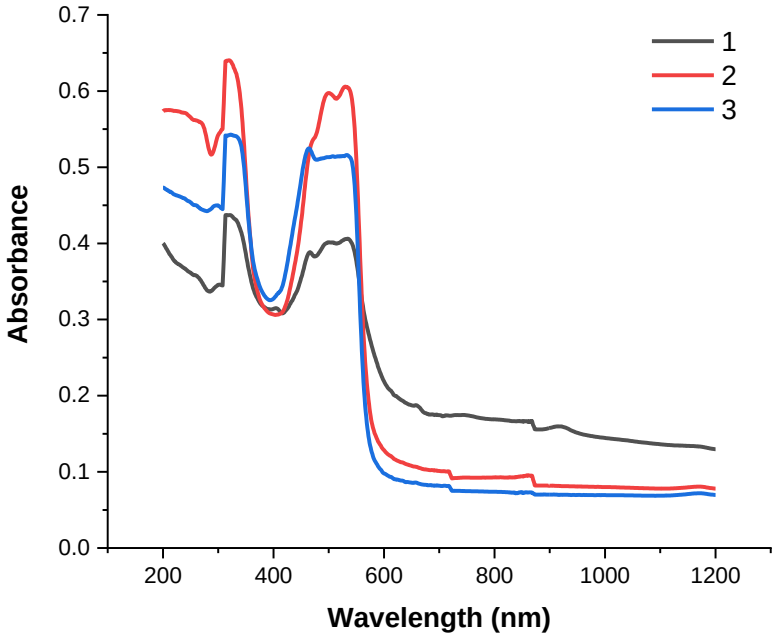

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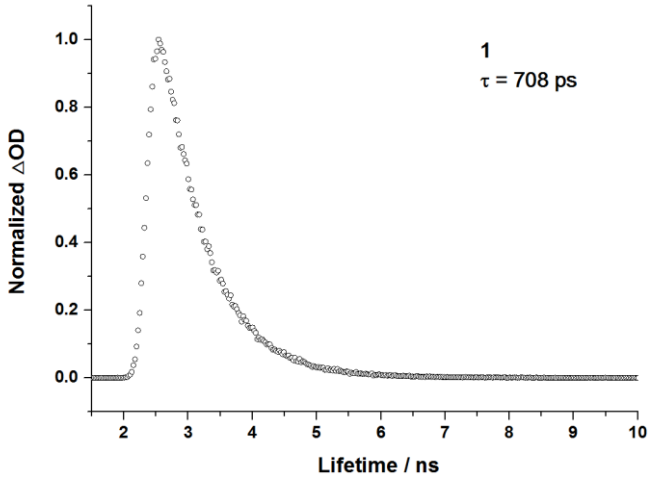

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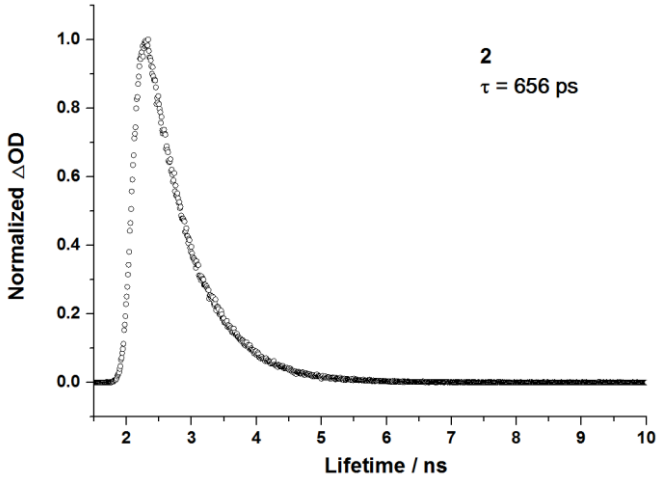

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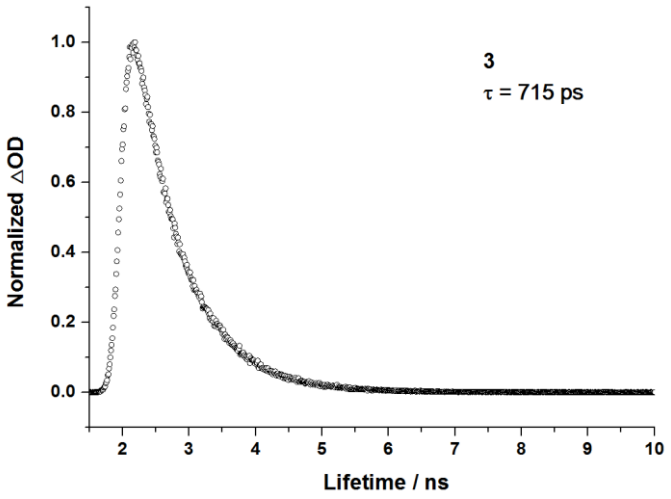

