

Supplementary Information

Constructing multicolored mechanochromic luminogen with high contrast through combination of large conjugation core and peripheral phenyl rings

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Experimental section

Tetrahydrofuran (THF) was purified by distillation over sodium/benzophenone under nitrogen before use. Other reagents were commercially obtained and used as received without additional purification.

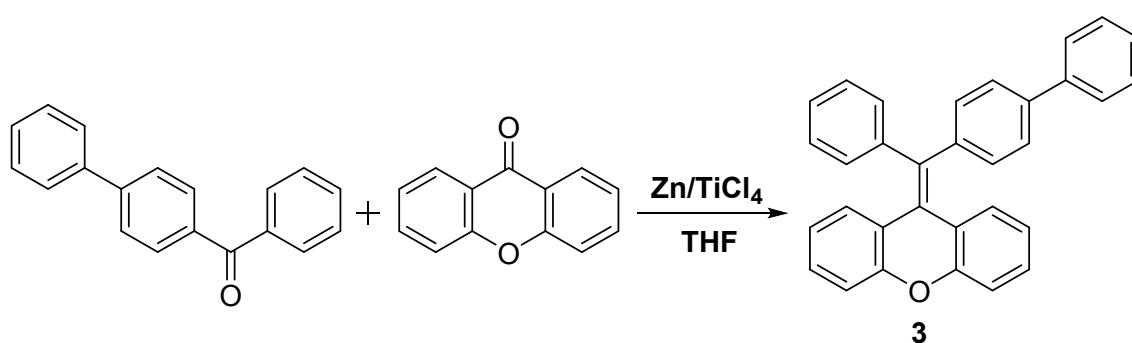
General Characterization Method

All the reactions were carried out under a nitrogen atmosphere using Schlenk technique. ¹H NMR spectra was recorded using a Bruker AV 400 Spectrometer at 400 MHz and ¹³C NMR spectra was recorded using a Bruker AVANCE 500 at 125 MHz in CDCl₃-d₃ solution, respectively. Mass spectra was recorded on a triple quadrupole mass spectrometer (Bruker micr OTOF-Q II) operating in a chemical ionization (CI) mode. Fluorescence spectra of all samples were measured by a Cary Eclipse spectrofluorometer. Quantum yield of solid were recorded on horiba fluoromax 4 with a calibrated intergrating sphere system. Infra-red (IR) spectra were obtained on a Nicolet fourier

spectrofluorometer. Differential scanning calorimetry (DSC) was carried out a Mettler DSC 1 instrument at a scanning rate of 10 K min⁻¹ under nitrogen atmosphere. Powder X-Ray diffraction (XRD) patterns were performed on a X' Pert PRO MPD diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 25 °C (scan range: 4.5 – 50 °). Melting points were measured by DSC analysis. All photographs were recorded on a FinePix S7000 digital camera.

Synthesis of luminogen **3**

Luminogens **3** was prepared according to Scheme S1 following the synthetic procedures given in the literature^[1], the reaction was carried out under a dry nitrogen atmospheres using Schlenk technique, which was a typical cross McMurry coupling reaction. Yield: 32%. M.p. 193-194 °C. ¹H-NMR (400 MHz, CD₃Cl-d₃, δ): 7.60-7.58 (2H), 7.53-7.51 (2H), 7.45-7.41 (2H), 7.37-7.29 (8H), 7.27-7.17 (4H), 6.74-6.69 (2H), 7.02-6.90 (2H). ¹³C-NMR (125 MHz, CD₃Cl-d₃, δ): 153.7, 143.1, 142.1, 140.7, 139.4, 138.1, 129.9, 129.5, 129.2, 128.9, 128.8, 128.7, 128.0, 127.3, 127.2, 126.9, 125.6, 124.5, 122.4, 122.3, 116.3. MS (CI): m/e 423.4 (M⁺, calcd. 422.2). IR (KBr, cm⁻¹): $\nu = 3437$ (s), 1608 (s), 1447 (s), 1251 (s), 1201 (m), 761 (s),



Scheme S1. Synthetic route of luminogen **3**.

