

Aggregation Enhanced Emissive Mechanofluorochromic Carbazole-Halogen Positional Isomers: Tunable Fluorescence via Conformational Polymorphism and Crystallization Induced Fluorescence Switching

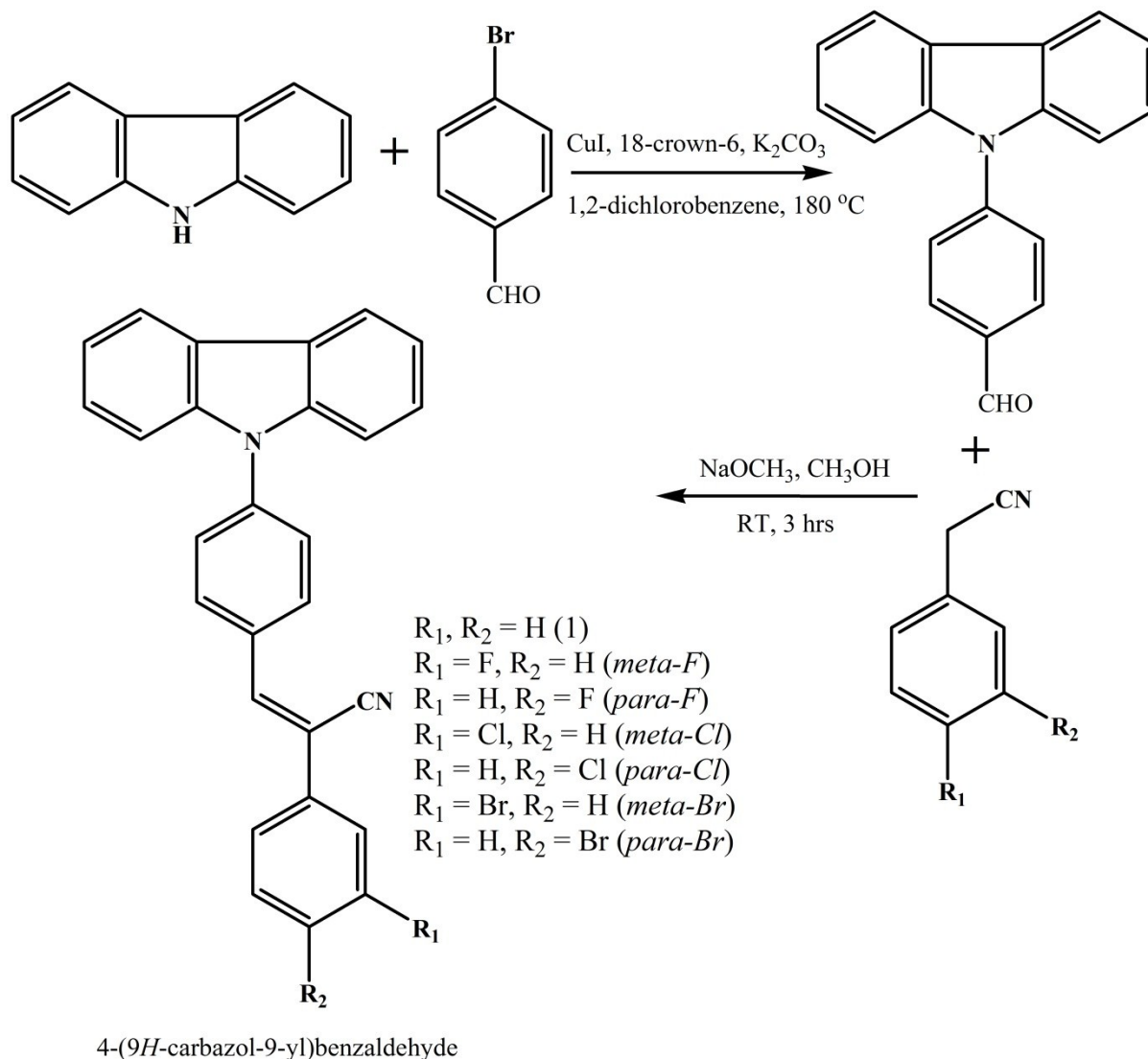
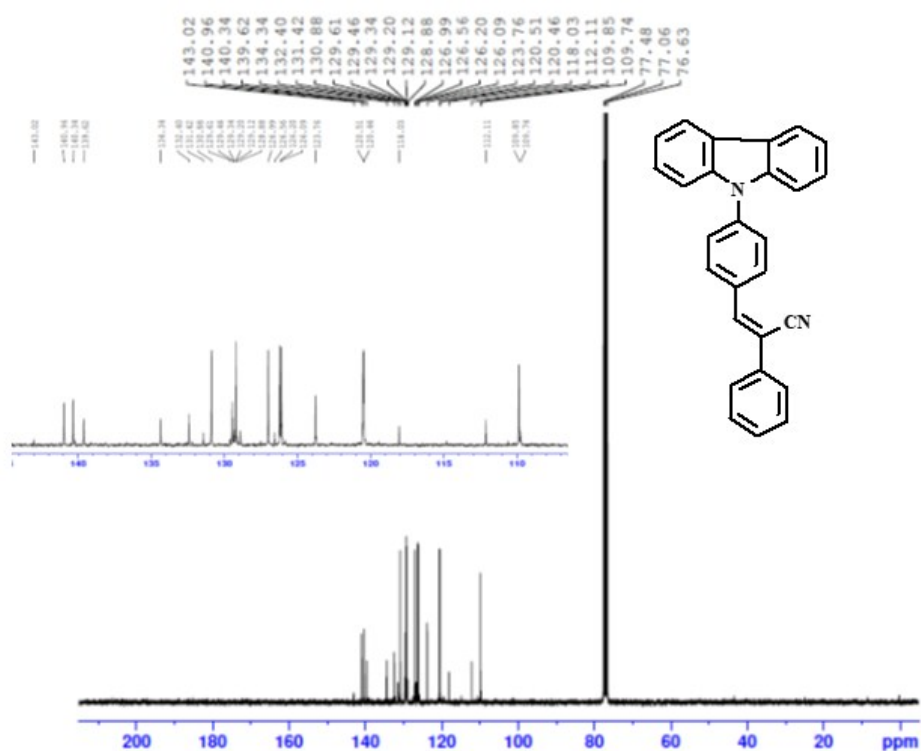
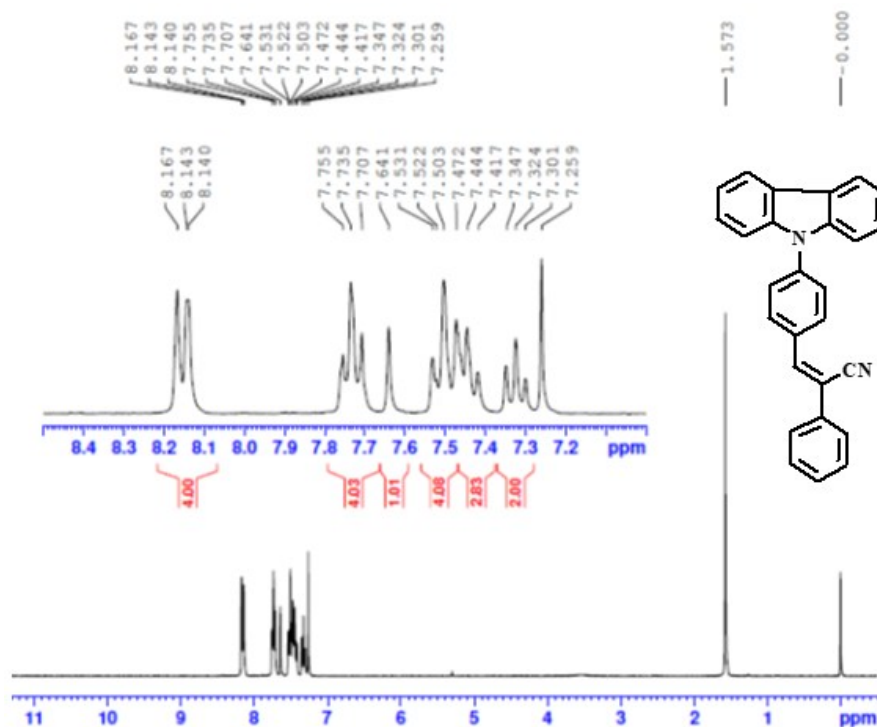
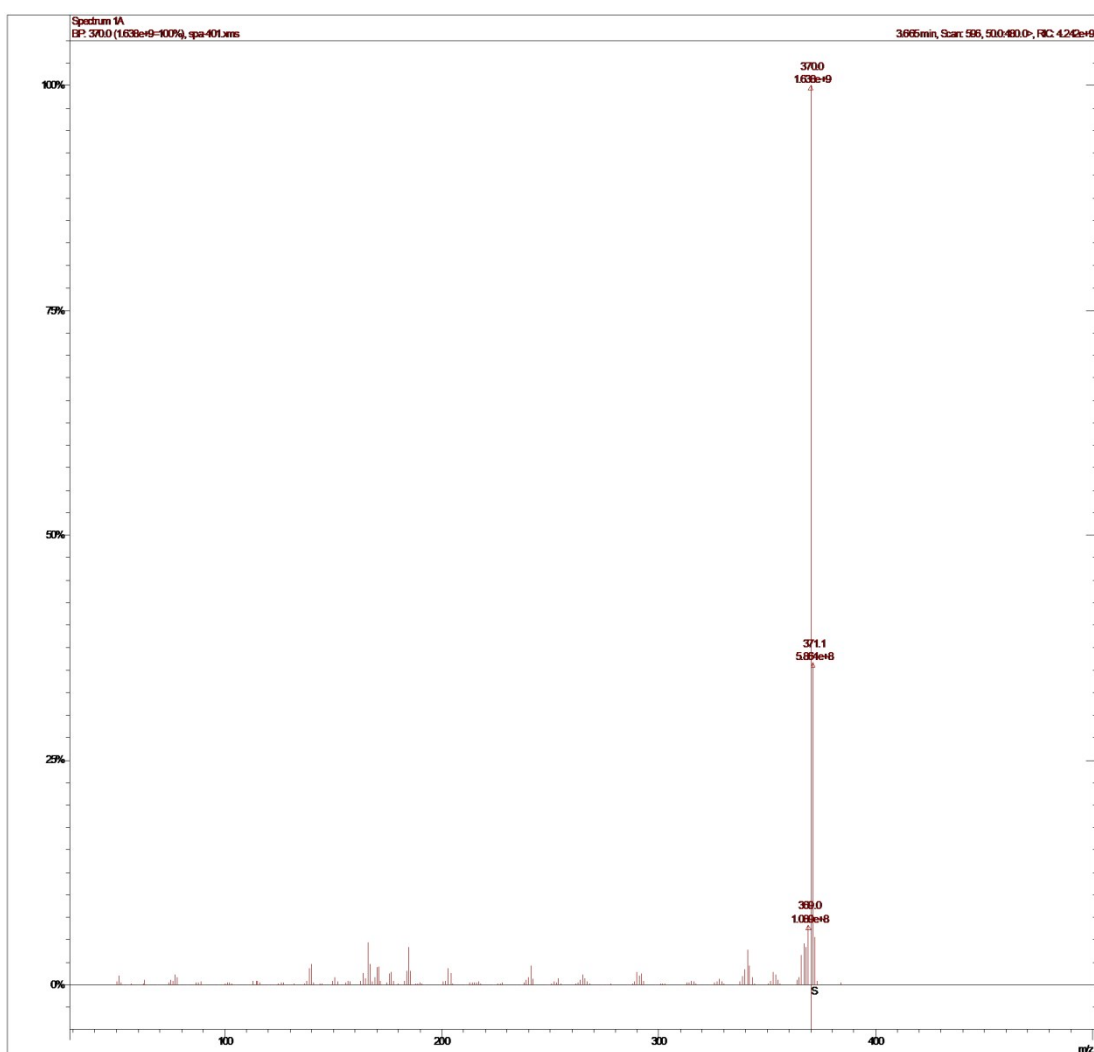
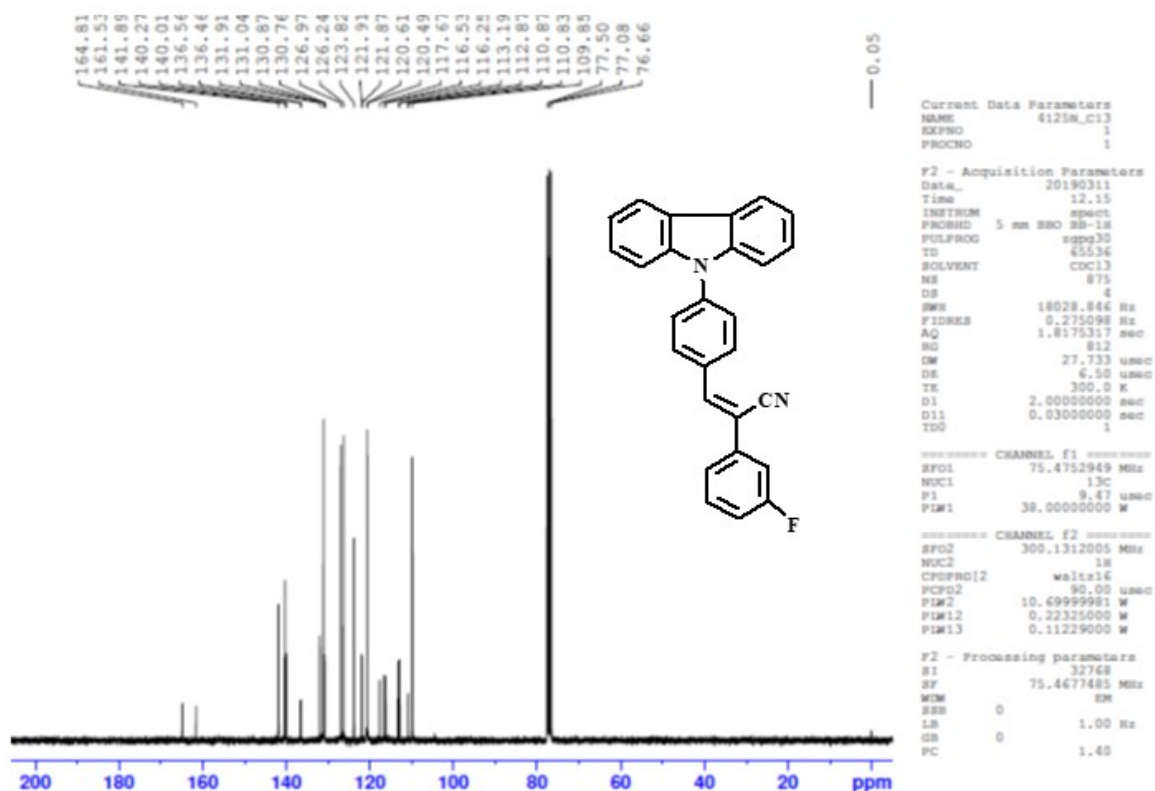
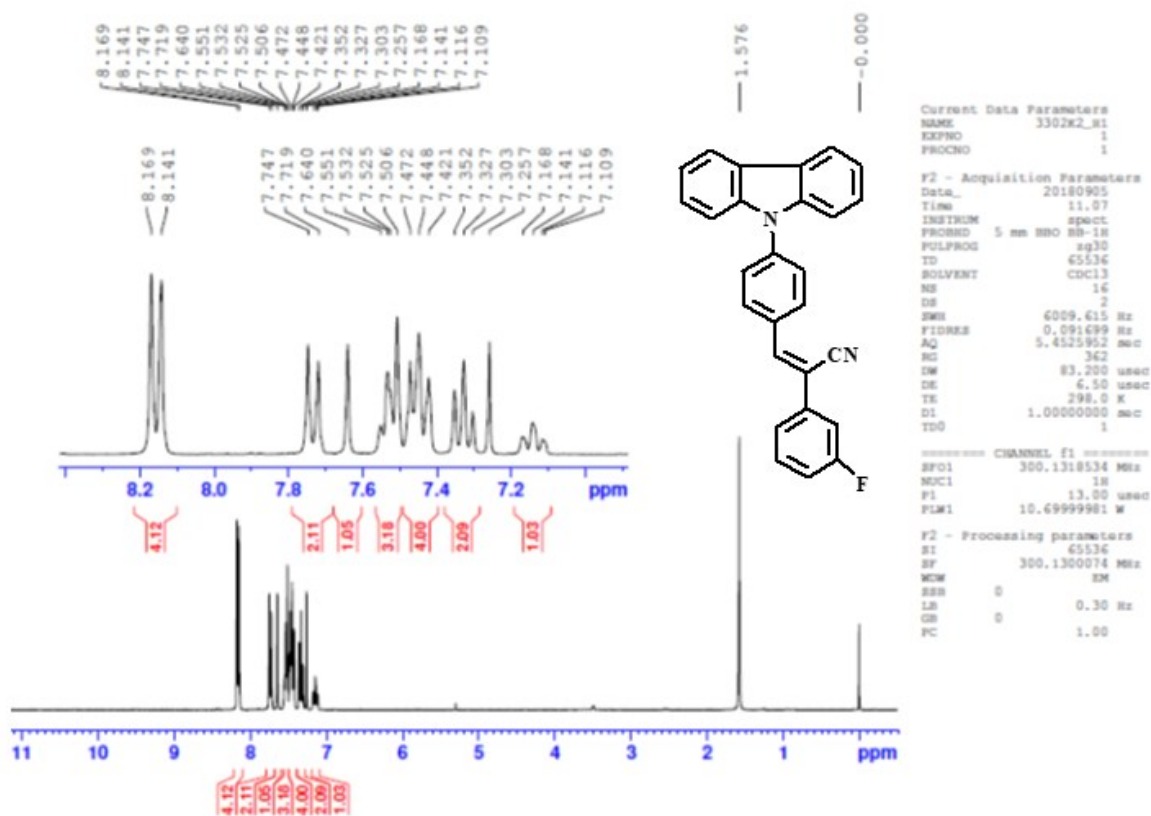
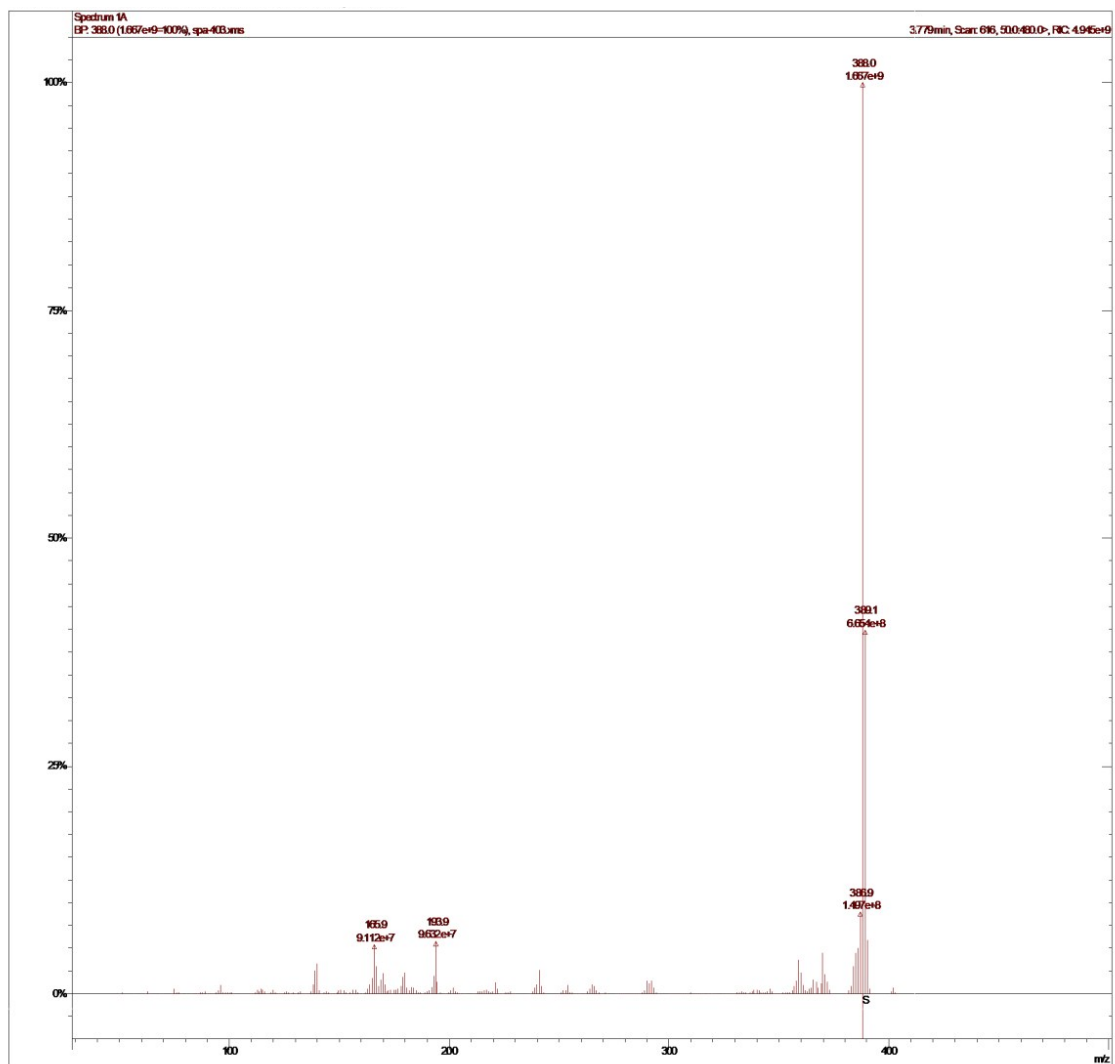


