

Supporting Information

Visible-light-excitable aqueous afterglow exhibiting long emission wavelength and ultralong afterglow lifetime of 7.64 s

Xiangxiang Zhai,^{a,b} Ying Zeng,^b Xinjian Deng,^b Qianqian Lou,^c Aizhi Cao,^c Limin Ji,^c Qianqian Yan,^{*b} Biaobing Wang^{*a} and Kaka Zhang^{*b}

^a Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou, People's Republic of China

^b Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

^c Shandong Longchang Animal Health Product CO. Ltd, Qihe Economic Development Zone, Qihe County, Dezhou City, Shandong Province, People's Republic of China

*Correspondence: yanqianqian@sioc.ac.cn; biaobing@cczu.edu.cn; zhangkaka@sioc.ac.cn.

Table of Contents

Materials

Physical measurements and instrumentation

The synthesis of D-coronene

The synthesis of SpirocurBF₂

Preparation of afterglow emulsions

Steady state and delay spectra and decay profiles of emulsions

NMR spectra of compounds

References

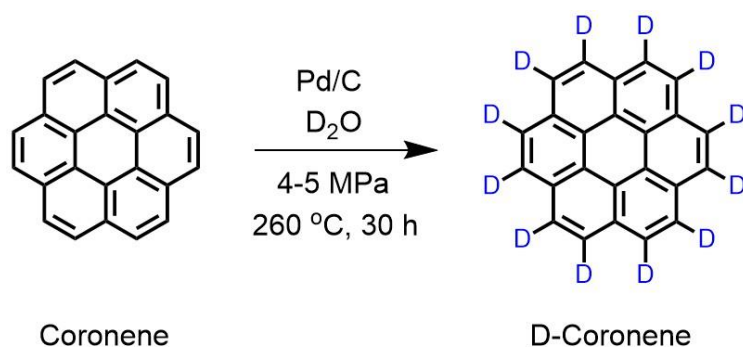
Materials

Unless otherwise stated, all commercially available chemicals were used without further purifications. Coronene (98%, Zhengzhou Alpha Chemical Co), methyl methacrylate (MMA) (99%, Adamas), potassium persulfate (KPS) (98%, Innochem), Pluronic F127 (poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), PEO₁₀₀-*b*-PPO₆₈-*b*-PEO₁₀₀ (the subscript represents the degree of polymerization of each block, Sigma-Aldrich), sodium cholate ($\geq 98\%$, Dibo), sodium deoxycholate (SDC) (98%, Meryer), 2,2'-azobis(2-methylpropionitrile) (AIBN) (99%, Macklin), polysorbate 40 (99%, Aladdin), sodium dodecyl benzene sulfonate (SDBS) (99%, Aladdin), hexadecyltrimethylammonium bromide (CTAB) ($\geq 97\%$, Bide Accela).