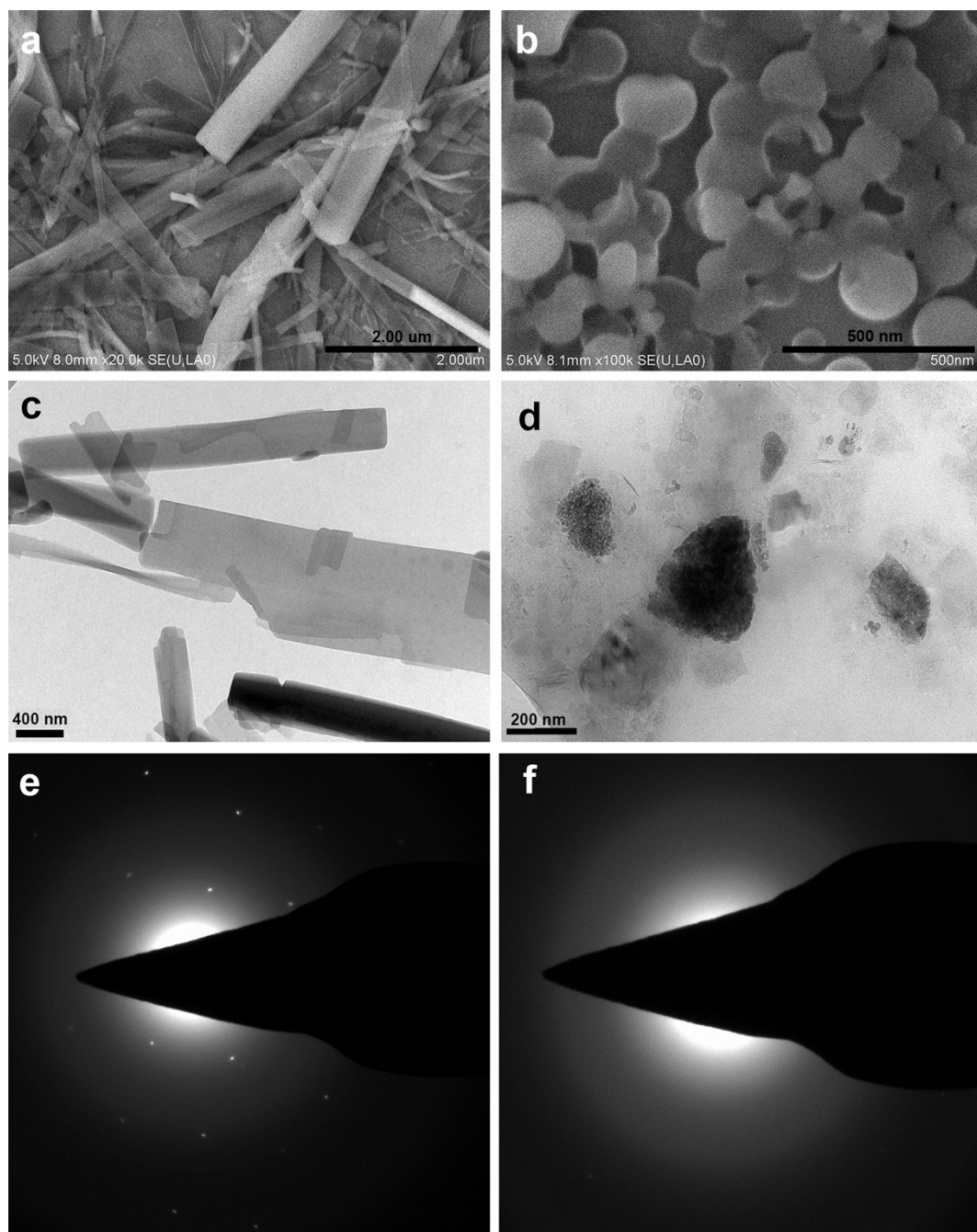


Fig. S1 (a, b) SEM, (c, d) TEM images and (e, f) ED patterns of aggregates of **3** formed in acetonitrile/water mixtures with $f_w =$ (a, c, e) 70%, and (b, d, f) 90%.