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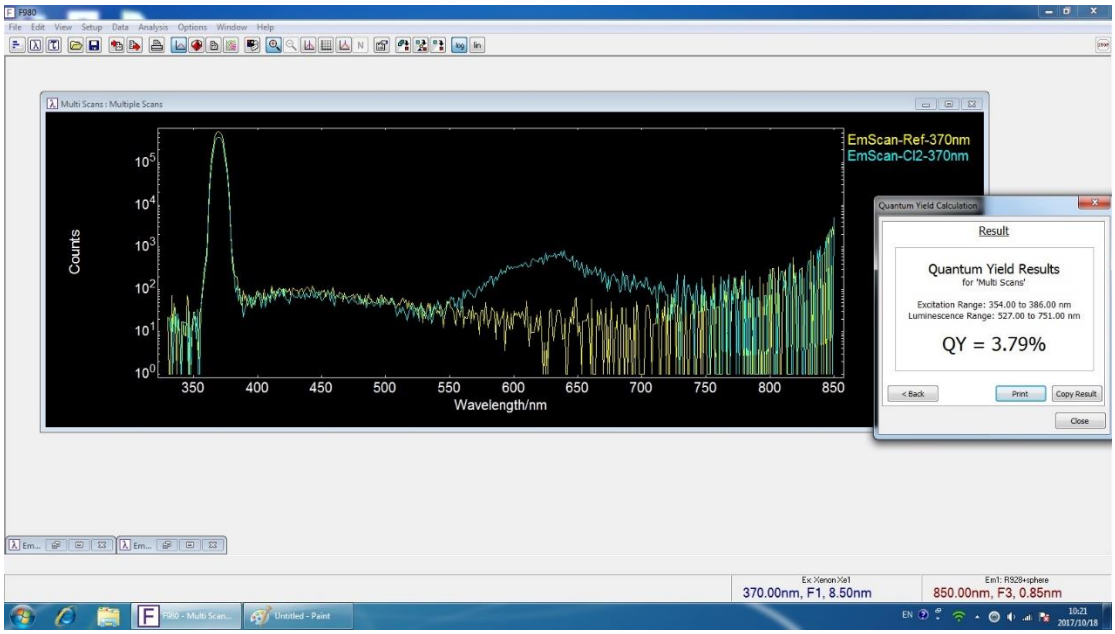

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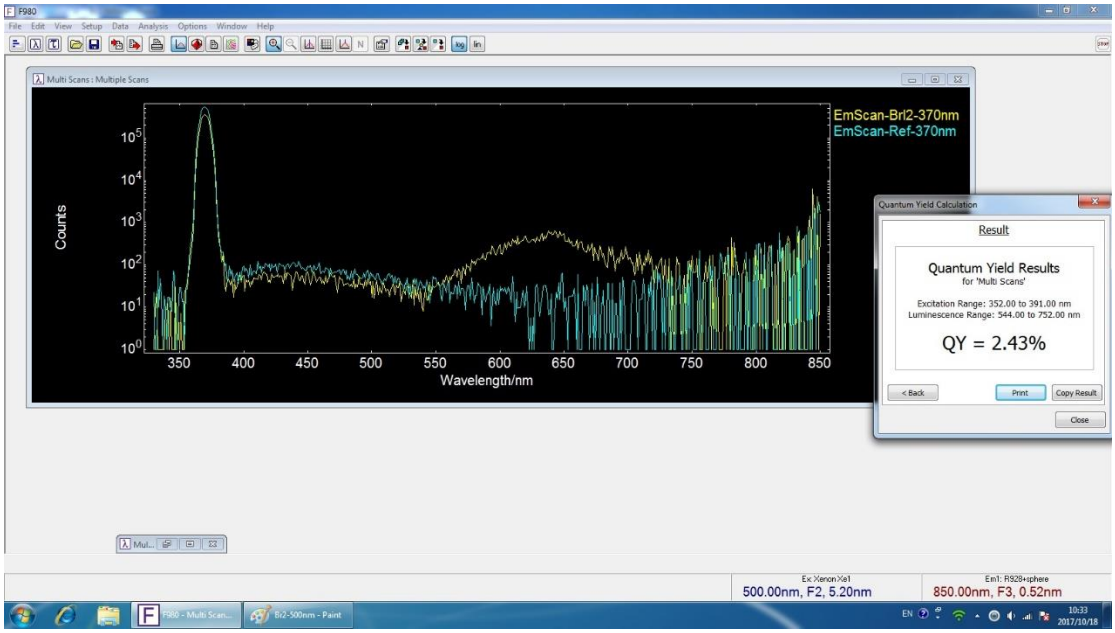

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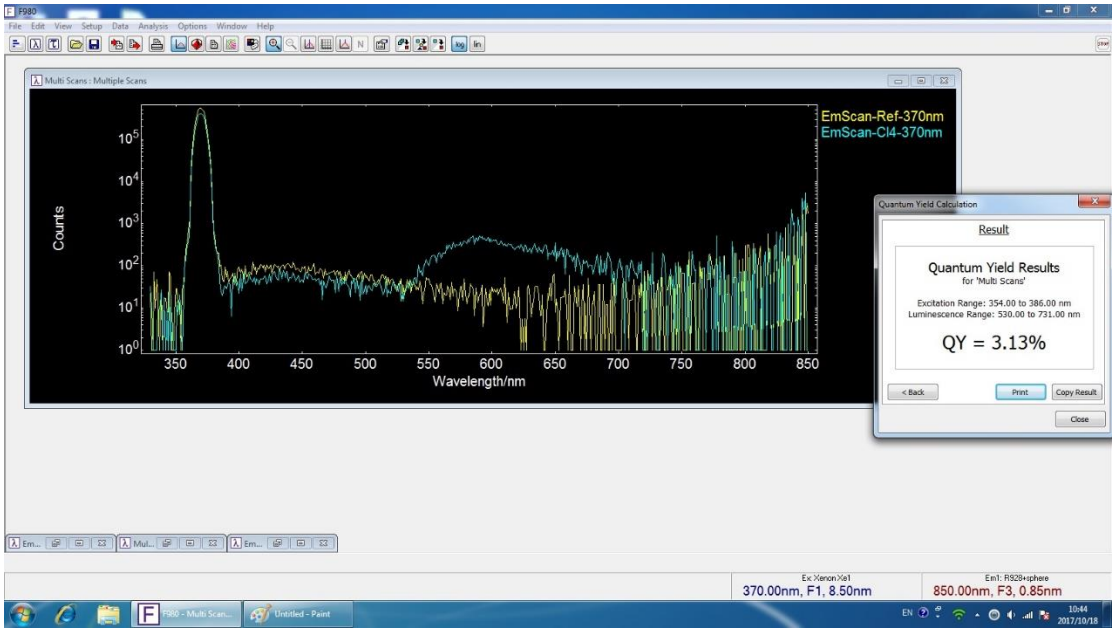