Figure S1. Synthesis of carbazole based halogen substituted positional isomers.

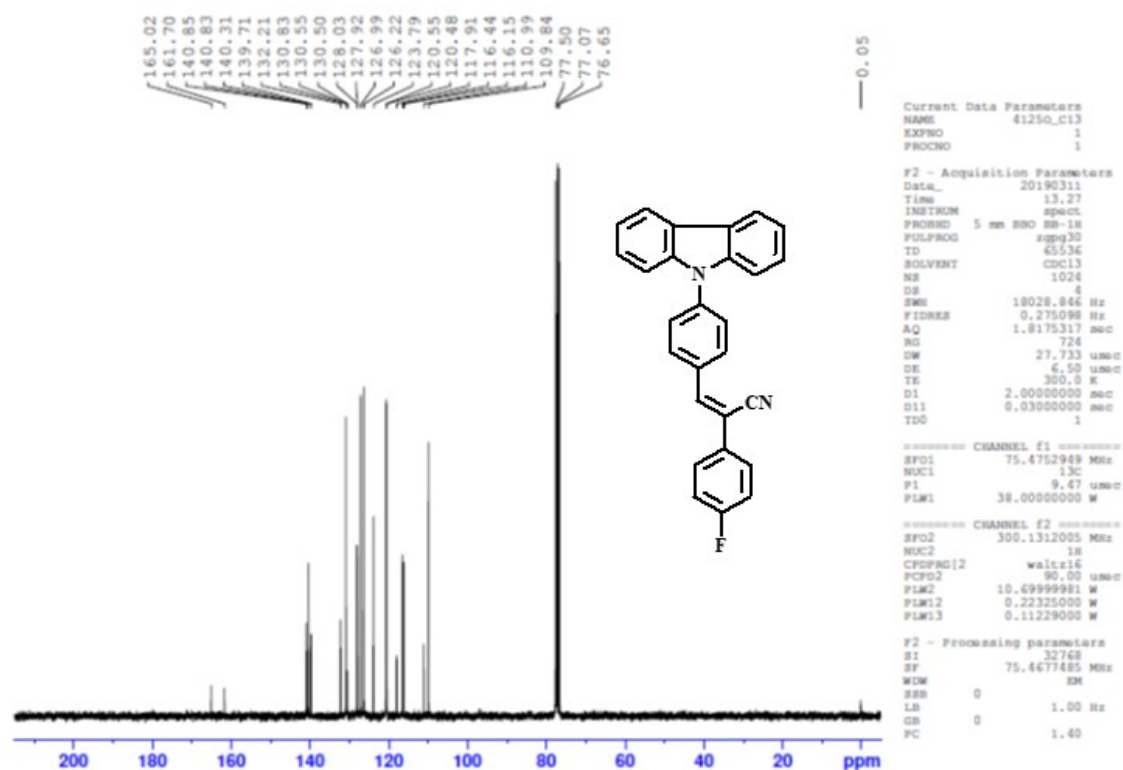
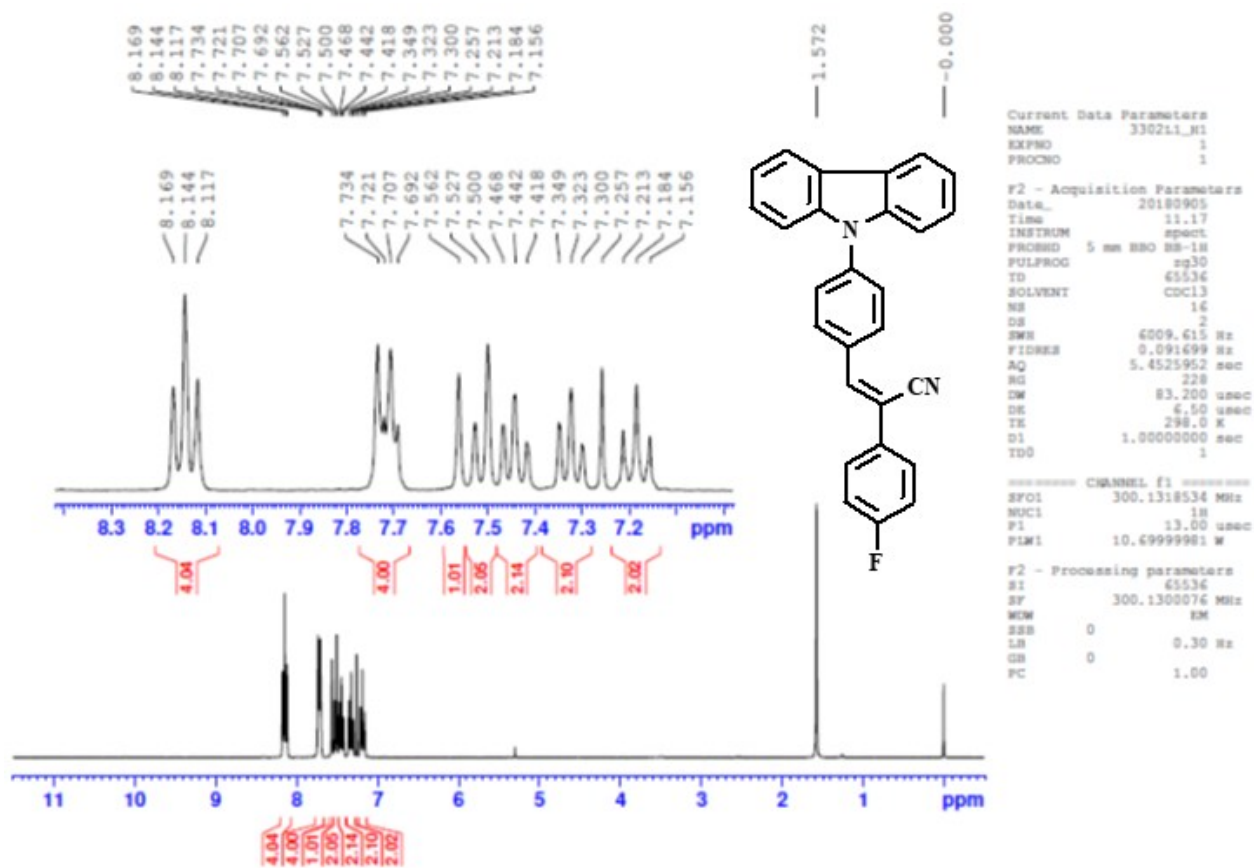


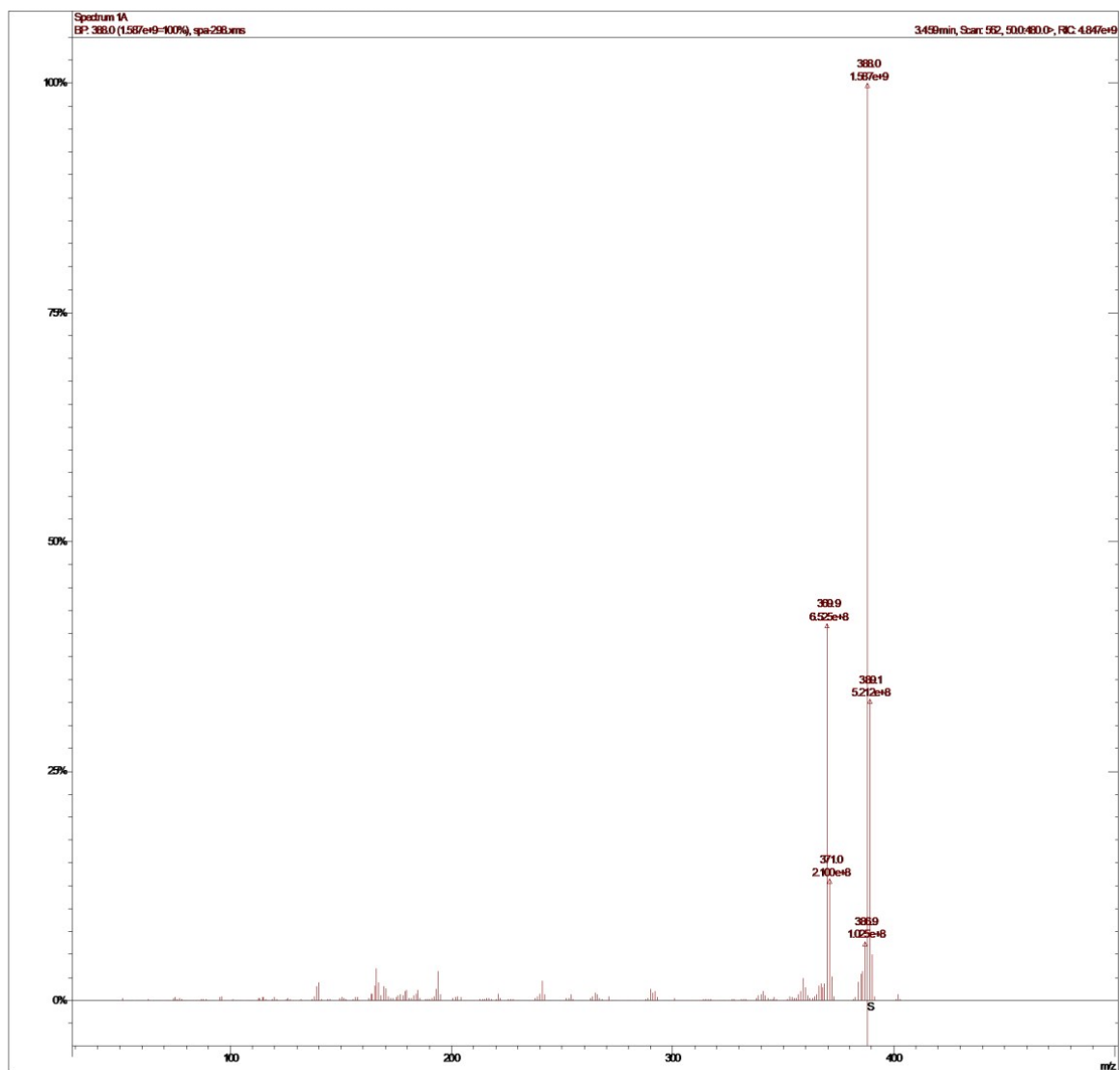
^1H and ^{13}C NMR of **1**Mass spectrum of **H**.