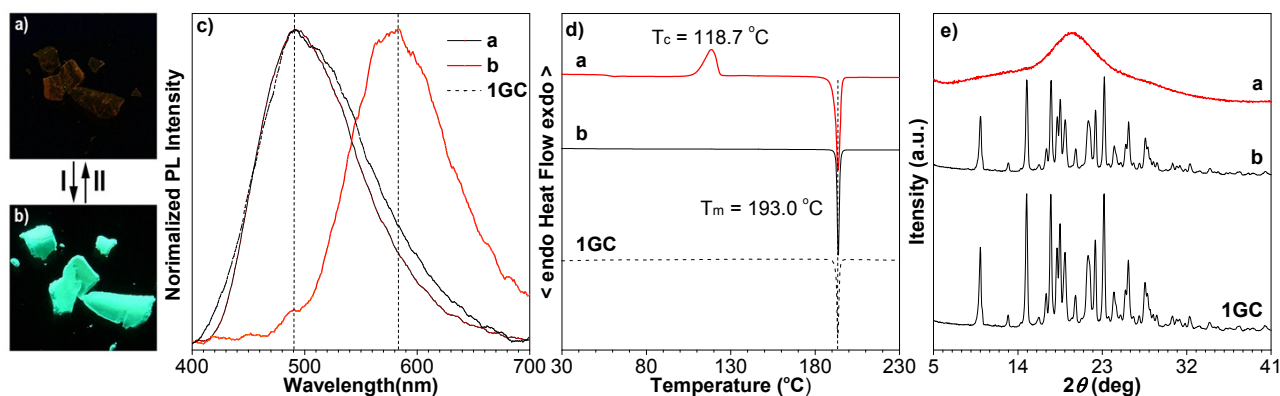


Fig. S2 Photos of (a) 3Am and (b) 3Am fumed with acetone, (c) Normalized PL spectra (Excitation wavelength: 360 nm), (d) DSC thermograms and (e) powder XRD patterns of samples (a) and (b) in the images. The curves of 3GC are also listed for comparison. Photos of sample (a) and (b) were taken under UV illumination. Conditions: I, fuming with acetone vapor, 5 min; II, heating to melt and quickly cooling.