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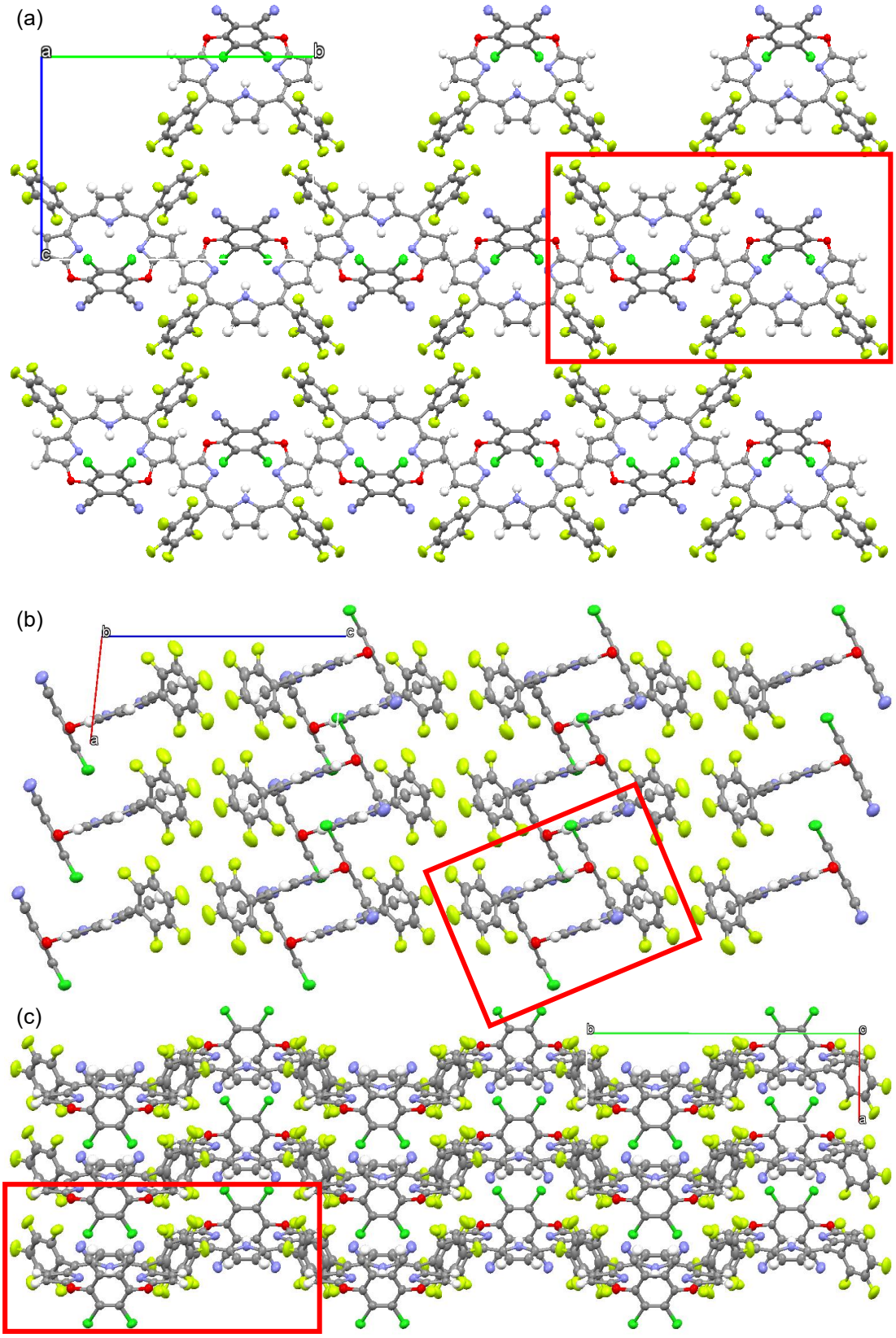

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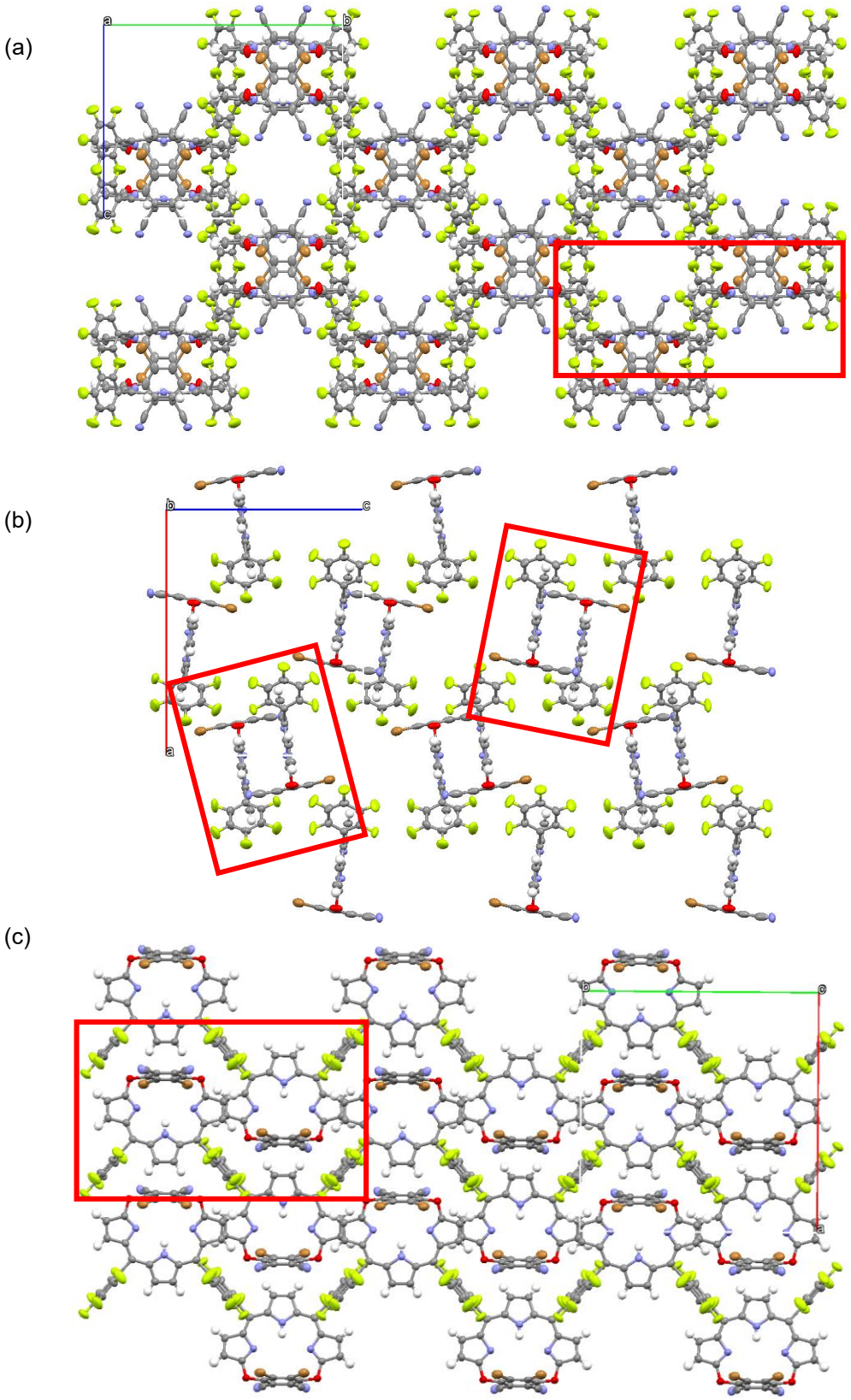