Physical measurements and instrumentation

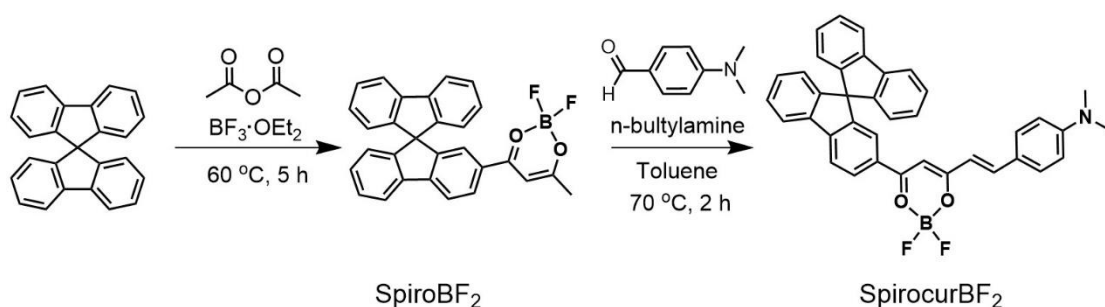
NMR spectra were recorded on a JEOL Fourier-transform NMR spectrometer (400 MHz). Chemical shifts for ^1H , ^{11}B , ^{13}C and ^{19}F spectra are reported in ppm on the δ scale and chemical shifts for ^1H and ^{13}C spectra relative to proton resonance resulting from incomplete deuteration of the solvents (CDCl_3 : 7.26 ppm, 77.16 ppm). UV-Vis absorption spectra were recorded on a Hitachi U-3310 UV-vis spectrophotometer and a Techcomp UV1050 UV-vis spectrophotometer. The steady-state and delayed emission spectra were collected by Hitachi FL-4700 fluorescence spectrometer equipped with chopping systems, the delayed emission spectra were obtained with a delay time of approximately 1 ms. The excited state decay profiles in millisecond to second region were collected by Hitachi FL-4700 fluorescence spectrometer equipped with chopping systems. Zeta-potential analysis and dynamic light scattering (DLS) experiments were performed on a Malvern Nano-ZS90 Zetasizer with an internal HeNe laser ($\lambda = 632.8 \text{ nm}$). Transmission electron microscopy (TEM) experiments were performed on a Hitachi TEM system at accelerating voltage of 100 kV. TEM samples were prepared by depositing a drop of sample solution onto a carbon-coated copper grid followed by drying under ambient conditions. The sizes of the nanoparticles were analyzed using ImageJ 1.53c software. Photographs and videos were captured by using Apple iPhone 12 cameras. Before the capture, samples were irradiated by a 365 nm UV lamp (5 W) for approximately 5 s at a distance of approximately 15 cm.

The synthesis of D-Coronene



200 mg undeuterated coronene, 150 mg Pd (10 wt%) on activated carbon and 30 mL D_2O were added into a teflon-lined autoclave. The autoclave was then sealed and heated in a safe laboratory in our institute. The deuteration reaction was performed at 260 °C and 4-5 MPa for 30 h. After deuteration, the autoclave was cooled to room temperature. The reaction mixture was then extracted with dichloromethane. The crude organic layer was dried over Na_2SO_4 , filtered and reduced under vacuum. The crude deuterated coronene was purified by column chromatography over silica using dichloromethane as eluent. After rotary evaporation and vacuum drying, the purified deuterated coronene was obtained with a yield of 50%. The deuteration yield of coronene was estimated from ^1H NMR results using 1,4-dioxane as an internal standard. The synthetic procedures are the same as our previous study.¹

The synthesis of SpirocurBF₂



9,9'-spirobifluorene (500 mg, 1.1 mmol), acetic anhydride (5 mL) and boron trifluoride diethyl etherate (0.8 mL) were added into a 50 mL round bottom flask. The reaction mixture was heated to 60 °C and stirred for 5 h. Then the reaction was quenched by adding the reaction mixture dropwise into cold water. The precipitates were washed by water for three times and dried under vacuum. The crude product was

purified by column chromatography over silica gel using petroleum ether/dichloromethane (1:1) as eluent to give yellow solids with an isolation yield of 53%. The obtained product spiroBF₂ was further purified by three cycles of recrystallization in spectroscopic grade dichloromethane/hexane. ¹H NMR (CDCl₃, 298 K, 400 MHz): δ 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.36 (d, *J* = 1.4 Hz, 1H), 7.22 (td, *J* = 7.6, 0.8 Hz, 1H), 7.13 (td, *J* = 7.5, 0.8 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 2H), 6.37 (s, 1H), 2.30 (s, 3H). ¹³C NMR (CDCl₃, 298 K, 101 MHz): δ 191.58, 182.28, 150.69, 149.90, 149.54, 147.29, 142.05, 139.80, 130.47, 130.29, 129.80, 128.41, 128.39, 128.26, 124.83, 124.50, 124.07, 121.58, 120.74, 120.52, 97.51, 65.96, 24.71. ¹⁹F NMR (CDCl₃, 298 K, 376 MHz): δ -140.06 (20%), -140.13 (80%). ¹¹B NMR (CDCl₃, 298 K, 128 MHz) δ -0.07. HRMS (positive ESI) *m/z*: calcd for C₂₉H₁₉O₂¹⁰BF₂+Na⁺: 470.1375, found: 470.1371. The synthetic procedures are the same as our previous study.²