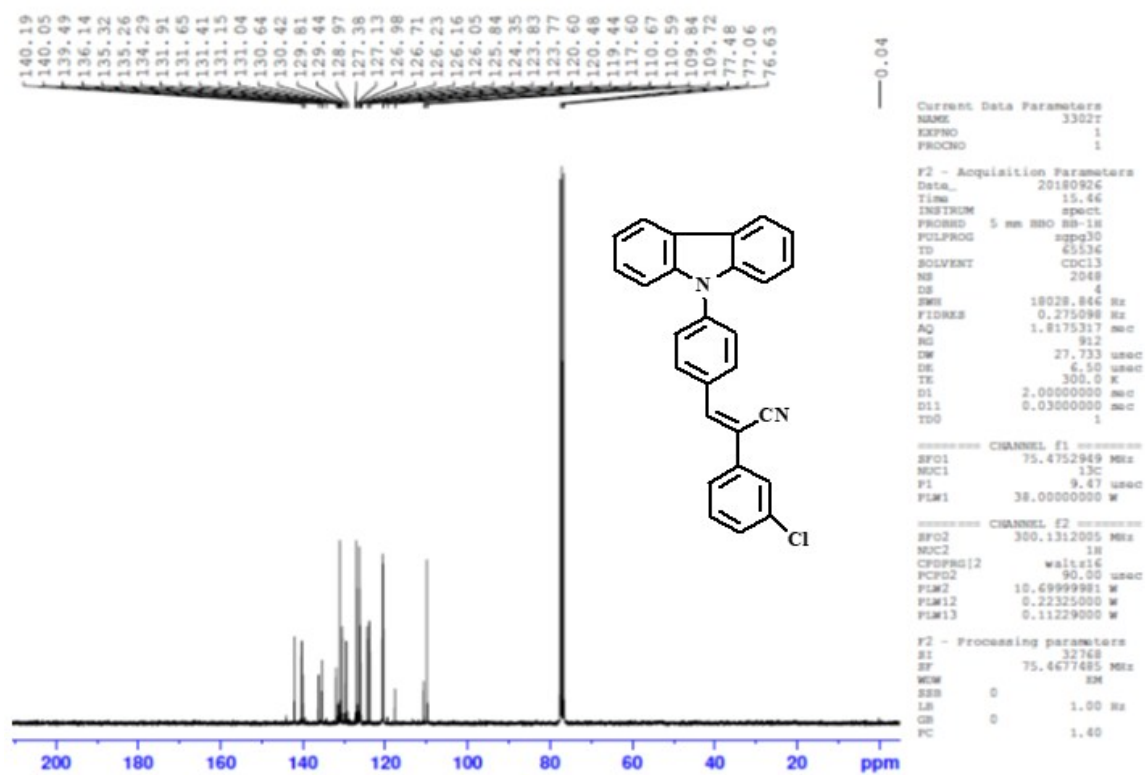
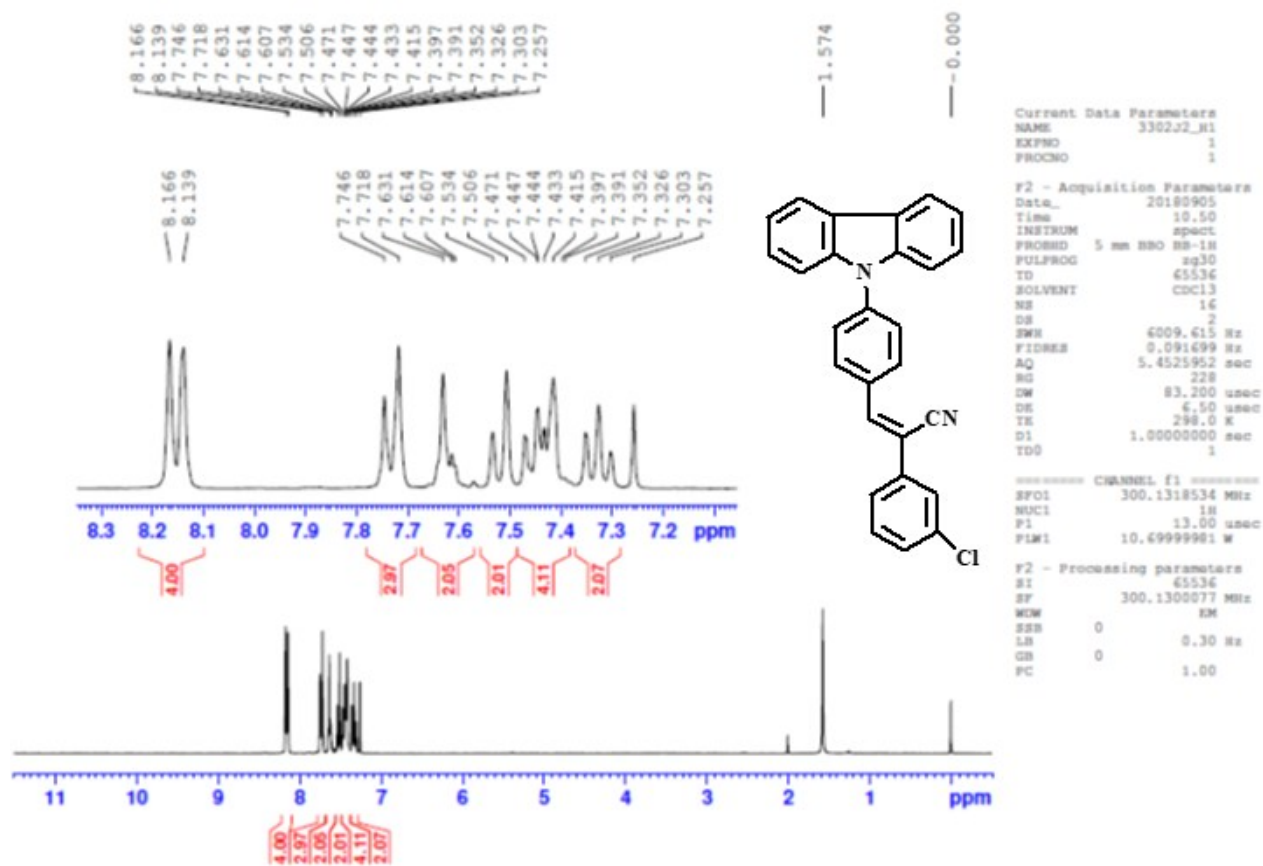


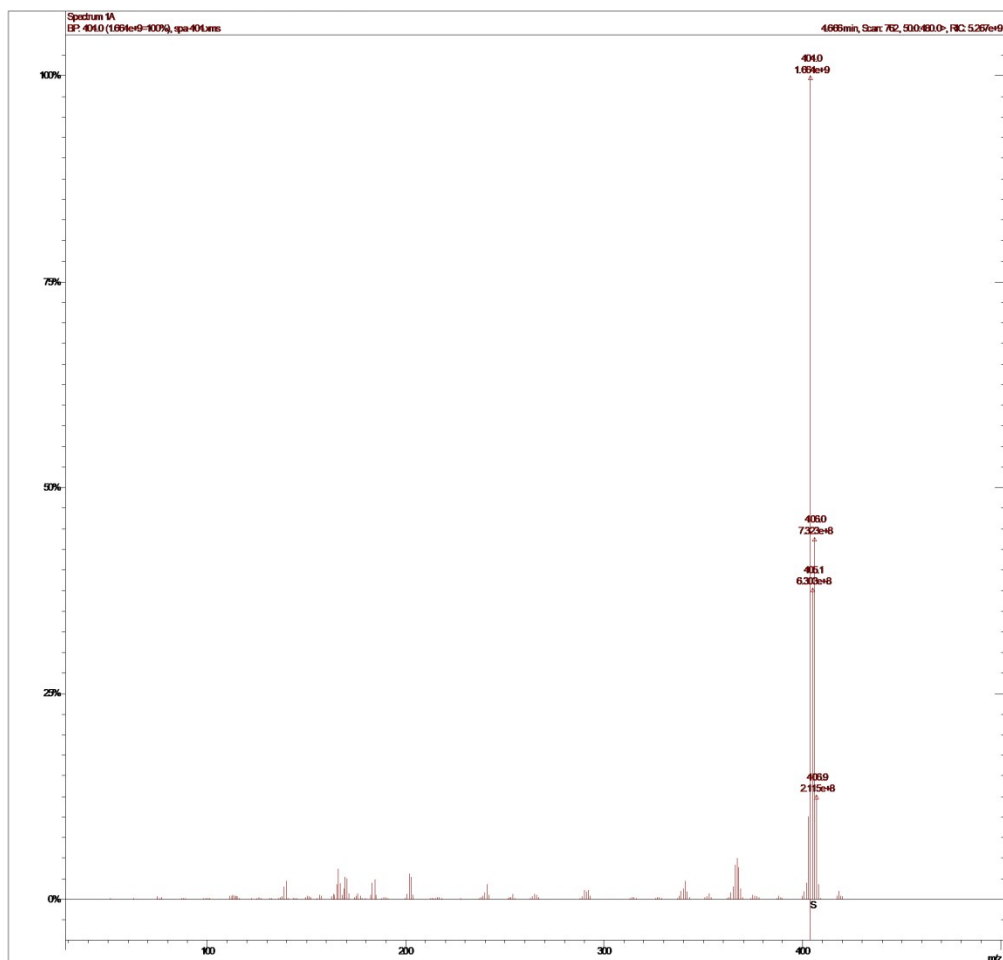
Mass spectrum of *meta-F*.

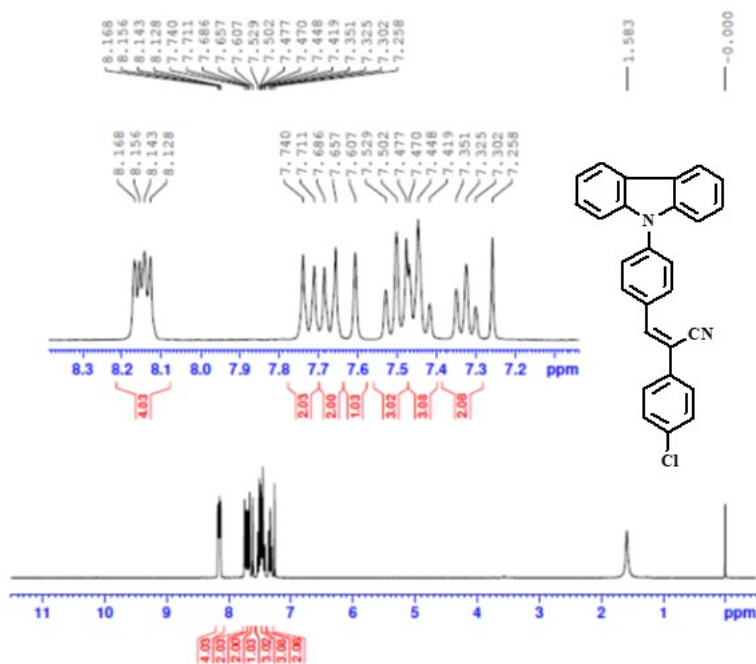




Mass spectrum of *para-F*.



^1H and ^{13}C NMR of *meta*-ClMass spectrum of *meta*-Cl.