Figure S28 Crystal packing of **2** along the (a) *a*, (b) *b* and (c) *c* directions with J-dimer in red box.

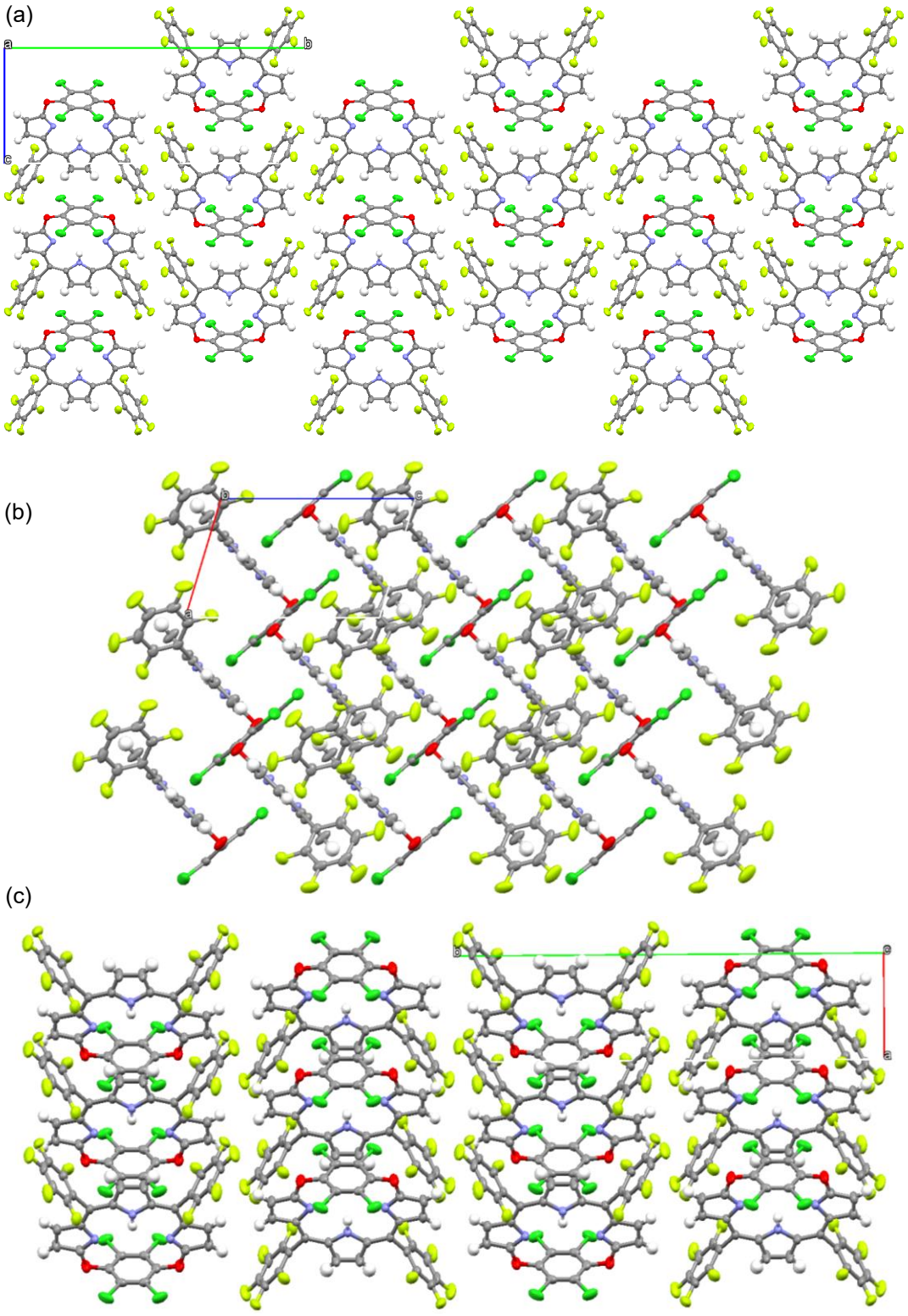
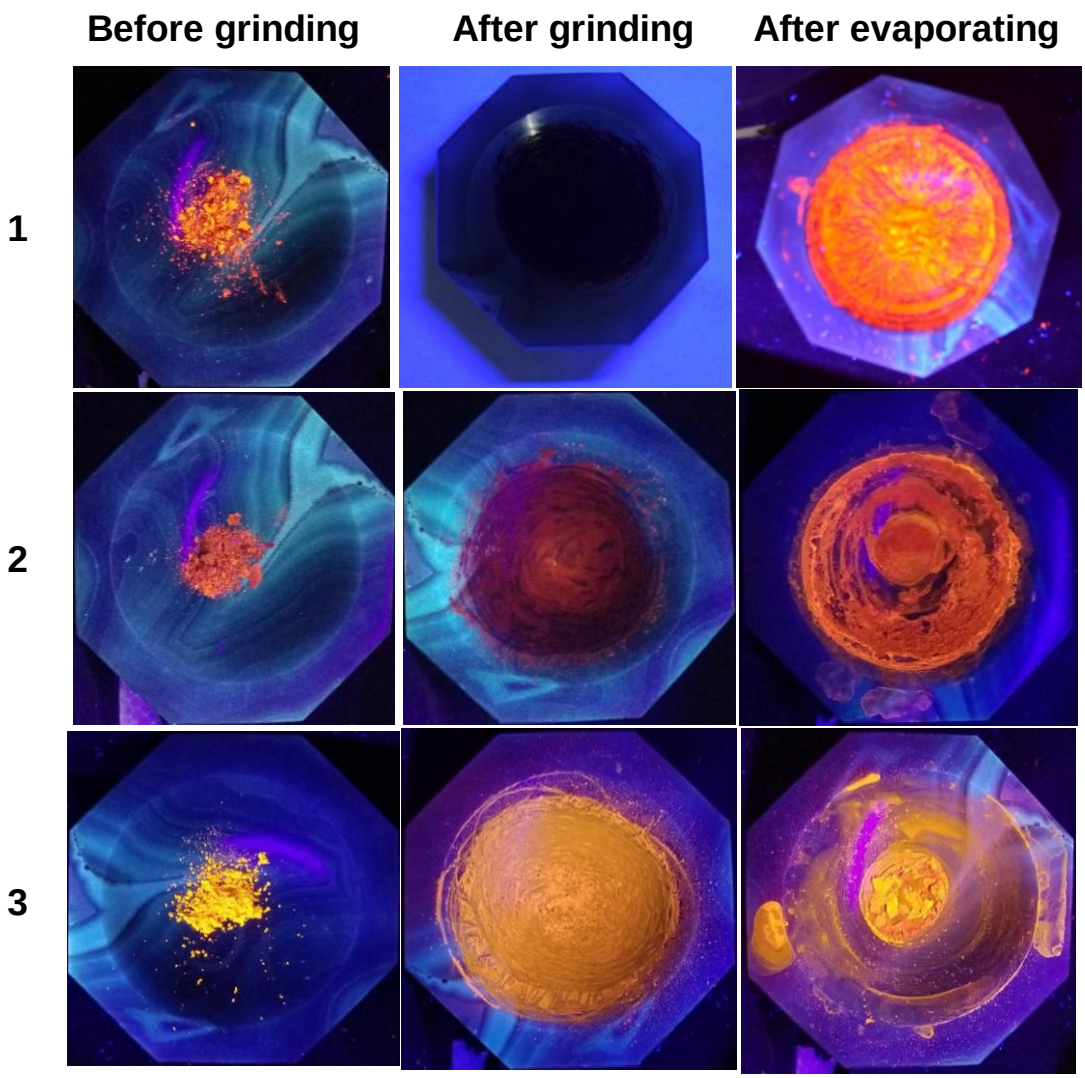