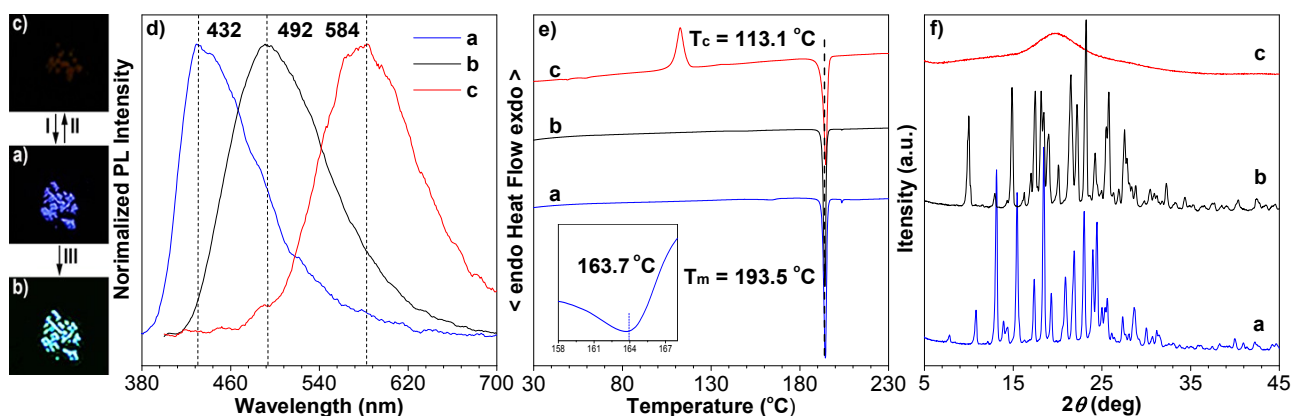


Fig. S3 Photos of (a) 3Am fumed by methanol, (b) heated sample (a), and (c) 3Am were taken under UV illumination. (d) Normalized PL spectra (Excitation wavelength: 360 nm), (e) DSC thermograms (scan rate: 10 °C min⁻¹) and (f) XRD patterns of samples (a), (b) and (c) in the images. Photos of (a), (b) and (c) were taken under UV illumination. Conditions: I, fuming with methanol vapor, 6 h; II, heating to melt and quickly cooling; III, annealed at 160 °C, 2 h.

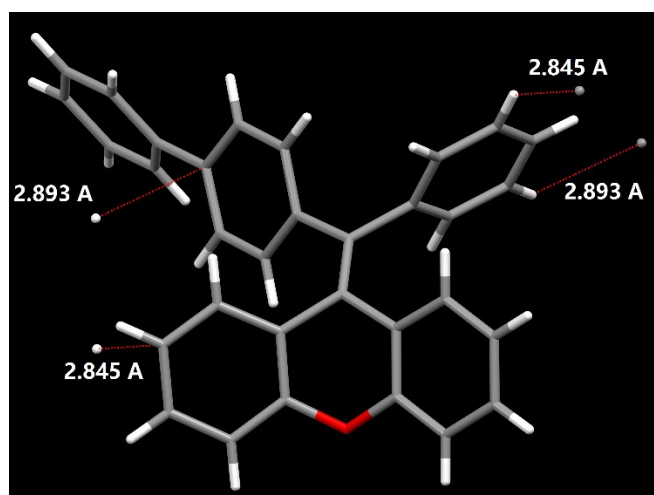


Fig. S4 View of molecular conformation and C-H... π interactions in **3GC**

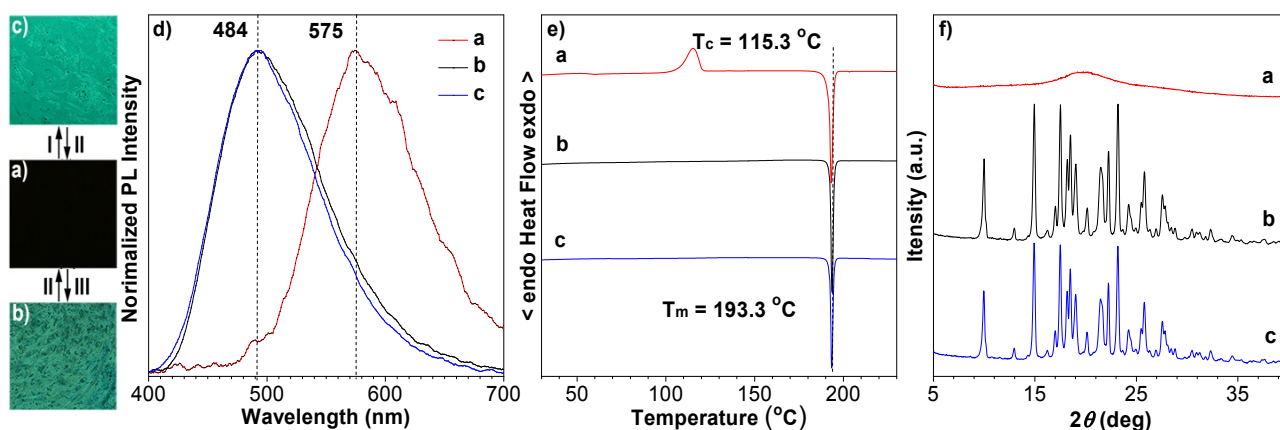


Fig. S5 Photos of (a) ground powder of **3**, (b) annealed ground powder of **3** (c) ground powder of **3** fumed with acetone. (d) Normalized PL spectra (Excitation wavelength: 360 nm), (e) DSC thermograms (scan rate: 10 °C min⁻¹) and (f) XRD patterns of samples (a), (b) and (c) in the images. Photos were taken under UV illumination. Conditions: I, fuming with acetone vapor, 5min; II, grinding; III, 120 °C, 1h.