SpiroBF₂ (56 mg, 0.125 mmol), 4-(dimethylamino)-benzaldehyde (56 mg, 0.375 mmol), 1-butylamine (2.5 μL) and toluene (2 mL) were added into a round bottom flask. The reaction was stirred at 70°C for 2 h. After cooling to room temperature, the solvent was removed by distillation under reduced pressure. Then the crude product was purified by column chromatography using petroleum ether/dichloromethane (1:1) as eluent to give black solids with an isolation yield of 48.5%. The spirocurBF₂ was further purified by three cycle of recrystallization in spectroscopic grade dichloromethane/hexane. ¹H NMR (CDCl₃, 298 K, 400 MHz): δ 8.15 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.99 (dd, *J* = 21.9, 11.6 Hz, 2H), 7.90 (t, *J* = 8.1 Hz, 3H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 3H), 7.36 (d, *J* = 1.6 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 15.2 Hz, 1H), 6.32 (s, 1H), 3.08 (s, 6H). ¹⁹F NMR (CDCl₃, 298 K, 376 MHz): δ -141.45 (20%), -141.51 (80%). HRMS *m/z*: calcd. for C₃₈H₂₈BF₂NO₂ + H⁺: 580.2254, found: 580.2274. The synthetic procedures are the same as our previous study.³

The preparation of Cor-PMMA organic afterglow emulsions

Methyl methacrylate (60 μ L), 60 μ L of coronene in methyl methacrylate (0.01 mg/mL), water (2 mL), 1 mL of surfactant (such as sodium cholate) in aqueous solution (25 mg/mL) were added into a 10 mL Schlenk tube to form the liquid precursor. The liquid precursor was treated by 30 min ultrasonication for pre-emulsification, and then 0.5 mL of potassium persulfate (2 mg/mL) was added into the liquid precursor. After three cycles of freeze-pump-thaw degassing procedures, the liquid precursor was treated by sonication and heated to 80°C for 1.5 h under magnetic stirring (130 rpm), leading to the formation of Cor-PMMA organic afterglow emulsions.

The preparation of D-Cor-PMMA organic afterglow emulsions

Methyl methacrylate (60 μ L), 60 μ L of deuterated coronene in methyl methacrylate (0.01 mg/mL), water (2 mL), 1 mL of sodium cholate in aqueous solution (25 mg/mL) were added into a 10 mL Schlenk tube to form the liquid precursor. The liquid precursor was treated by 30 min ultrasonication for pre-emulsification, and then 0.5 mL of potassium persulfate (2 mg/mL) was added into the liquid precursor. After three cycles of freeze-pump-thaw degassing procedures, the liquid precursor was treated by sonication and heated to 80°C for 1.5 h under magnetic stirring (130 rpm), leading to the formation of D-Cor-PMMA organic afterglow emulsions.

The preparation of D-Cor-spirocurBF₂-PMMA organic afterglow emulsions

60 μ L of spirocurBF₂ in methyl methacrylate (0.4 mg/mL), 60 μ L of deuterated coronene in methyl methacrylate (0.01 mg/mL), water (2 mL), 1 mL of sodium cholate in aqueous solution (25 mg/mL) were added into a 10 mL Schlenk tube to form the liquid precursor. The liquid precursor was treated by 30 min ultrasonication for pre-emulsification, and then 0.5 mL of potassium persulfate (2 mg/mL) was added into the liquid precursor. After three cycles of freeze-pump-thaw-degassing procedures, the liquid precursor was treated by sonication and heated to 80°C for 1.5 h under magnetic stirring (130 rpm), leading to the formation of D-Cor-SpirocurBF₂-PMMA organic afterglow emulsions.