Figure S29 Crystal packing of **3** along the (a) *a*, (b) *b* and (c) *c* directions.



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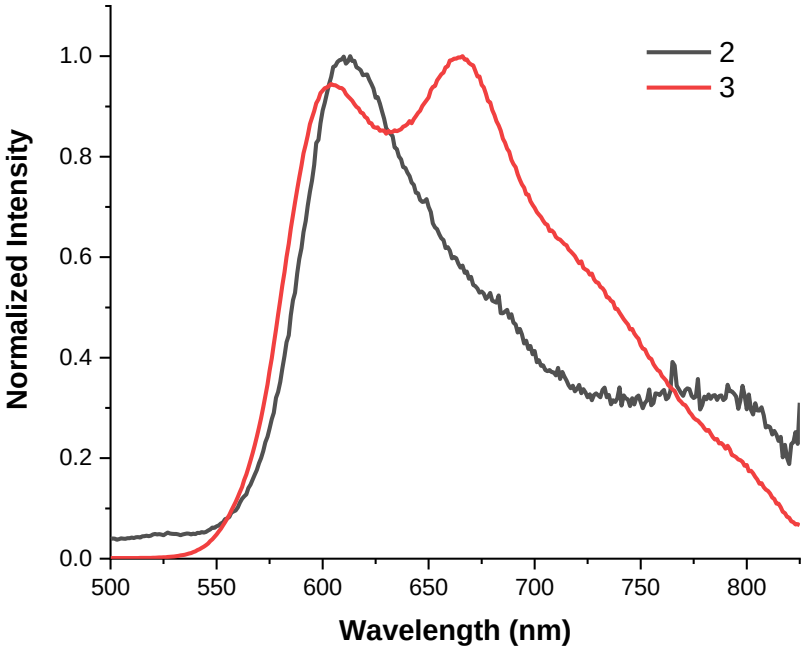


Figure S31 Normalized emission spectra of **2**-**3** in amorphous state.