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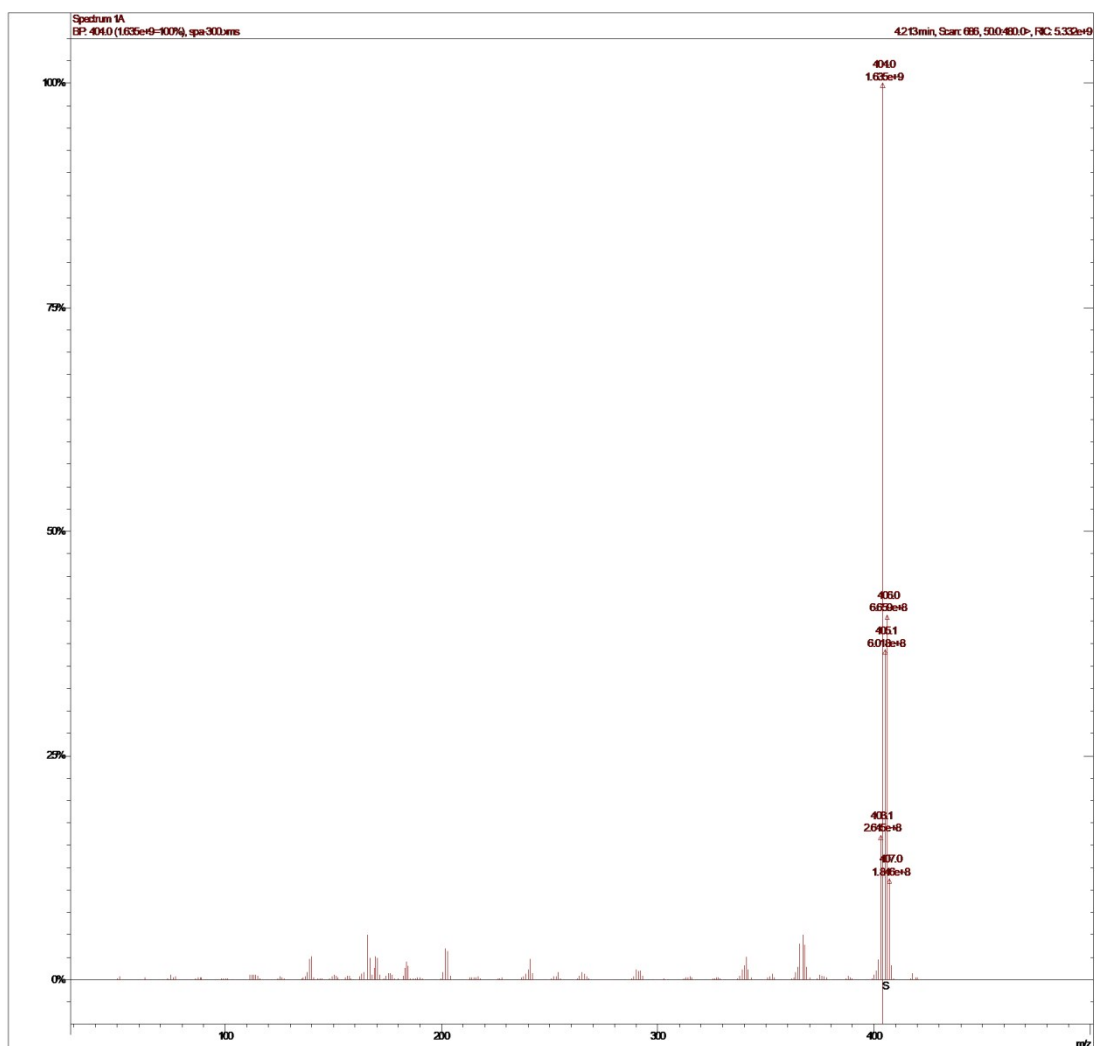
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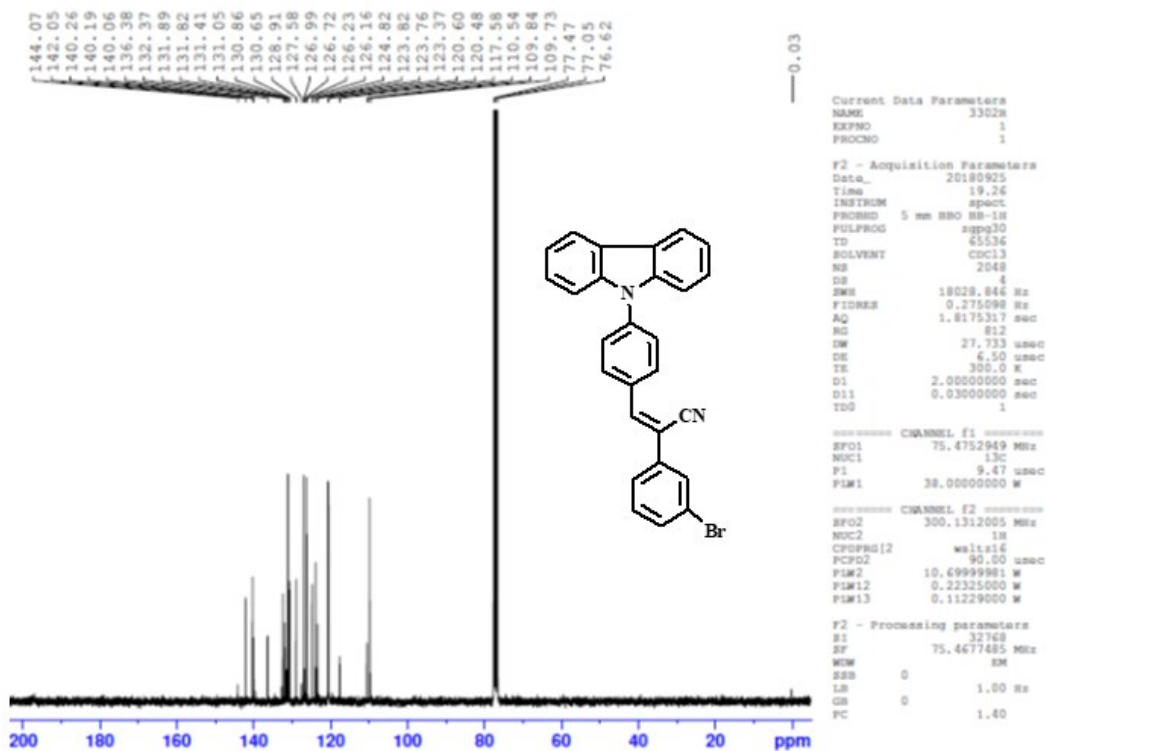
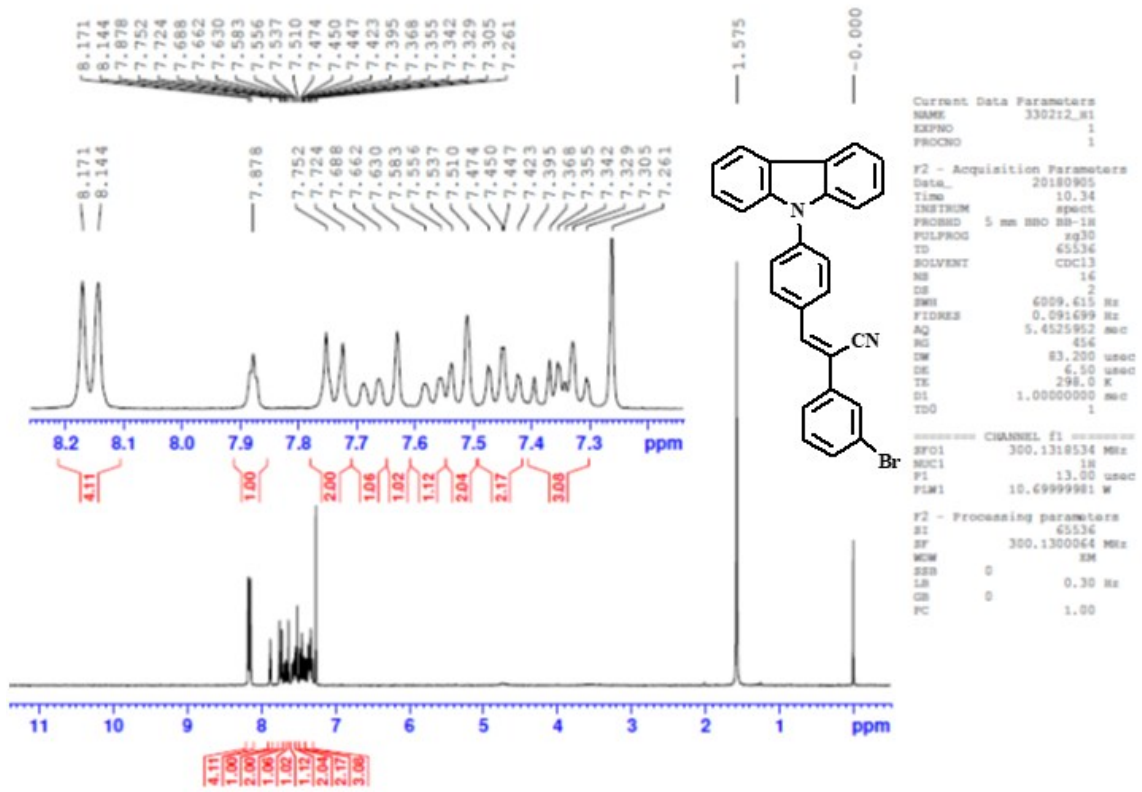
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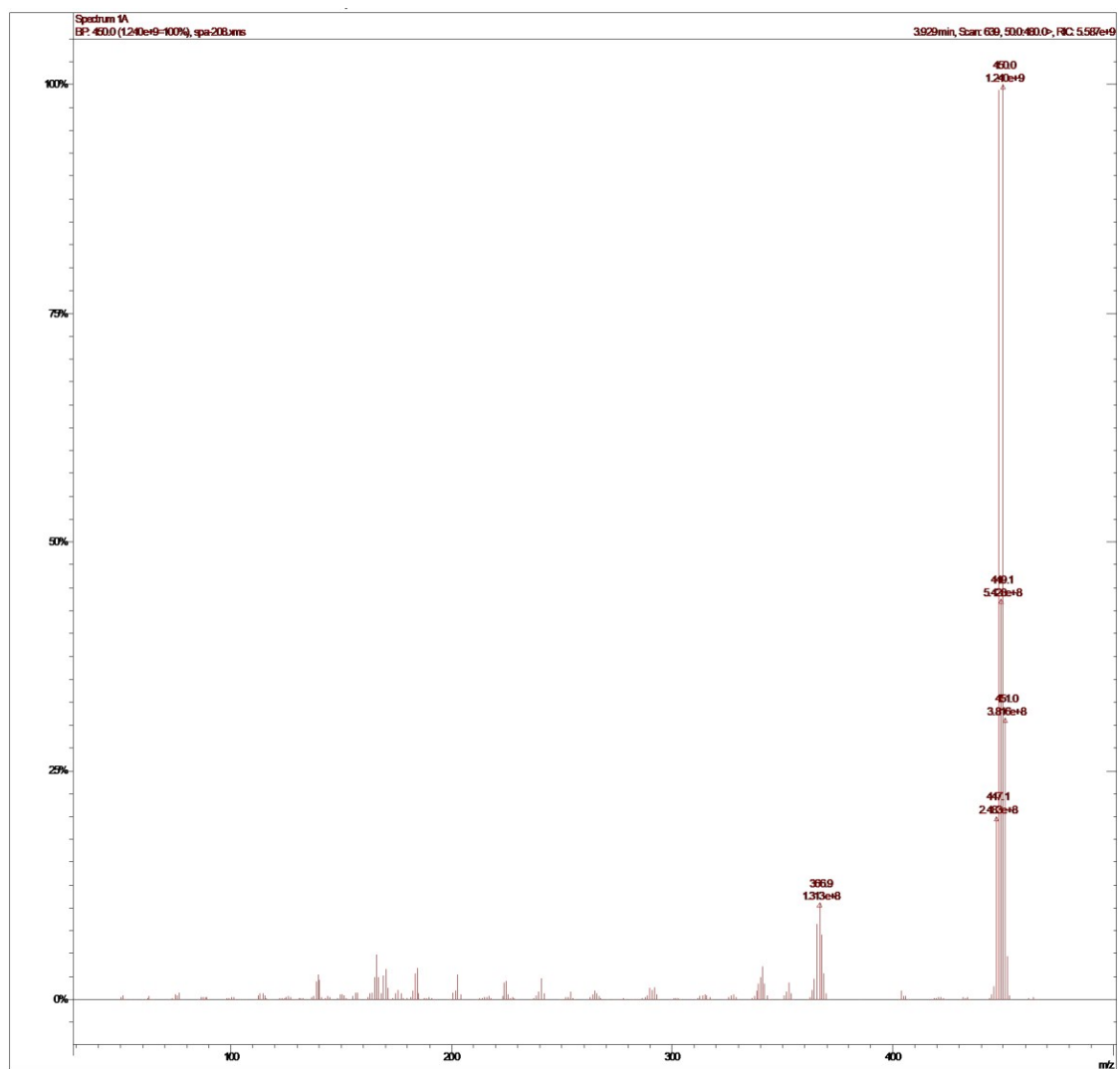
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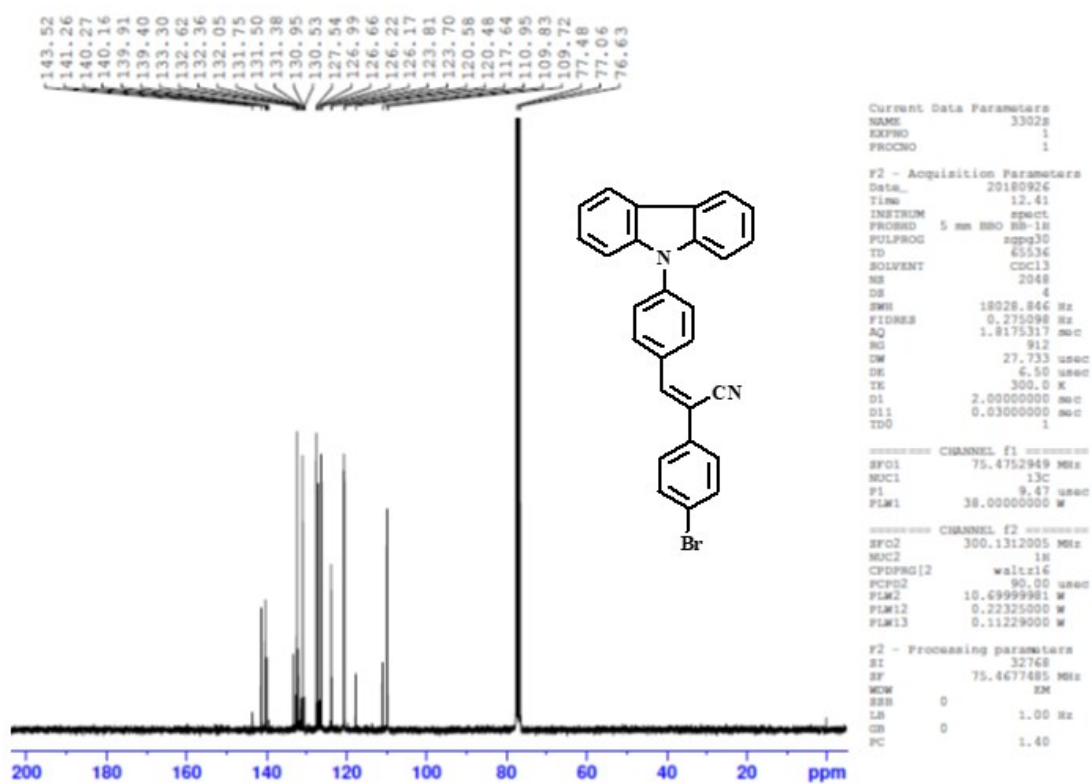
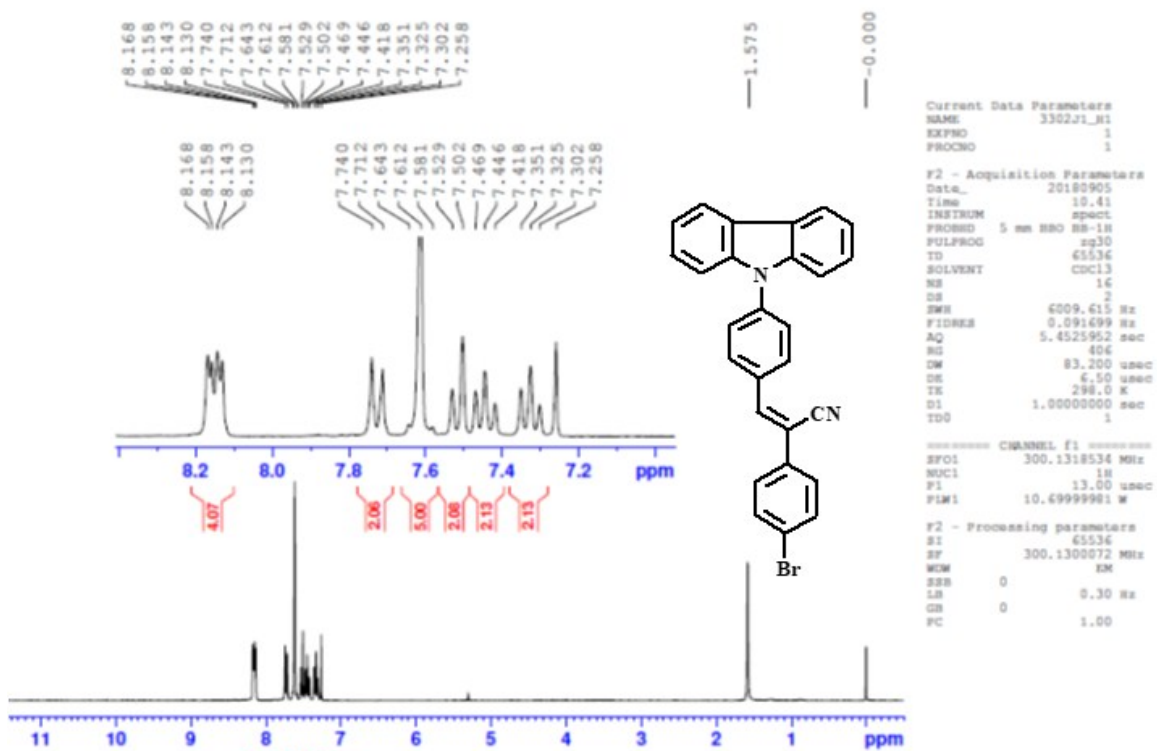
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^1H and ^{13}C NMR of *para*-ClMass spectrum of *para*-Cl.

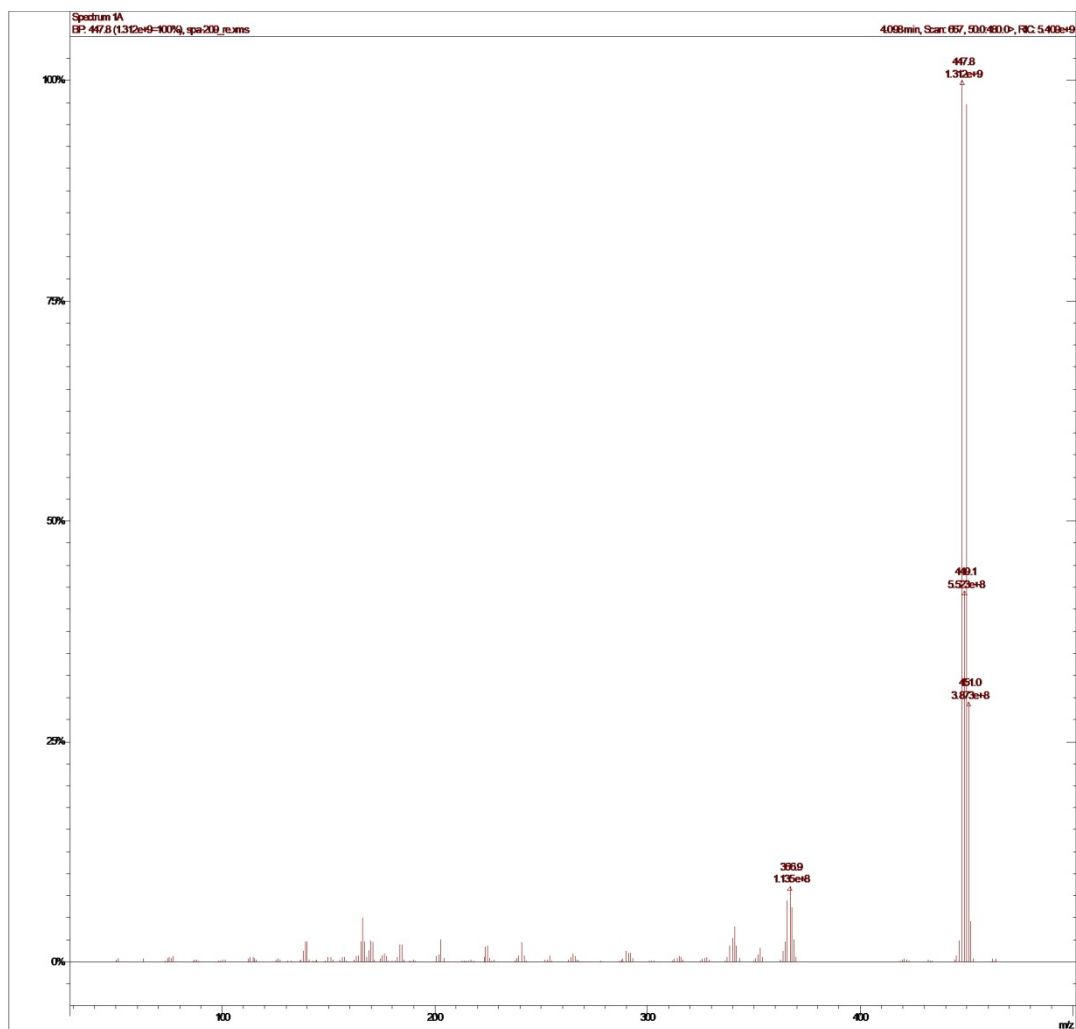


^1H and ^{13}C NMR of *meta*-Br

Mass spectrum of *meta-Br*.