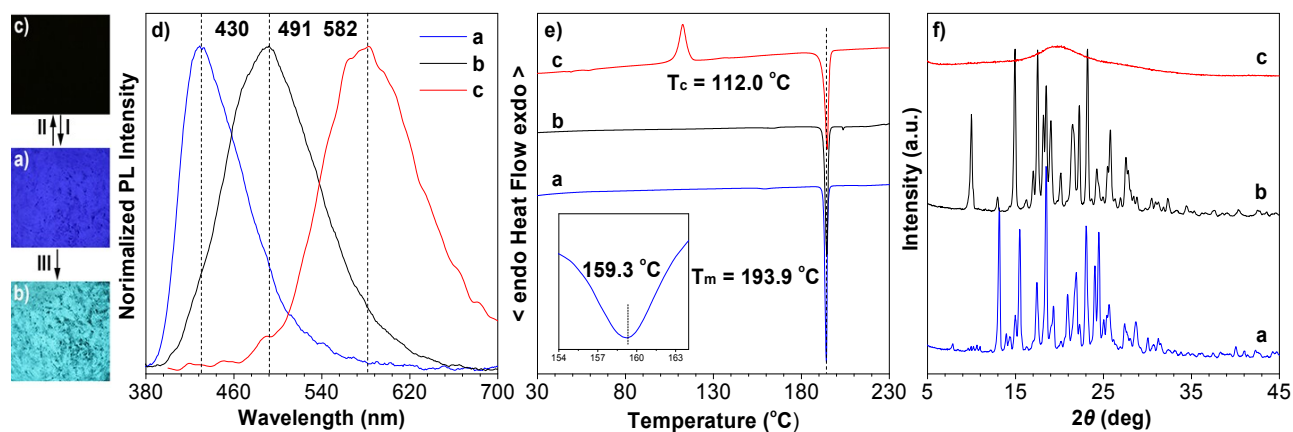


Fig. S6 Photos of (a) ground solid of **3** fumed by methanol, (b) sample (a) annealed at 160 °C, (c) ground solid of **3**. (d) Normalized PL spectra (Excitation wavelength: 360 nm), (e) DSC thermograms (scan rate: 10 °C min⁻¹) and (f) XRD patterns of samples in the images. Photos were taken under UV illumination. Condition: I, fumed with methanol vapor, 3 h; II, grinding; III, annealed at 160 °C, 1 h.

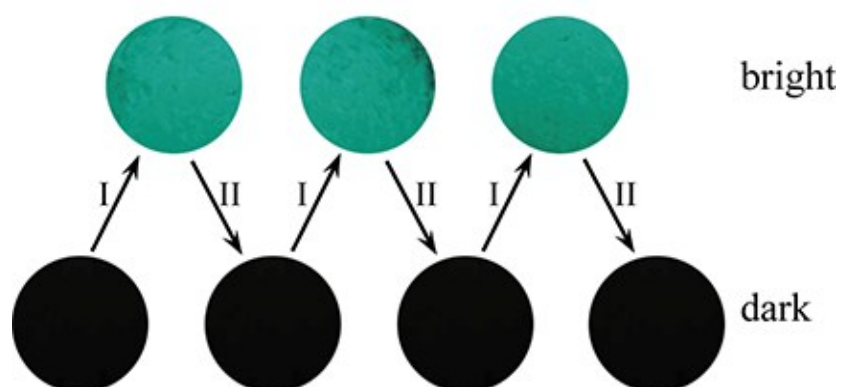


Fig. S7 Repeated switching emission of **3** between dark and bright green by grinding-heating cycles. The photos were taken under illumination. I: 120 °C, 1 h; II: grinding.