The preparation of SpirocurBF₂-PMMA organic emulsions

60 μ L of spirocurBF₂ in methyl methacrylate (0.4 mg/mL), 60 μ L methyl methacrylate, water (2 mL), 1 mL of surfactant (sodium cholate) in aqueous solution (25 mg/mL) were added into a 10 mL Schlenk tube to form the liquid precursor. The liquid precursor was treated by 30 min ultrasonication for pre-emulsification, and then 0.5 mL of potassium persulfate (2 mg/mL) was added into the liquid precursor. After three cycles of freeze-pump-thaw-degassing procedures, the liquid precursor was treated by sonication and heated to 80°C for 1.5 h under magnetic stirring (130 rpm), leading to the formation of SpirocurBF₂-PMMA organic afterglow emulsions.

The preparation of PMMA organic emulsions

Methyl methacrylate (120 μ L), water (2 mL), 1 mL of sodium cholate in aqueous solution (25 mg/mL) were added into a 10 mL Schlenk tube to form the liquid precursor. The liquid precursor was treated by 30 min ultrasonication for pre-emulsification, and then 0.5 mL of potassium persulfate (2 mg/mL) was added into the liquid precursor. After three cycles of freeze-pump-thaw-degassing procedures, the liquid precursor was treated by sonication and heated to 80°C for 1.5 h under magnetic stirring (130 rpm), leading to the formation of PMMA organic afterglow emulsions

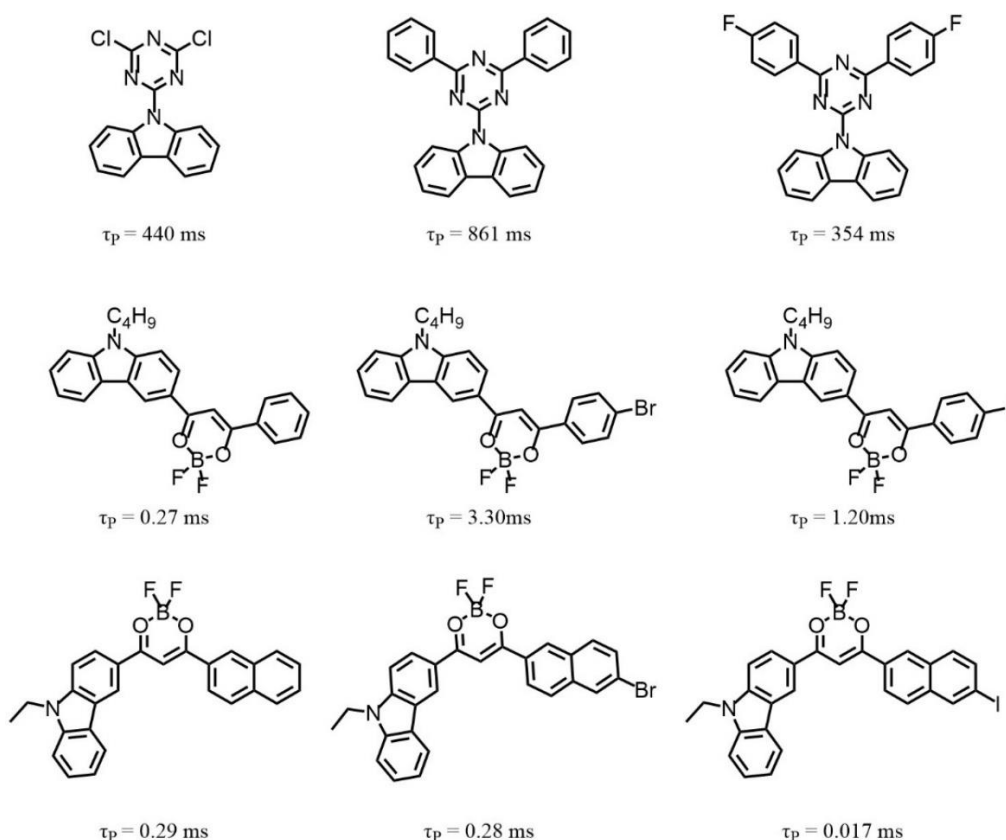


Figure S1. Selected examples of aqueous RTP and afterglow dispersions in the reported studies.⁴⁻⁶