^1H and ^{13}C NMR of *para*-Br



Mass spectrum of *para-Br*.

Table S1. Absolute quantum yield (Φ_f) of halogen positional isomers at different stimuli.

	Absolute quantum yield (Φ_f)						
	Crystals	Crushed	Heated	Melted	Heated	Slightly scratched	Heated
H-B	25.37	21.97	27.20	7.39	19.18	13.32	23.85
H-G	31.32						
<i>meta</i> -F-B	21.10	18.25	20.99	6.03	17.65	14.97	23.36
<i>meta</i> -F-G	19.46						
<i>para</i> -F-B	19.36	18.25	20.46	9.23	18.95	13.78	23.69
<i>para</i> -F-G	20.72						
<i>meta</i> -Cl-B	25.13	18.37	26.36	8.12	26.56	15.55	23.39
<i>meta</i> -Cl-G	28.40						
<i>para</i> Cl-B	26.37	20.18	25.21	7.69	18.89	14.63	22.87
<i>para</i> Cl-G	25.81						
<i>meta</i> -Br	15.67	5.39	13.23	2.89	6.65	5.69	10.25
<i>para</i> -Br-B	21.55	12.67	20.01	2.54	15.50	11.54	19.23
<i>para</i> -Br-G	20.72						

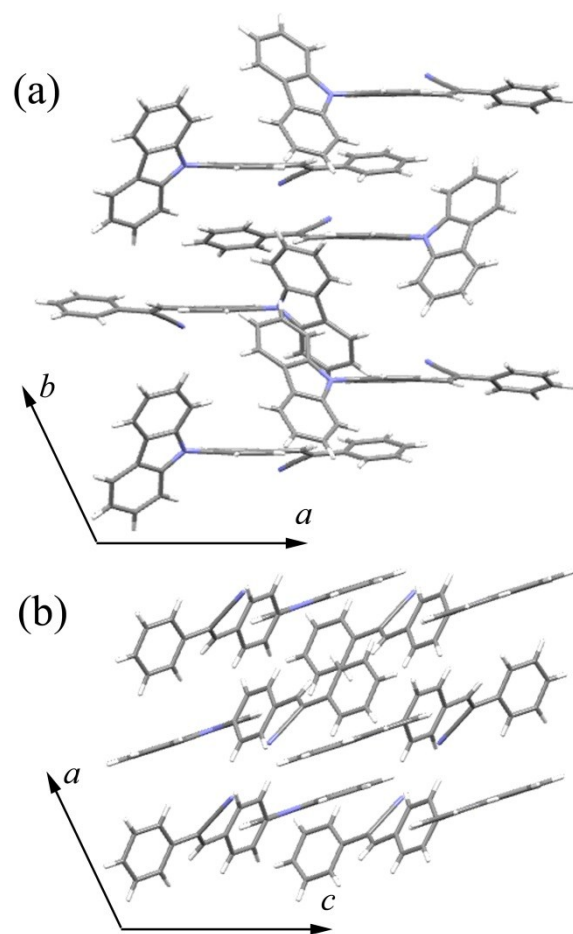


Figure S2. Molecular packing of (a) H-B and (b) H-G in the crystal lattice. C (grey), N (blue) and H (white).

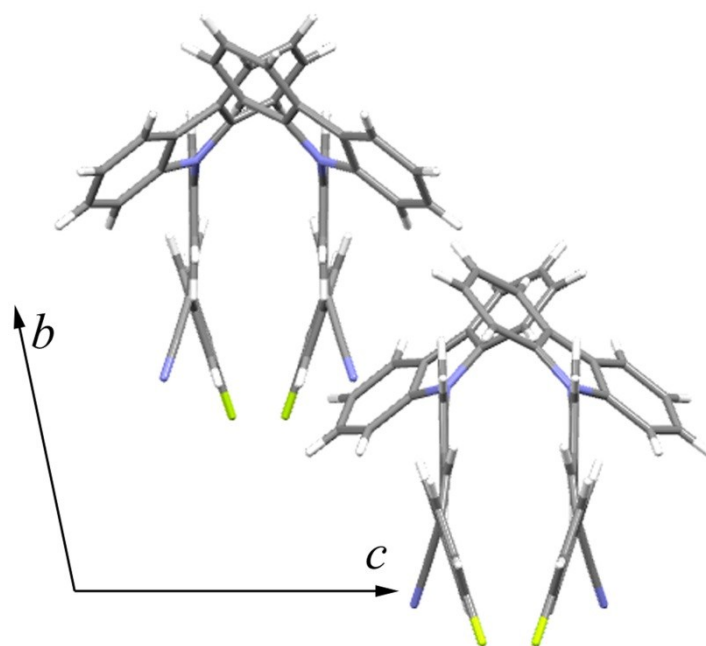


Figure S3. Molecular packing of *meta*-F-B in the crystal lattice. C (grey), N (blue), H (white) and F (yellow).

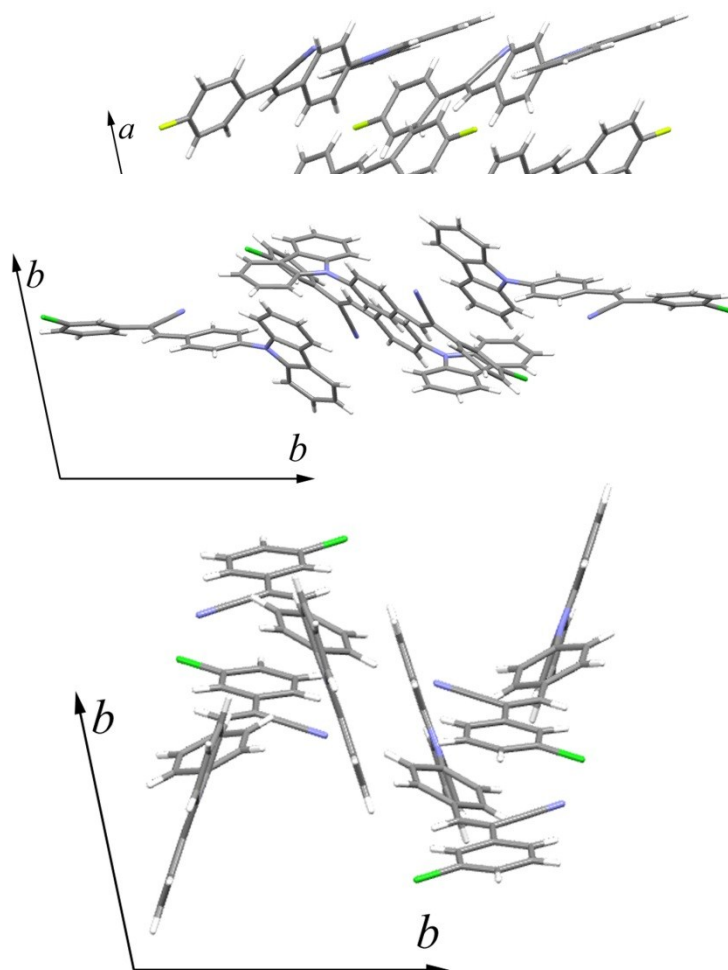


Figure
packing
of (a)
F-G. C

S4. Molecular
in the crystal lattice
para-F-B and *para*-
(grey), N (blue), H

(white) and F (yellow).

Figure S5. Molecular packing in the crystal lattice of (a) *meta*-Cl-B and *meta*-Cl-G. C (grey), N (blue), H (white) and Cl (green).

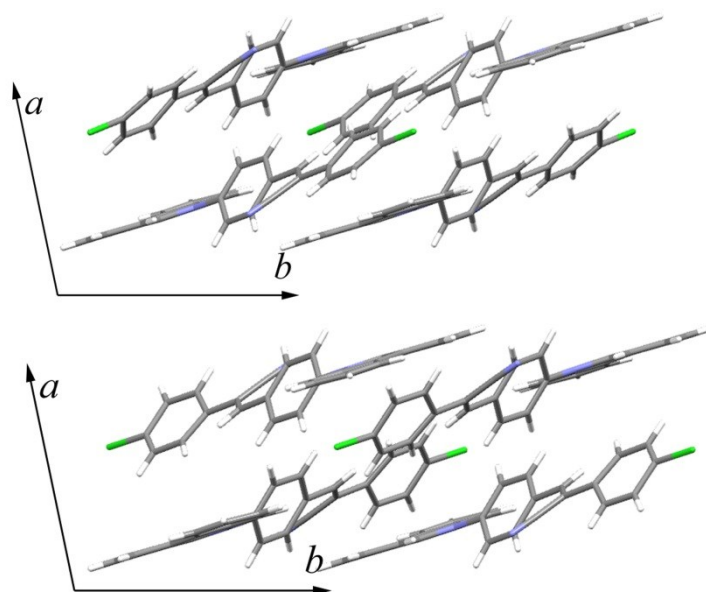


Figure S6. Molecular packing in the crystal lattice of (a) *para*-Cl-B and *para*-Cl-G. C (grey), N (blue), H (white) and Cl (green).

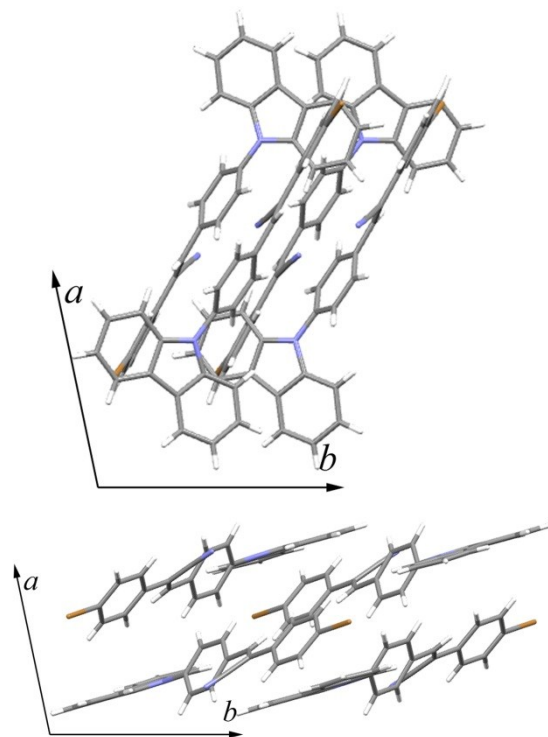


Figure S7. Molecular packing in the crystal lattice of (a) *meta*-Br and *para*-Br-B. C (grey), N (blue), H (white) and Br (orange).

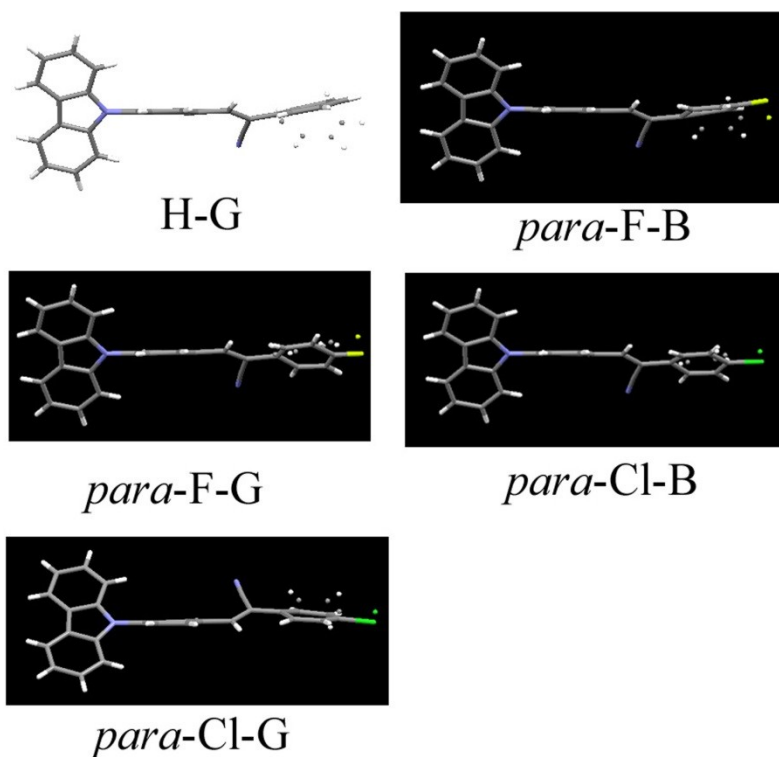


Figure S8. Disorder in the crystal lattice of different derivatives.

Table S2. Computationally calculated optical band gap of H and halogen isomers.

B3PW91/ 6-31+G(d,p)	HOMO	LUMO	band gap (eV)
H-B	-5.738	-2.427	3.31
H-G	-5.741	-2.475	3.27
<i>meta</i> -F-B	-5.454	-2.221	3.23
<i>para</i> -F-B	-5.807	-2.517	3.29
<i>para</i> -F-G	-5.776	-2.515	3.26
<i>meta</i> -Cl-B	-5.830	-2.662	3.17
<i>meta</i> -Cl-G	-5.797	-2.636	3.16
<i>para</i> -Cl-B	-5.813	-2.578	3.24
<i>para</i> -Cl-G	-5.777	-2.617	3.16
<i>meta</i> -Br	-5.516	-2.281	3.24
<i>para</i> -Br-B	-5.489	-2.417	3.07

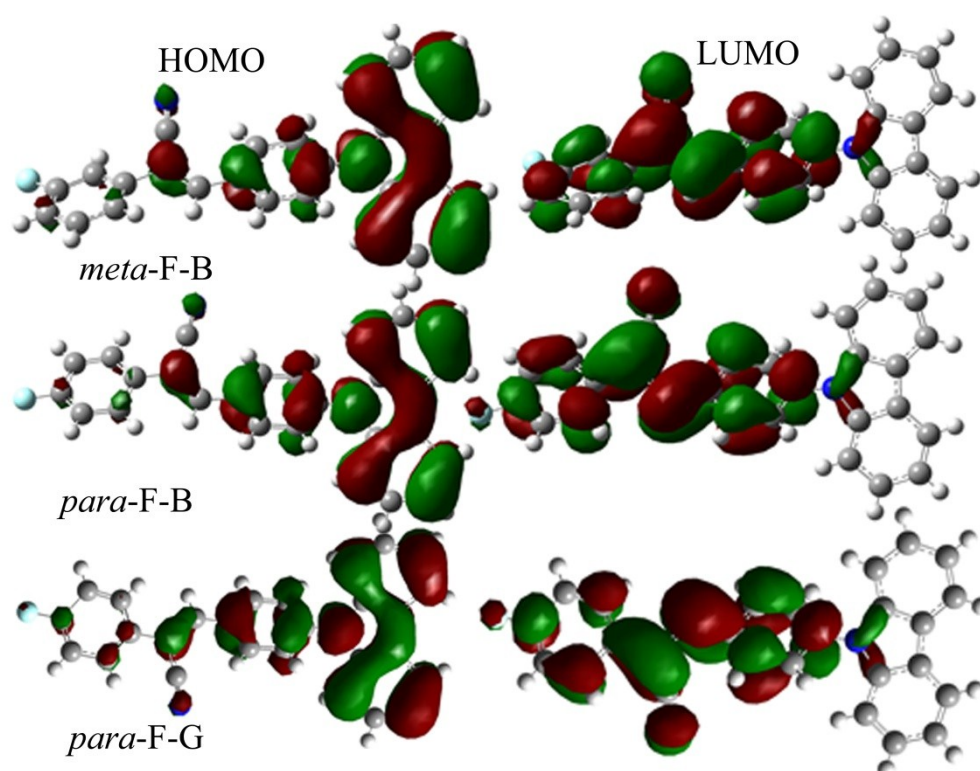


Figure S9. HOMO-LUMO molecular orbital diagram.