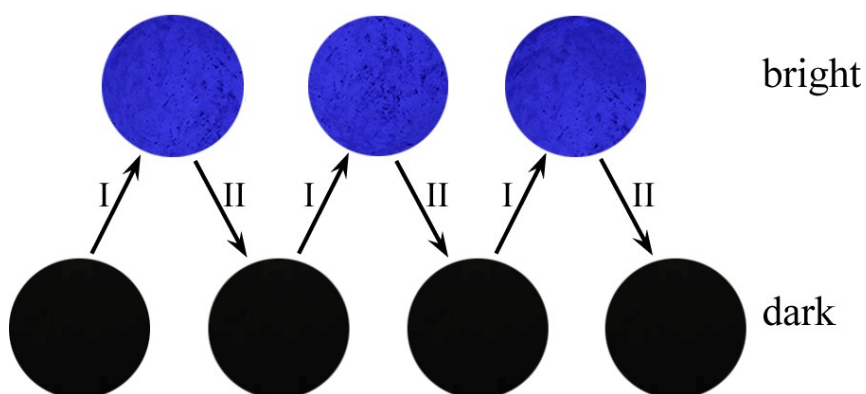


Fig. S8 Repeated switching emission of **3** between dark and bright deep blue by grinding-fuming with methanol cycles. The photos were taken under illumination. I: fuming with methanol vapor, 6 h; II: grinding.