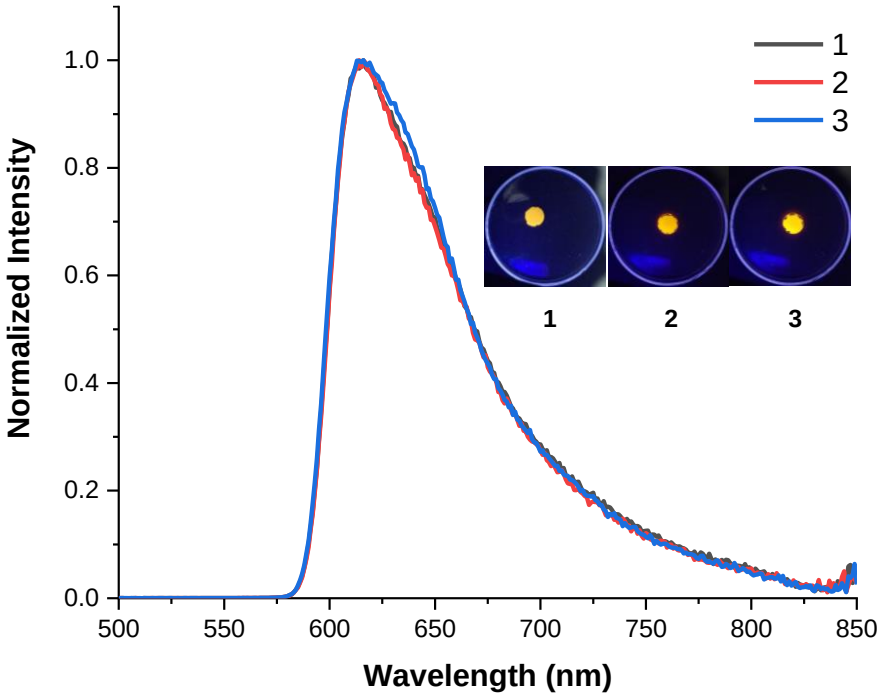
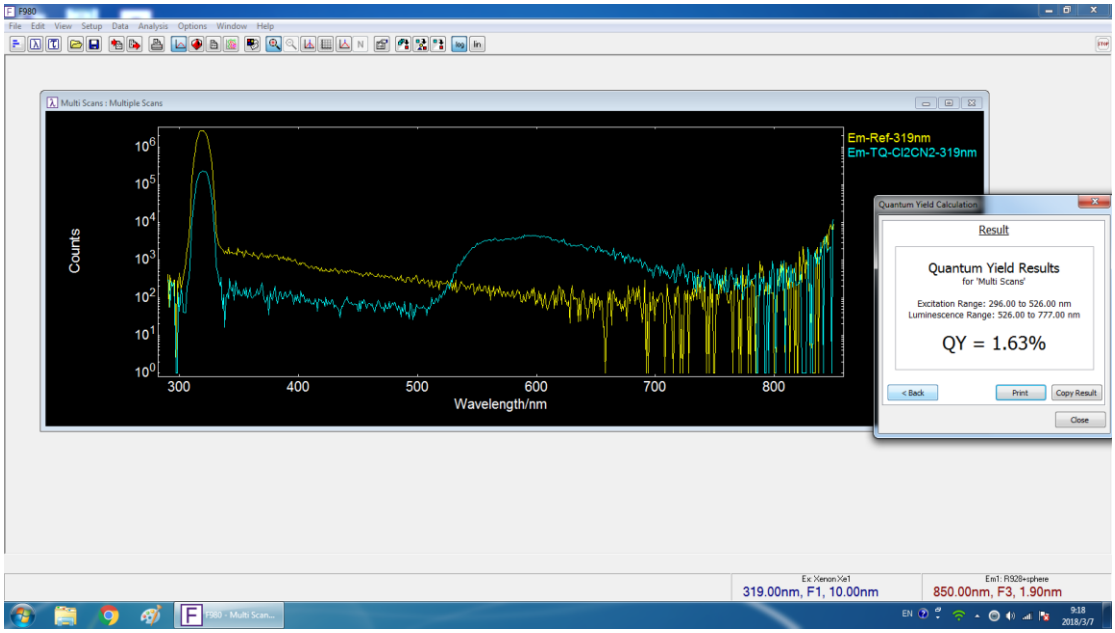


Figure S32 Normalized emission spectra of **1**-**3** in PMMA films. Insert: photograph taken under the 365 nm UV lamp.



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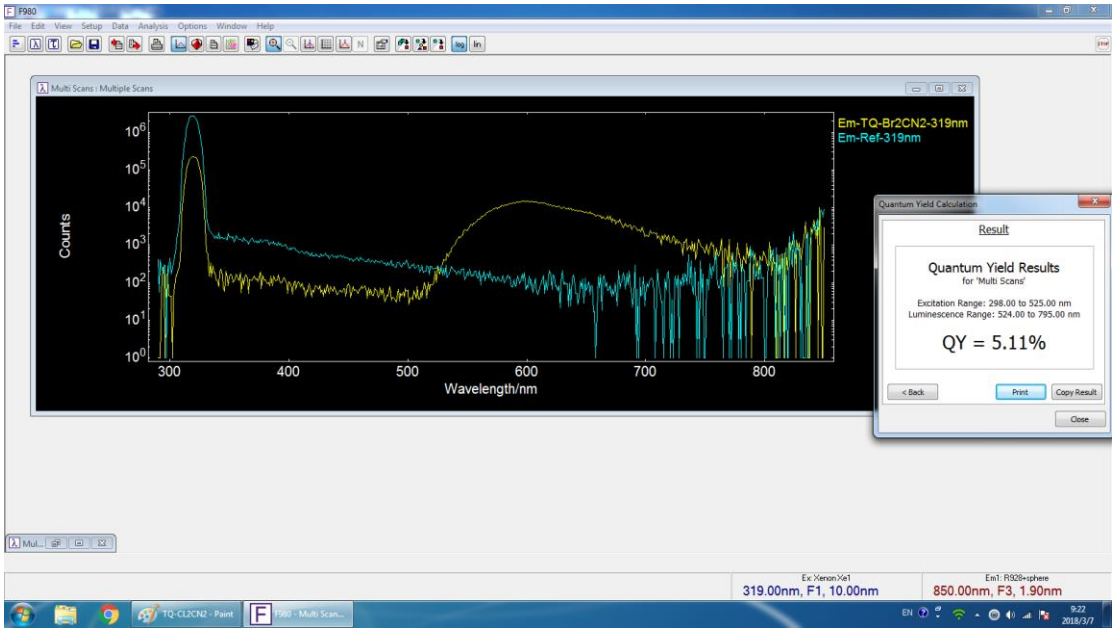