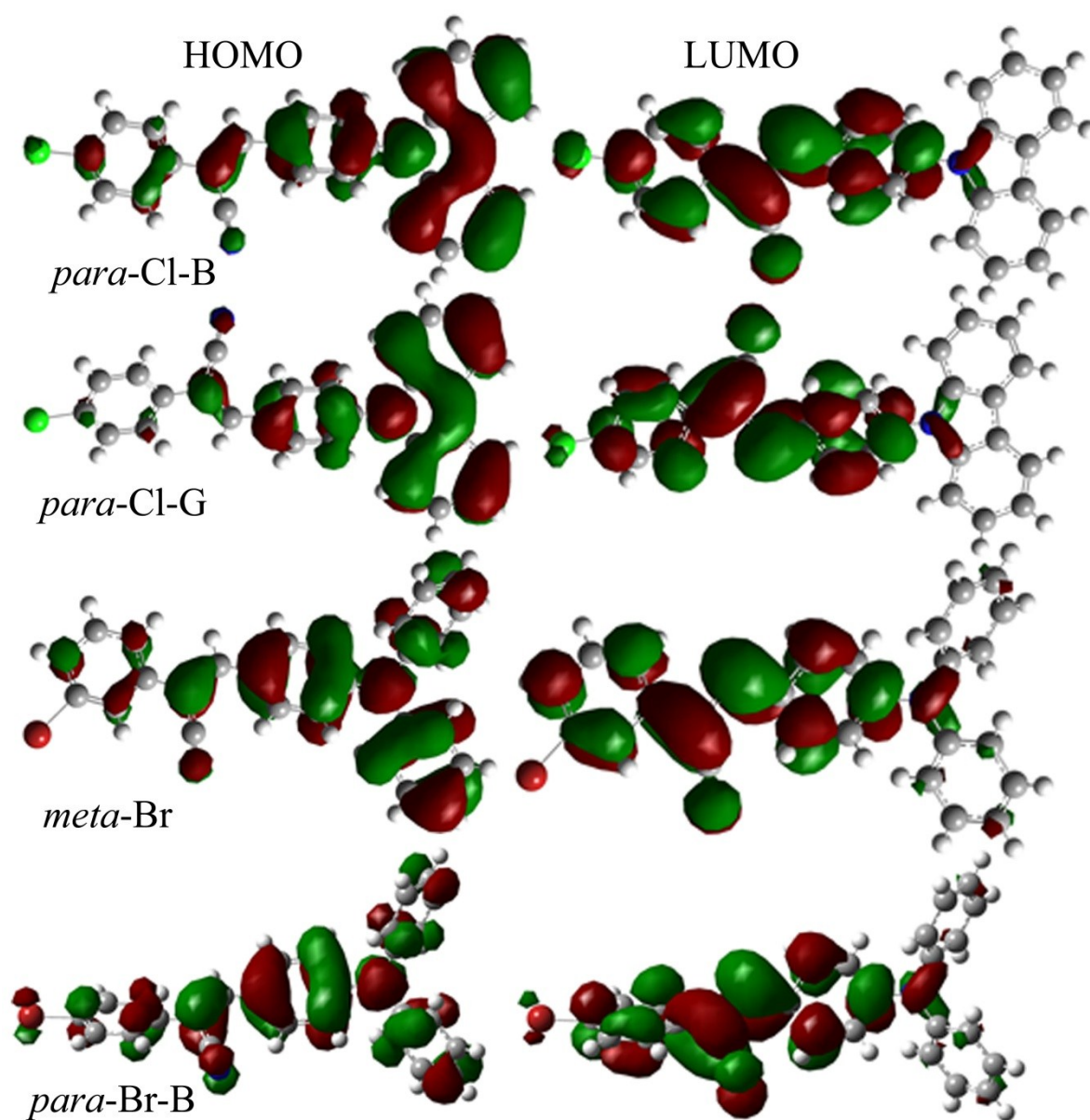


Figure S10. HOMO-LUMO molecular orbital diagram.

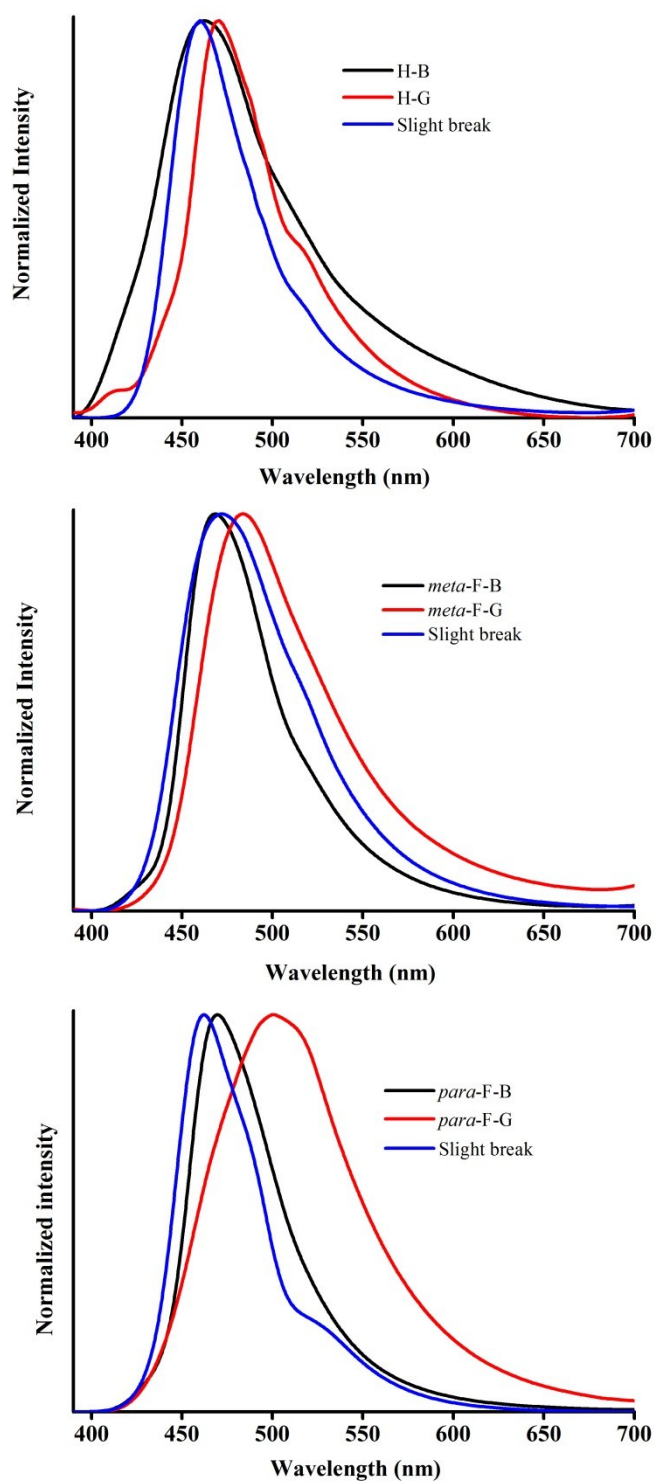


Figure S11. Solid state fluorescence spectra of blue, green and slight breaking of green polymorphs. $\lambda_{\text{ex}} = 360$ nm.

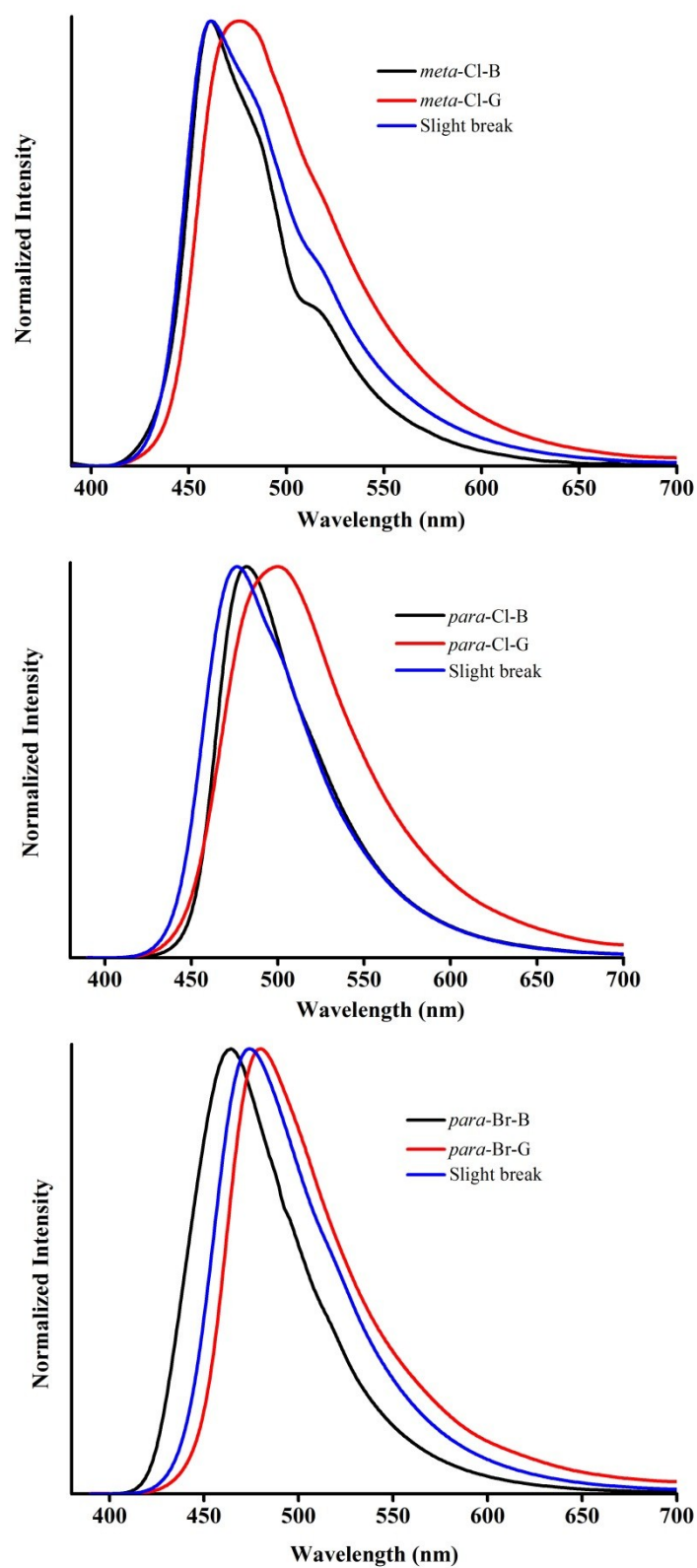


Figure S12. Solid state fluorescence spectra of blue, green and slight breaking of green polymorphs. $\lambda_{\text{ex}} = 360$ nm.

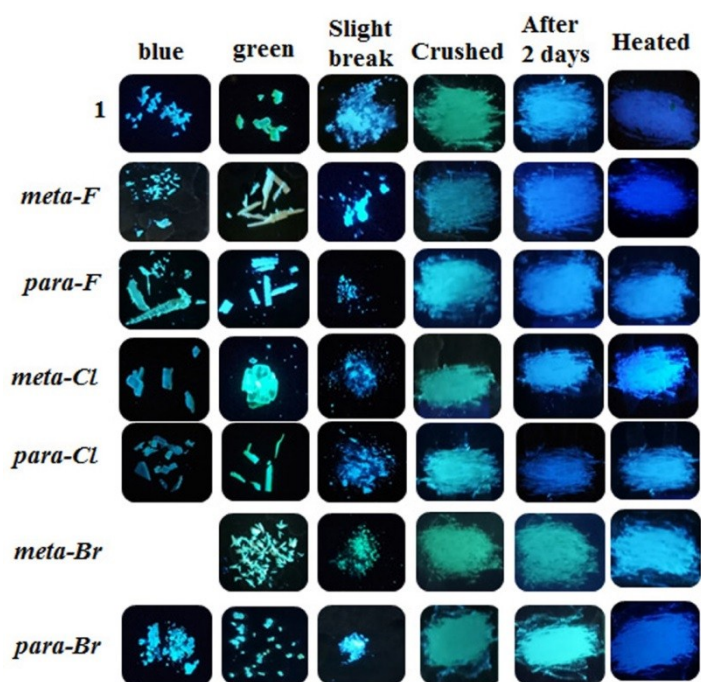


Figure S13. Digital images of stimuli responsive fluorescence changes of halogen positional isomers. $\lambda_{\text{ex}} = 365 \text{ nm}$.

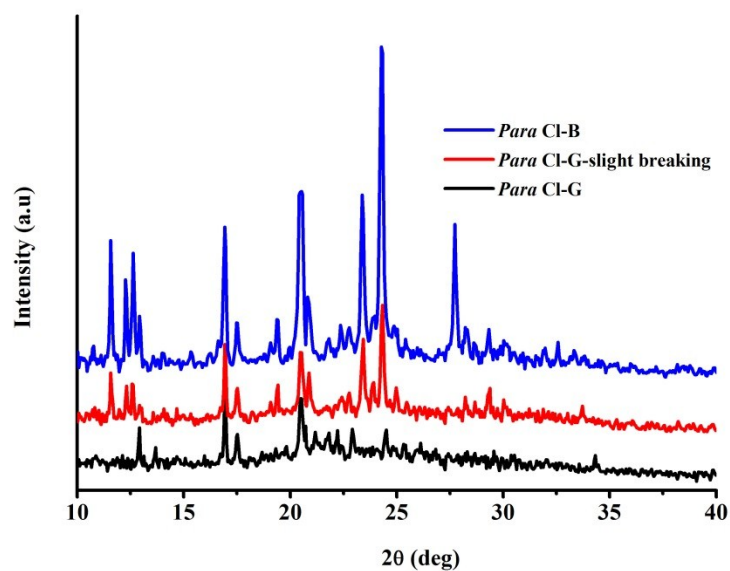


Figure S14. PXRD pattern of *para*-Cl-G before and after slight breaking and comparison with *para*-Cl-B.

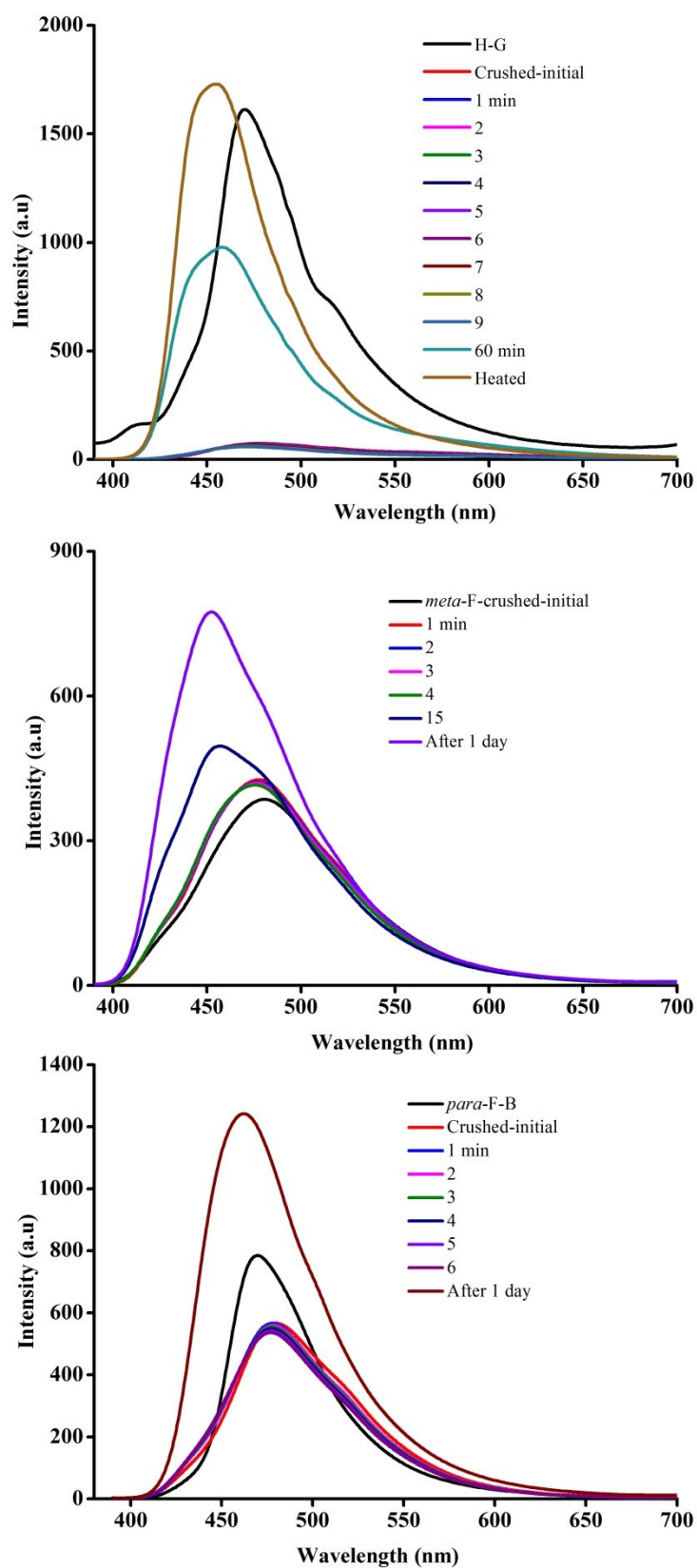


Figure S15. Self-reversible mechanofluorochromism. $\lambda_{\text{ex}} = 360$ nm.