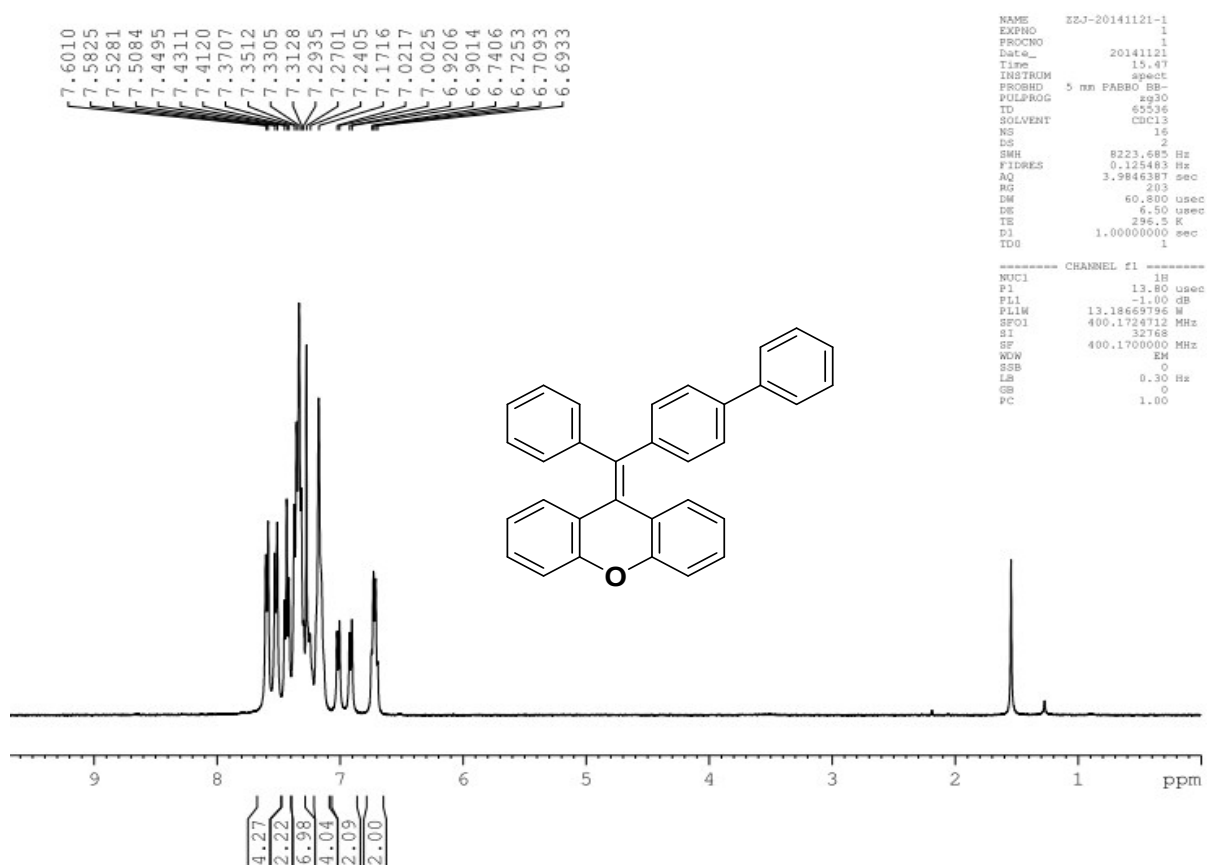


Fig. S9 The ¹H-NMR spectrum of **3** in Chloroform-d₃ solution.

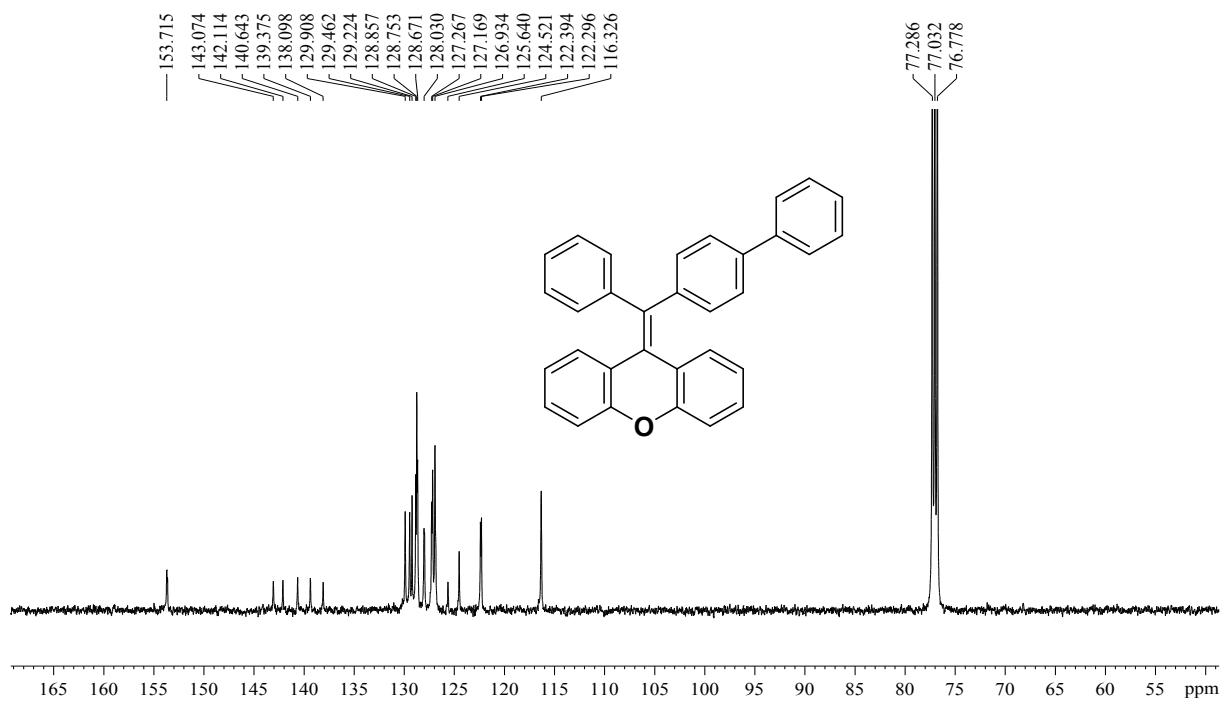


Fig. S10 The ^{13}C -NMR spectrum of **3** in Chloroform- d_3 solution.

References

1. J. Mcmurry, *Acc. Chem. Res.* 1983, 16, 405-411