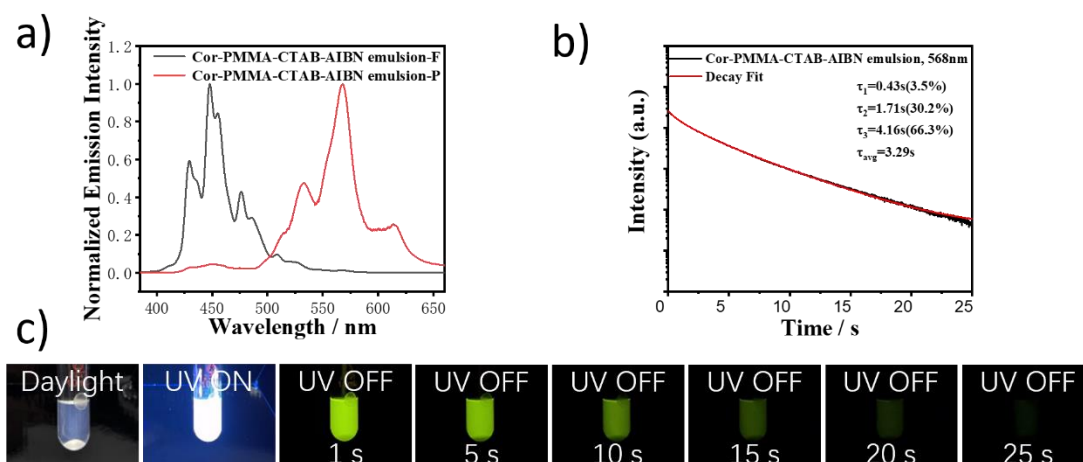


Figure S2. a) Room-temperature steady-state and delayed emission (1 ms delay) spectra of Cor-PMMA-CTAB-AIBN emulsions. b) Room-temperature emission decay profile of Cor-PMMA-CTAB-AIBN emulsions. c) Photographs of Cor-PMMA-CTAB-AIBN afterglow emulsions obtained under 365 nm UV and after switching-off the UV lamp at room temperature.

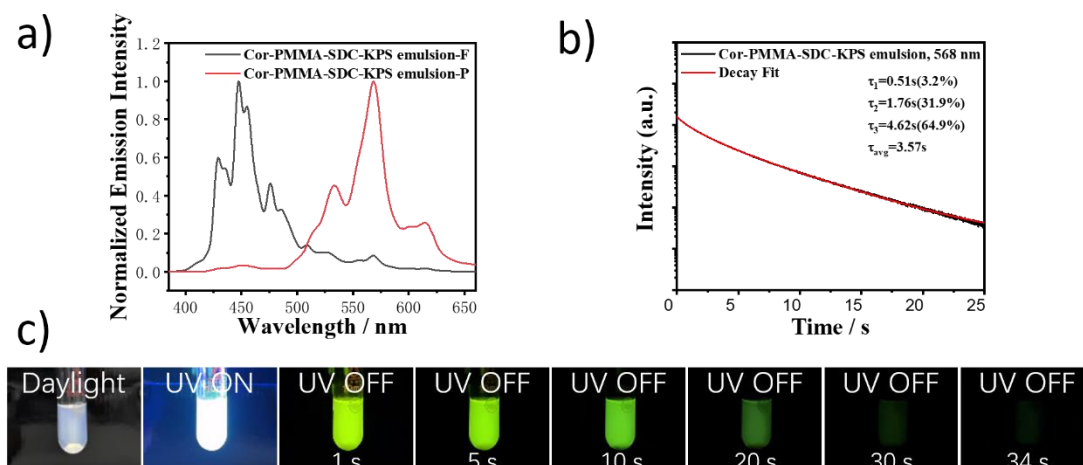


Figure S3. a) Room-temperature steady-state and delayed emission (1 ms delay) spectra of Cor-PMMA-SDC-KPS emulsions. b) Room-temperature emission decay profile of Cor-PMMA-SDC-KPS emulsions. c) Photographs of Cor-PMMA-SDC-KPS afterglow emulsions obtained under 365 nm UV and after switching-off the UV lamp at room temperature.