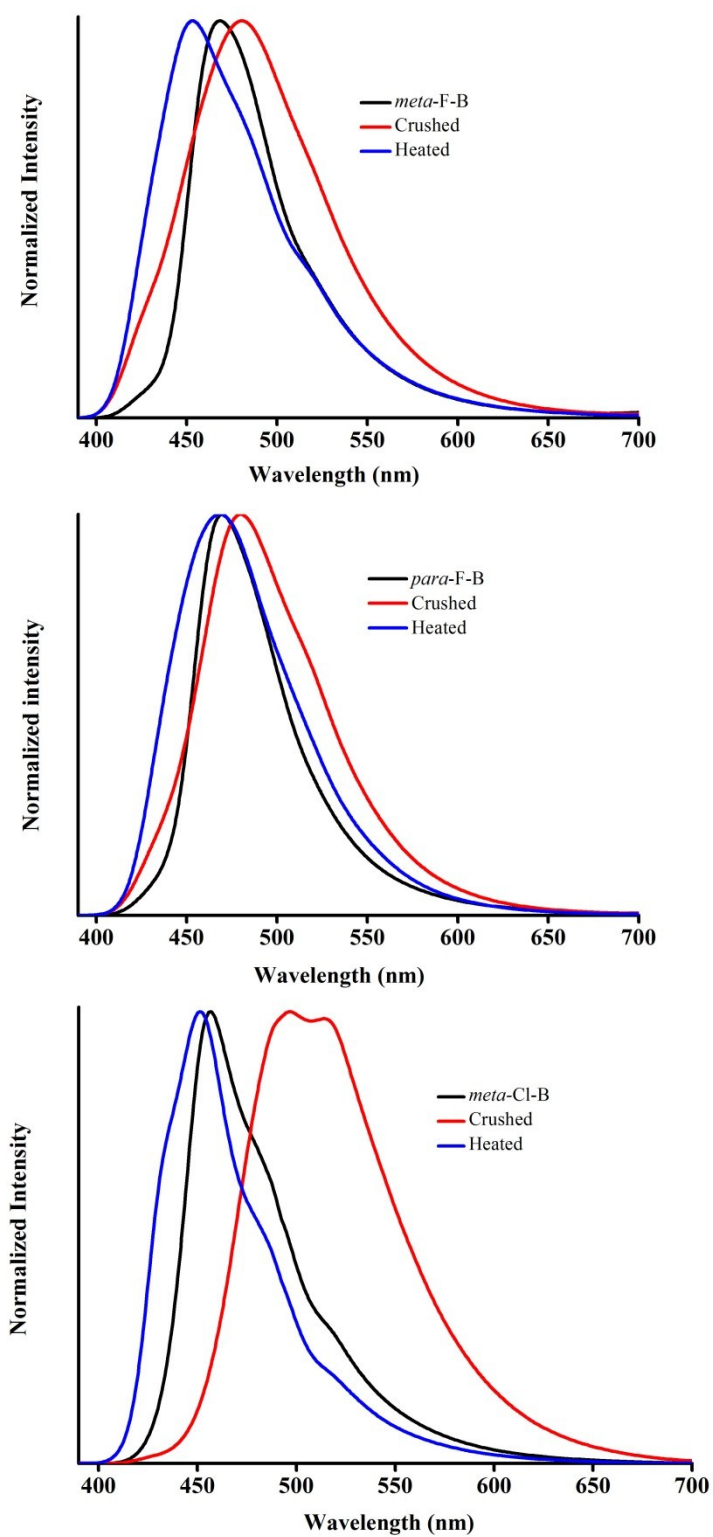


Figure S16. Reversible mechanofluorochromism. $\lambda_{\text{ex}} = 360 \text{ nm}$.

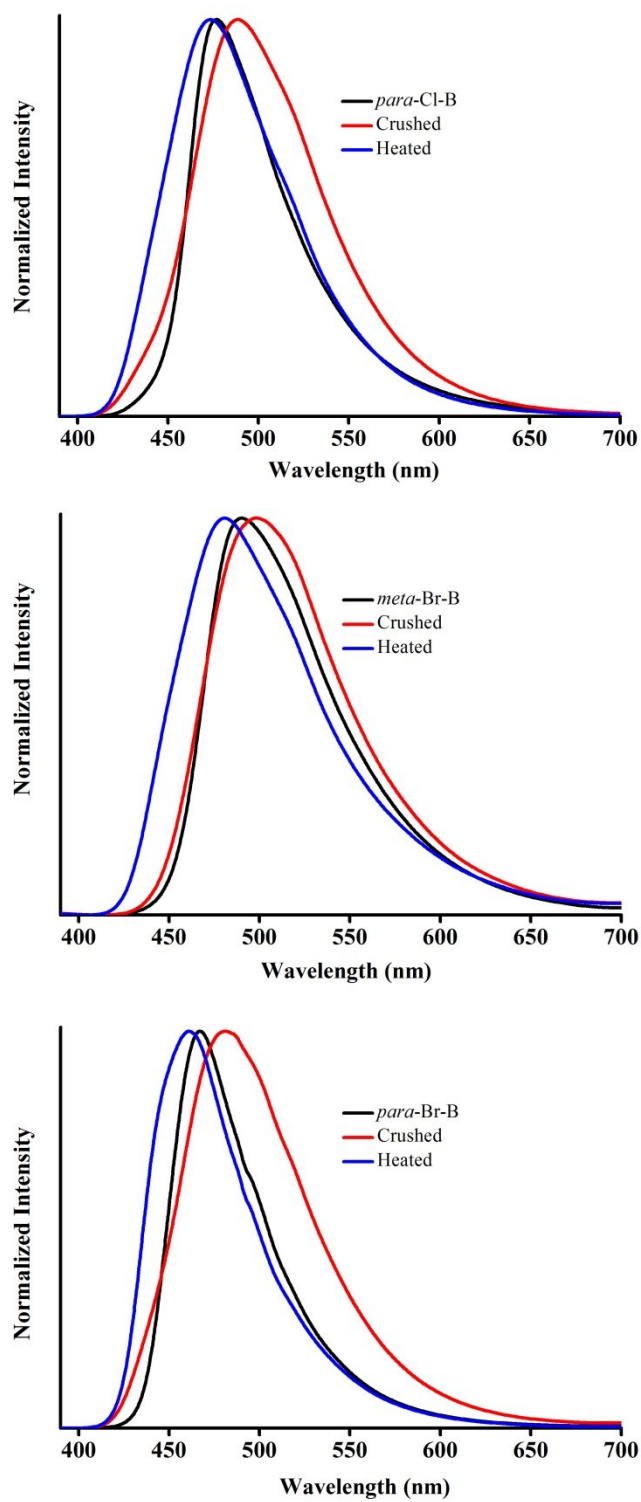


Figure S17. Reversible mechanofluorochromism. $\lambda_{\text{ex}} = 360$ nm.

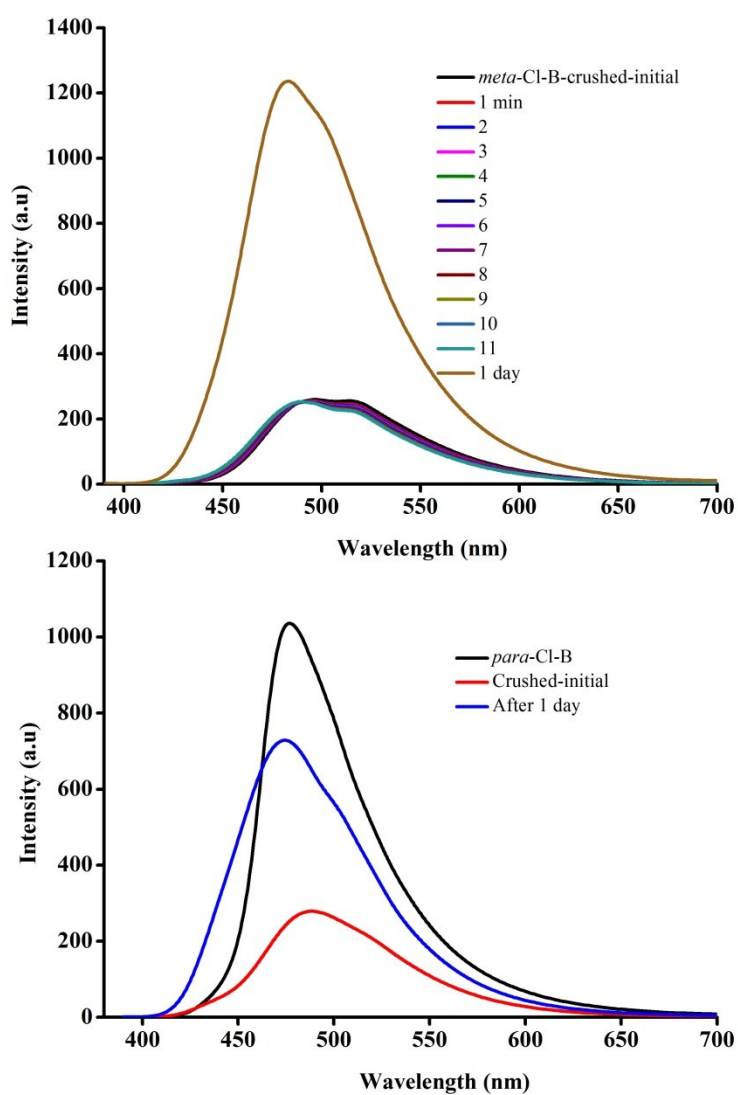


Figure S18. Self-reversible mechanofluorochromism. $\lambda_{\text{ex}} = 360$ nm.

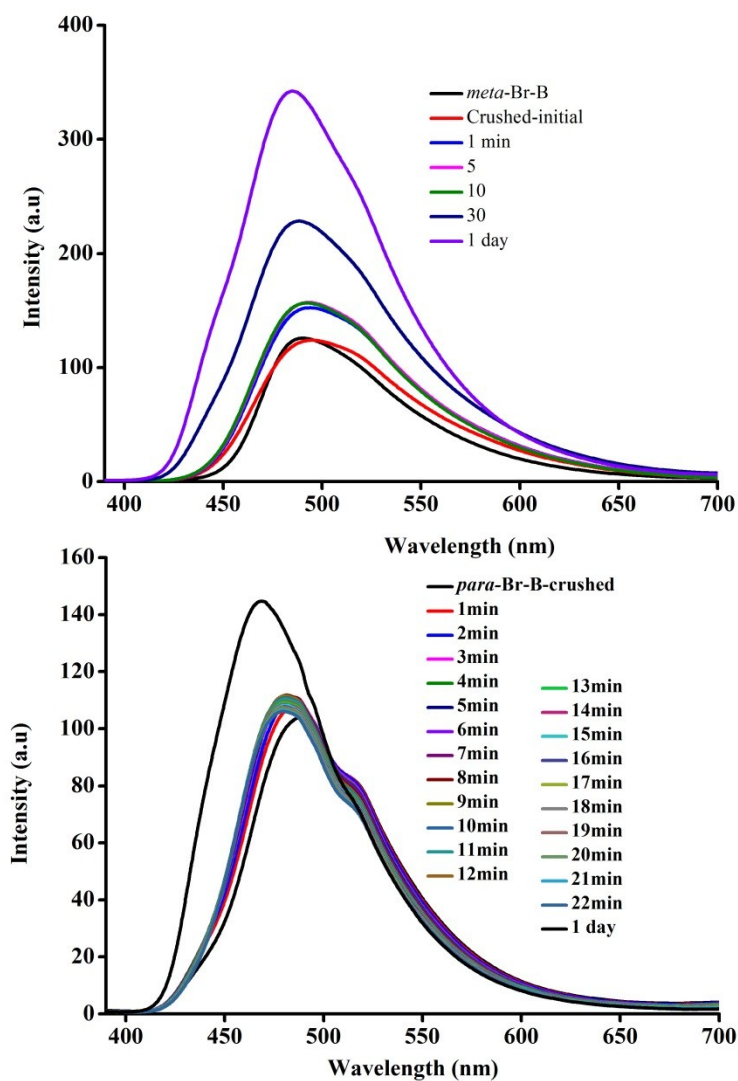


Figure S19. Self-reversible mechanofluorochromism. $\lambda_{\text{ex}} = 360$ nm.

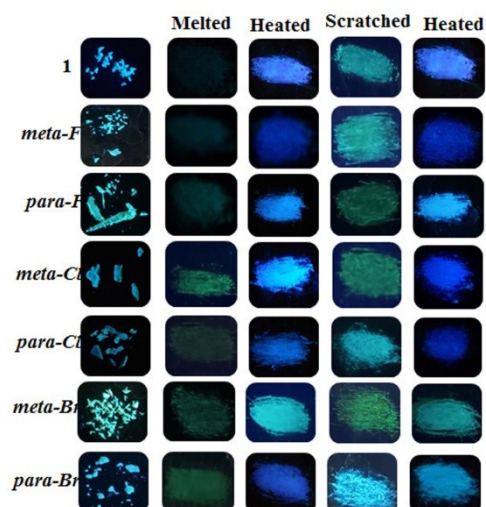


Figure S20. Digital images of crystallization induced fluorescence switching. $\lambda_{\text{ex}} = 365$ nm.