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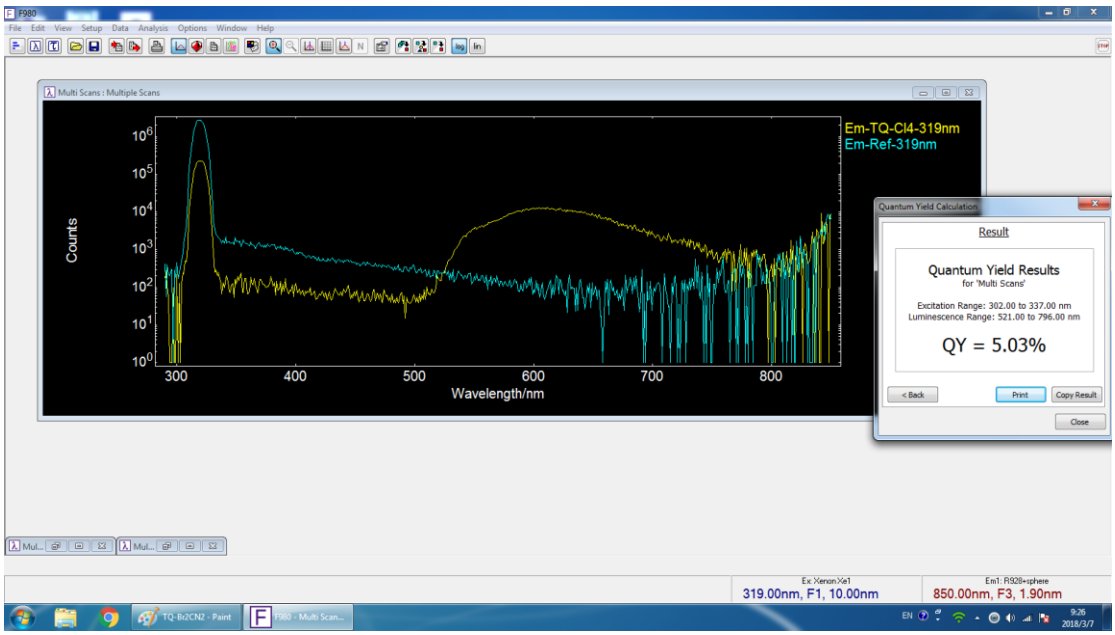

Figure S35 Absolute quantum yield of **3** in PMMA films.

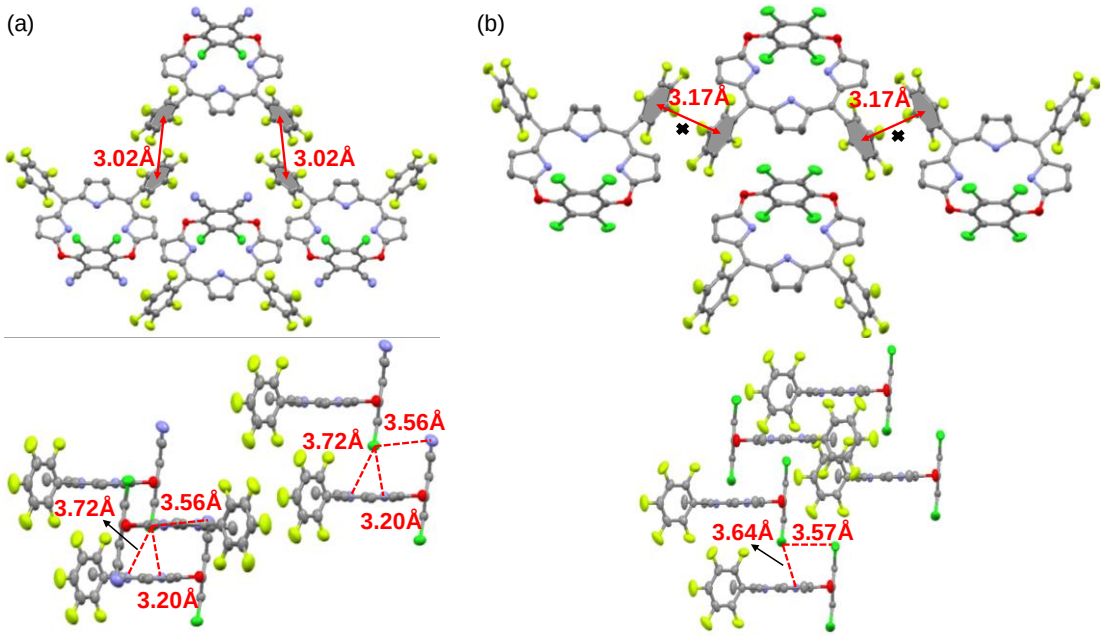

Figure S36 Weak halogen bonds and π-π interaction of **1** (a) and **3** (b) in crystal. Up: top view in perpendicular direction of intramolecular N_3-plane, down: side view in parallel direction of intramolecular N_3-plane.