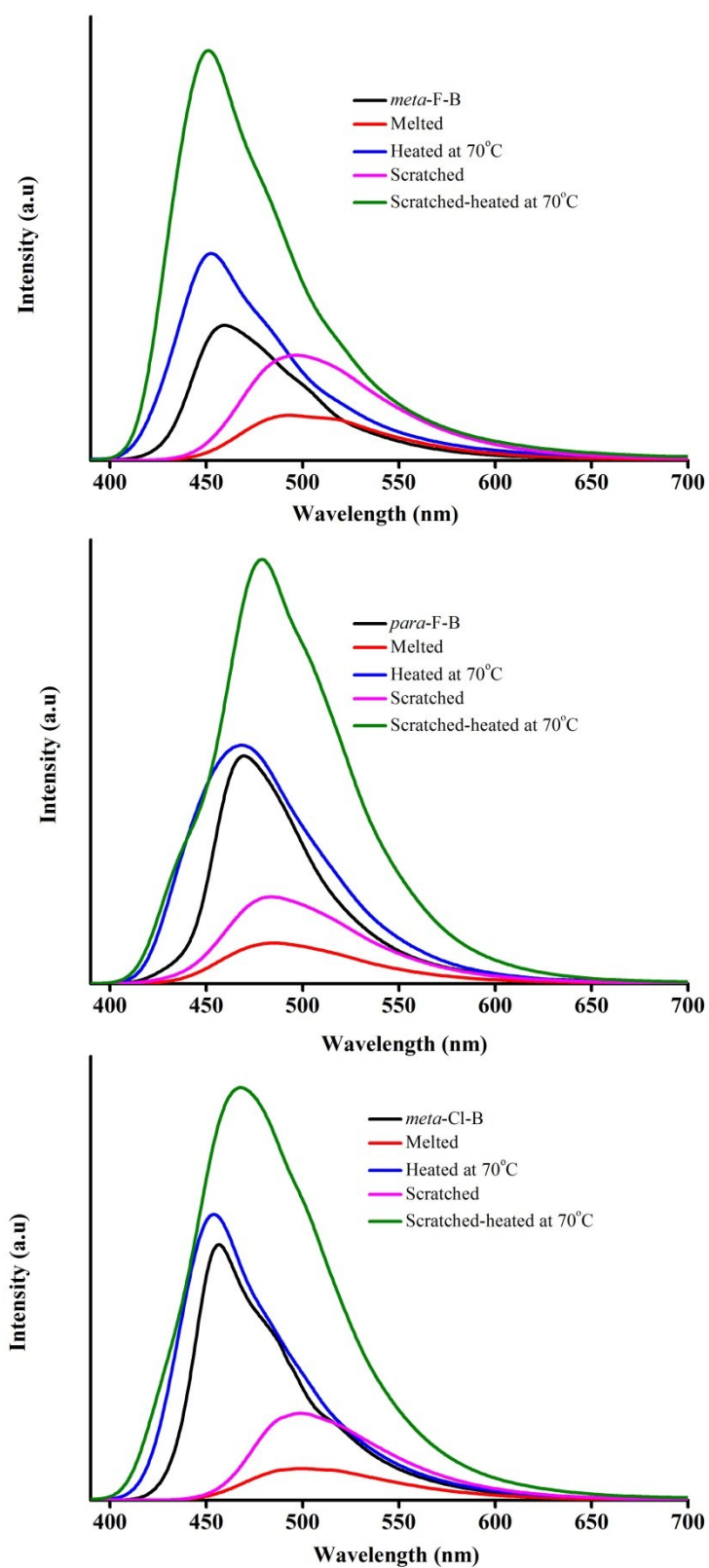


Figure S21. Fluorescence spectra of crystallization induced fluorescence switching. $\lambda_{\text{ex}} = 360$ nm.

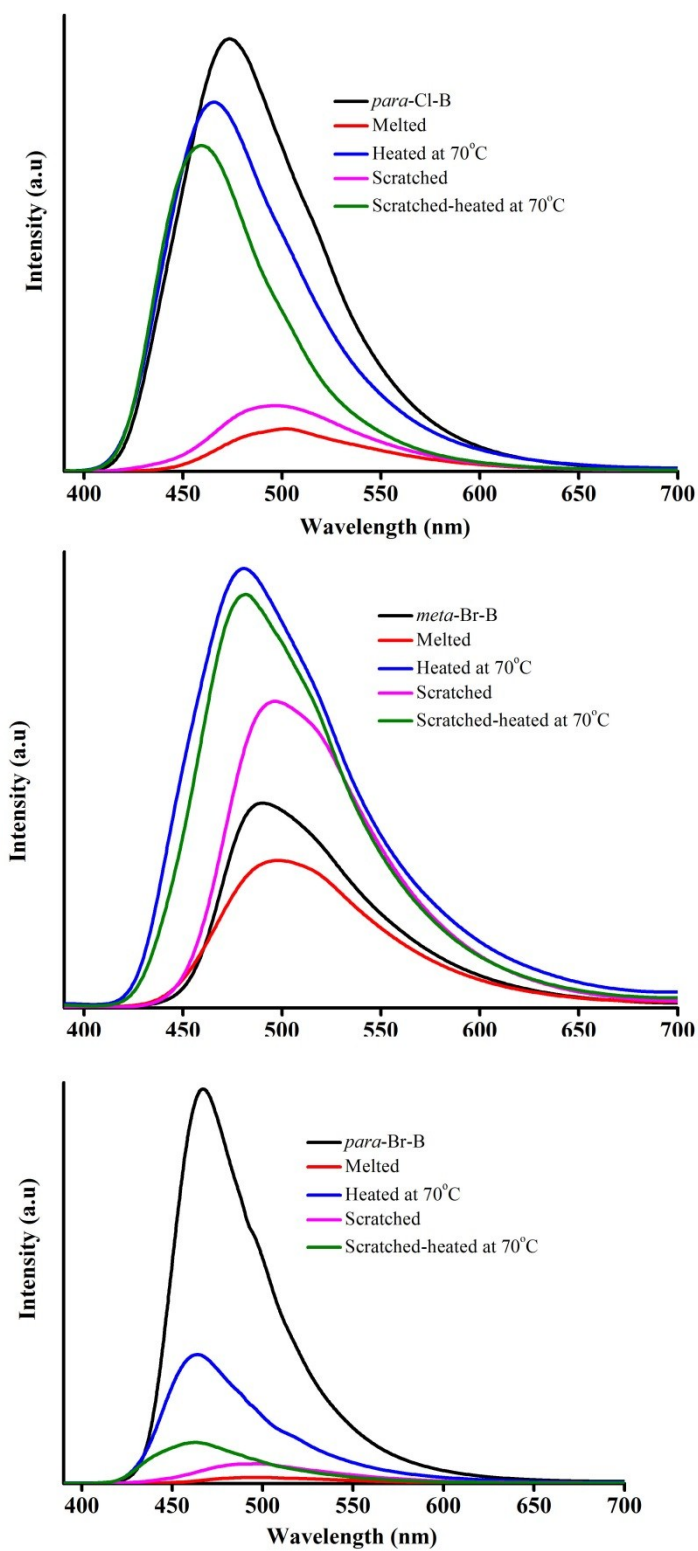


Figure S22. Fluorescence spectra of crystallization induced fluorescence switching. $\lambda_{\text{ex}} = 360$ nm.

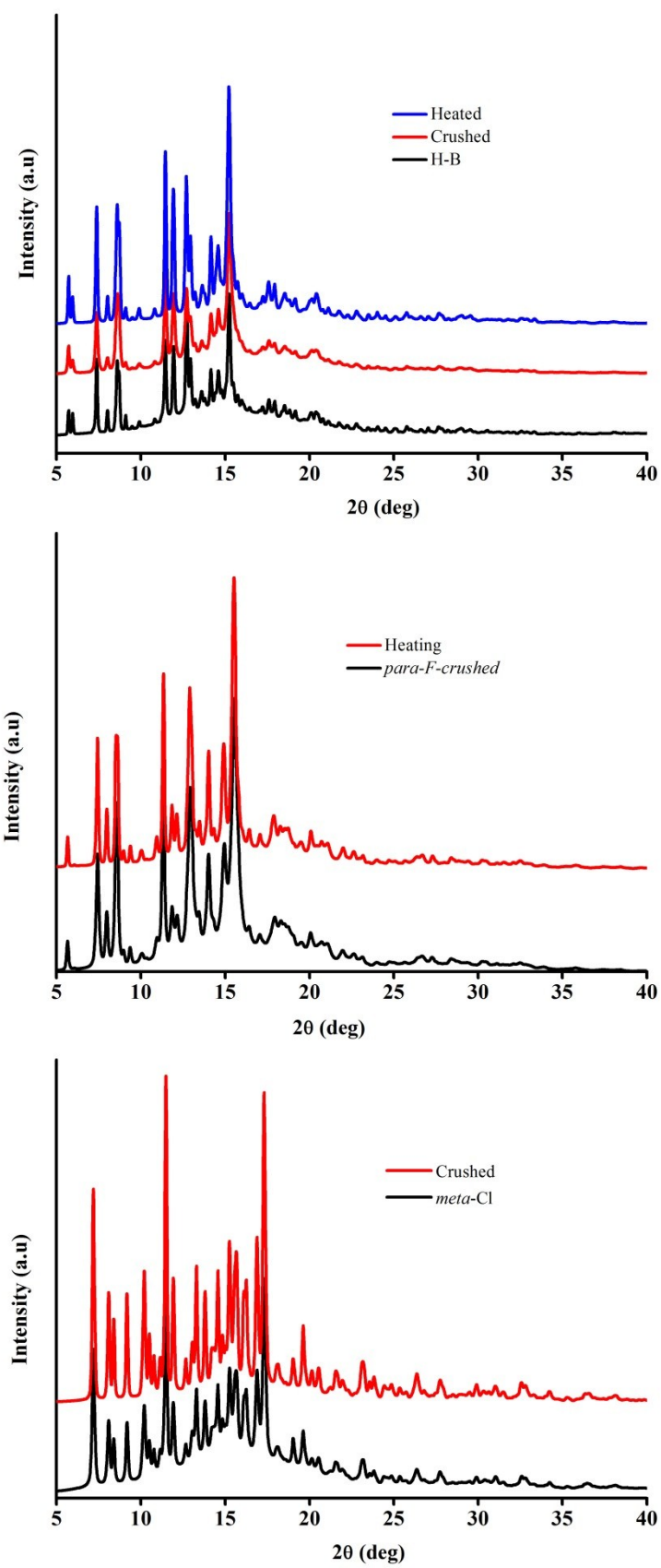


Figure S23. PXR D pattern.

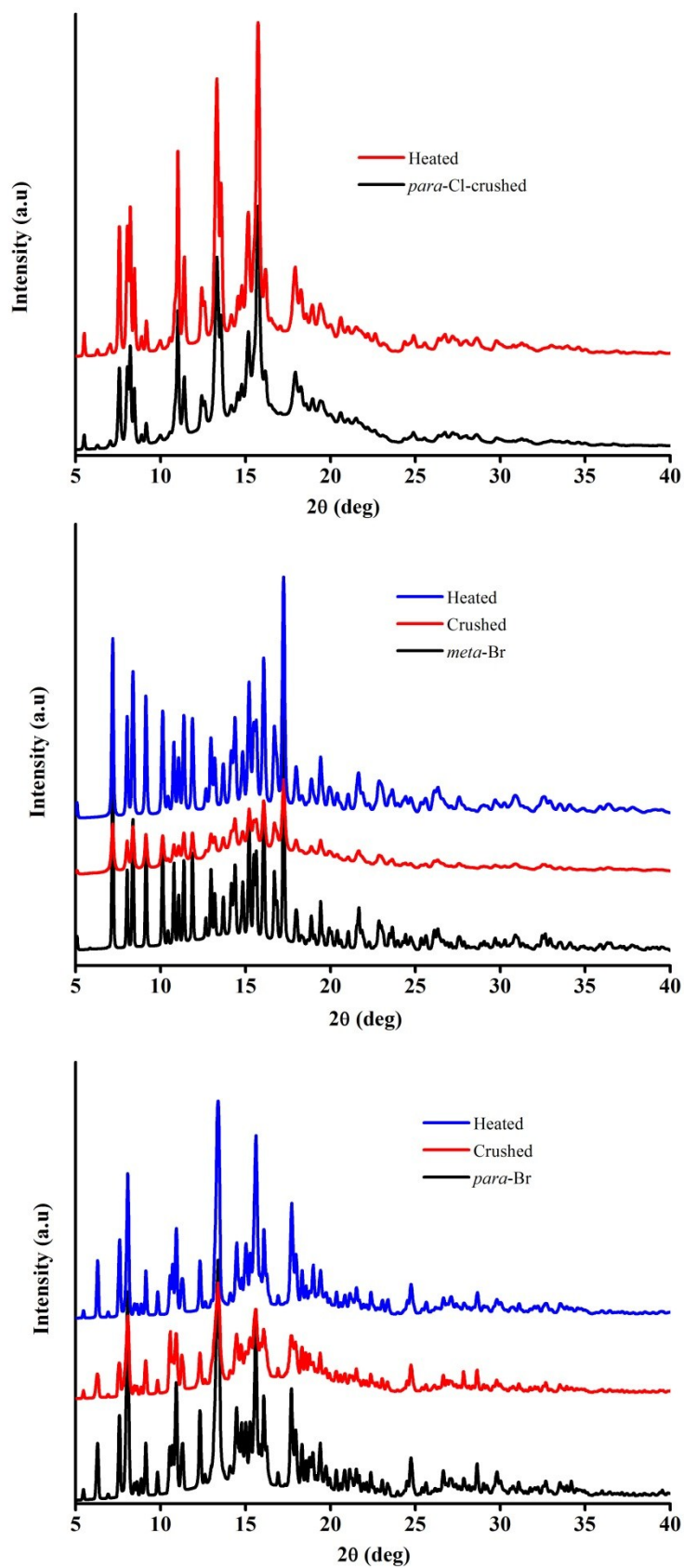


Figure S24. PXR D pattern.

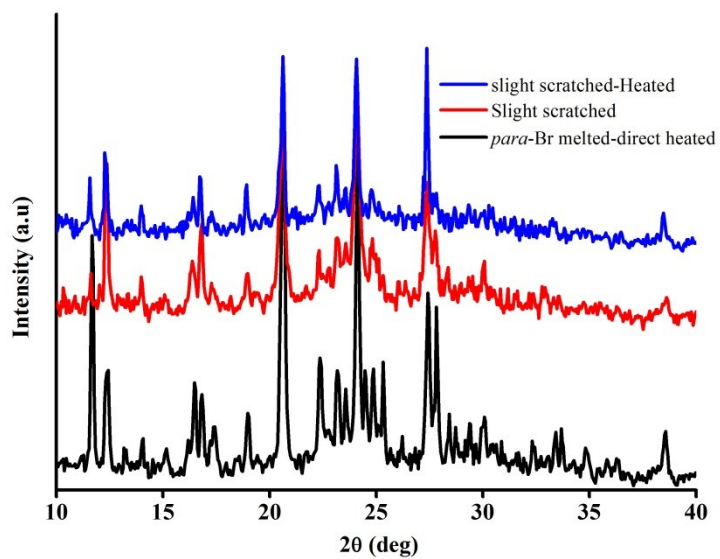


Figure S25. PXRD pattern.

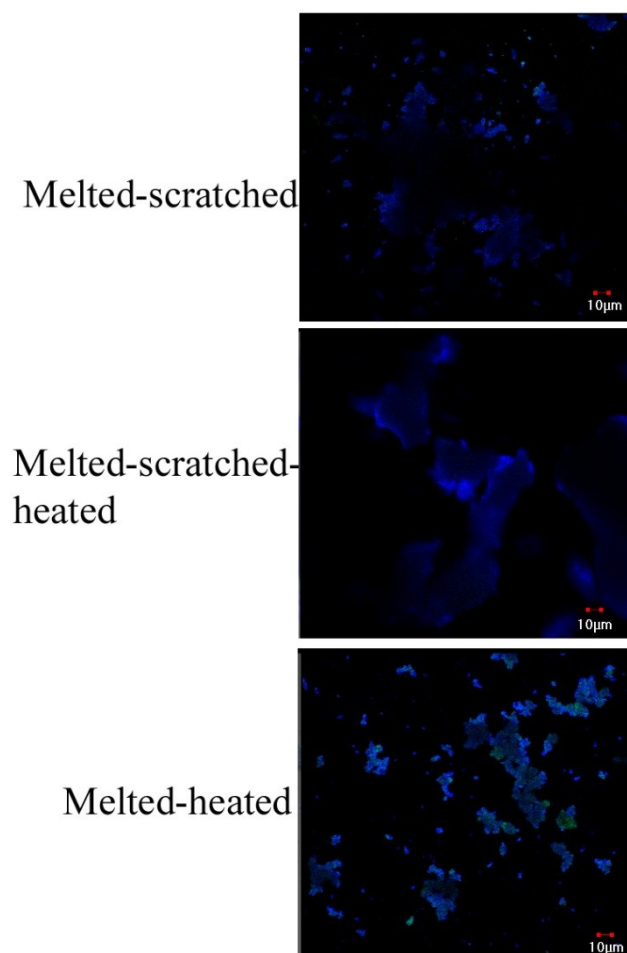


Figure S26. Confocal fluorescence image of *para*-Br-B.