Table S1. X-ray crystallographic data of **1** (CCDC 1581723)

Complex	**1**·0.5THF
molecular formula	$C_{36}H_{11}Cl_2F_{10}N_5O_{2.5}$
formula wt. (g mol^{-1})	814.40
temperature (K)	180.01(10)
radiation (λ, Å)	0.71073
crystal system	monoclinic
space group	P 2_1/m
a (Å)	6.3689(5)
b (Å)	19.2075(10)
c (Å)	14.4005(9)
α (°)	90
β (°)	96.153(7)
γ (°)	90
Volume ($Å^3$)	1751.5(2)
Z	2
ρ_{calcd} (g cm^{-3})	1.544
μ (mm^{-1})	0.282
F(000)	812
crystal size (mm^3)	0.41×0.25× 0.03
Theta range	3.214 to 24.997°
reflections collected	10154
independent reflections	3185 [R(int) = 0.0429]
Completeness	99.64 %
goodness-of-fit on F^2	1.117
final R indices	$R1^a$ = 0.0683
R indices (all data)	$R1^a$ = 0.0931
largest diff. peak and hole (e $Å^{-3}$)	1.57 and -0.26

Table S2. X-ray crystallographic data of **2** (CCDC 1581724)

Complex	**2**·THF
molecular formula	$C_{38}H_{15}Br_2F_{10}N_5O_3$
formula wt. (g mol^{-1})	939.37
temperature (K)	180(2)
radiation (λ, Å)	0.71073
crystal system	orthorhombic
space group	P_{nma}
a (Å)	18.5573(10)
b (Å)	18.3335(13)
c (Å)	14.8419(10)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	5049.5(5)
Z	4
ρcalcd (g cm^{-3})	1.225
μ (mm^{-1})	1.676
F(000)	1816
crystal size (mm^3)	0.35×0.25× 0.24
Theta range	3.512 to 24.996°
reflections collected	52350
independent reflections	4591 [R(int) = 0.0646]
Completeness	99.58 %
goodness-of-fit on F^2	1.065
final R indices	$R1^a$ = 0.0702
R indices (all data)	$R1^a$ = 0.0938
largest diff. peak and hole (e $Å^{-3}$)	0.68 and -0.62

Table S3. X-ray crystallographic data of **3** (CCDC 1581725)

Complex	**3**
molecular formula	$C_{32}H_7Cl_4F_{10}N_3O_2$
formula wt. (g mol^{-1})	797.21
temperature (K)	180.01(10)
radiation (λ, Å)	0.71073
crystal system	monoclinic
space group	P 2_1/m
a (Å)	6.4792(4)
b (Å)	25.1943(14)
c (Å)	10.1094(6)
α (°)	90
β (°)	106.673(6)
γ (°)	90
Volume ($Å^3$)	1580.88(16)
Z	2
ρcalcd (g cm^{-3})	1.675
μ (mm^{-1})	0.471
F(000)	788
crystal size (mm^3)	0.27×0.24× 0.06
Theta range	3.207 to 27.453°
reflections collected	11013
independent reflections	3708 [R(int) = 0.0325]
Completeness	99.73 %
goodness-of-fit on F^2	1.025
final R indices	$R1^a$ = 0.0441
R indices (all data)	$R1^a$ = 0.0694
largest diff. peak and hole (e $Å^{-3}$)	0.37 and -0.35

Table S4. Calculated energy levels of **1**-**3**

	1	**2**	**3**
LUMO+1/eV	-2.72	-2.70	-2.05
LUMO/eV	-3.38	-3.36	-3.16
HOMO/eV	-5.94	-5.91	-5.72

Table S5. Calculated vertical excitation and configuration analysis of **1**

No.	λ (nm)	Exp. (nm)	f	Major Contribution
S_1	500.33	530	0.4395	HOMO -> LUMO (99.9%)
S_2	466.28	500	0.0006	HOMO -> L+1 (99.8%)
…	…	…	…	…
S_{24}	284.35	319	0.8392	H-10 -> LUMO (27.7%)
				HOMO -> L+2 (20.9%)
				H-5 -> LUMO (15.0%)
				HOMO -> L+5 (14.5%)
				H-1 -> LUMO (7.1%)
				H-9 -> LUMO (4.7%)
				H-3 -> LUMO (2.4%)

Table S6. Calculated vertical excitation and configuration analysis of **2**

No.	λ (nm)	Exp. (nm)	f	Major Contribution
S_1	502.80	530	0.4184	HOMO -> LUMO (99.8%)
S_2	466.56	500	0.0008	HOMO -> L+1 (99.8%)
…	…	…	…	…
S_{26}	283.21	319	0.7708	H-10 -> LUMO (33.2%)
				HOMO -> L+6 (19.9%)
				HOMO -> L+2 (17.7%)
				H-5 -> LUMO (9.0%)
				H-1 -> LUMO (7.9%)
				H-9 -> LUMO (4.4%)

Table S7. Calculated vertical excitation and configuration analysis of **3**

No.	λ (nm)	Exp. (nm)	f	Major Contribution
S_1	500.98	530	0.4445	HOMO -> LUMO (100%)
…	…	…	…	…
S_{18}	283.96	319	0.8495	H-10 -> LUMO (32.9%)
				HOMO -> L+1 (19.2%)
				H-7 -> LUMO (16.3%)
				HOMO -> L+5 (10.2%)
				H-2 -> LUMO (5.3%)
				H-9 -> LUMO (4.9%)
				H-1 -> LUMO (4.5%)
				HOMO -> L+6 (2.1%)

Table S8. Photophysical properties of **1**-**3**

	1	**2**	**3**
UV/nm	532	533	529
FL/nm	560	560	551
QY/% [a]	8.2	7.3	8.5
τ/ps [b]	708	656	715
Solid FL/nm	627	622	582
Solid QY/% [c]	3.8	2.4	3.1
Solid τ/ps [d]	364 (68%), 1014 (32%)	304 (51%), 808 (49%)	227 (65%), 770 (35%)

[a] Fluorescein as reference, excitation = 470 nm. [b] Lifetime experiments use 590 nm as emission.

[c] Absolute quantum yield. [d] **1** and **2** use 620 nm as emission, **3** uses 580 nm as emission.