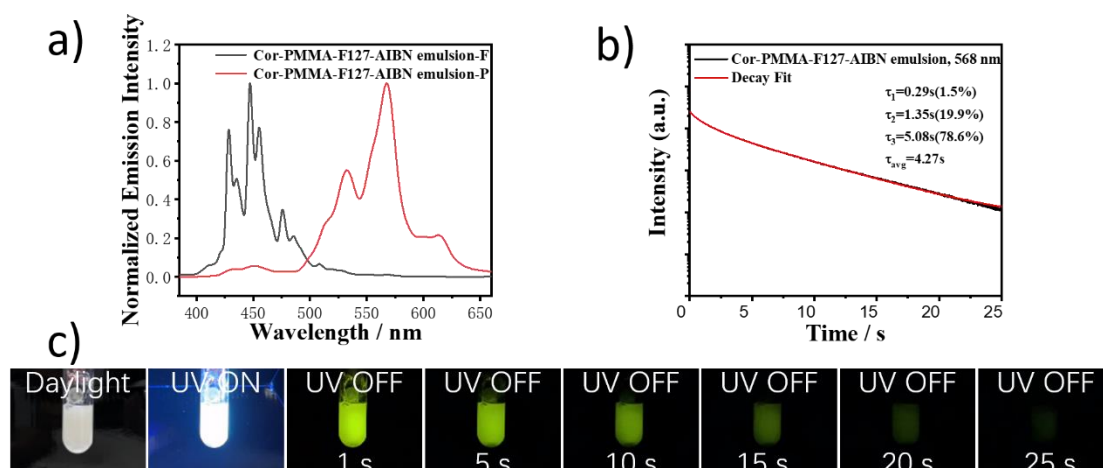


Figure S4. a) Room-temperature steady-state and delayed emission (1 ms delay) spectra of Cor-PMMA-F127-AIBN emulsions. b) Room-temperature emission decay profile of Cor-PMMA-F127-AIBN emulsions. c) Photographs of Cor-PMMA-F127-AIBN afterglow emulsions obtained under 365 nm UV and after switching-off the UV lamp at room temperature.

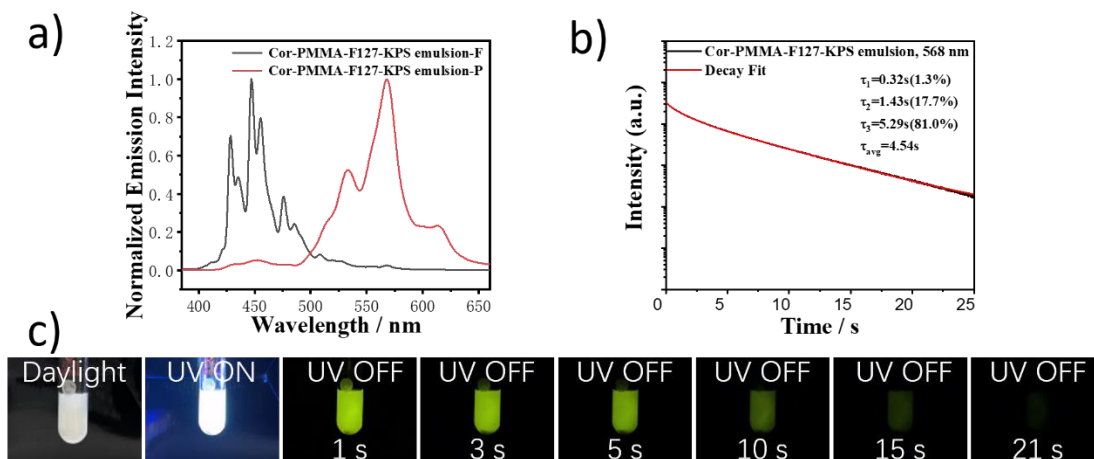


Figure S5. a) Room-temperature steady-state and delayed emission (1 ms delay) spectra of Cor-PMMA-F127-KPS emulsions. b) Room-temperature emission decay profile of Cor-PMMA-F127- KPS emulsions. c) Photographs of Cor-PMMA-F127-KPS afterglow emulsions obtained under 365 nm UV and after switching-off the UV lamp at room temperature.

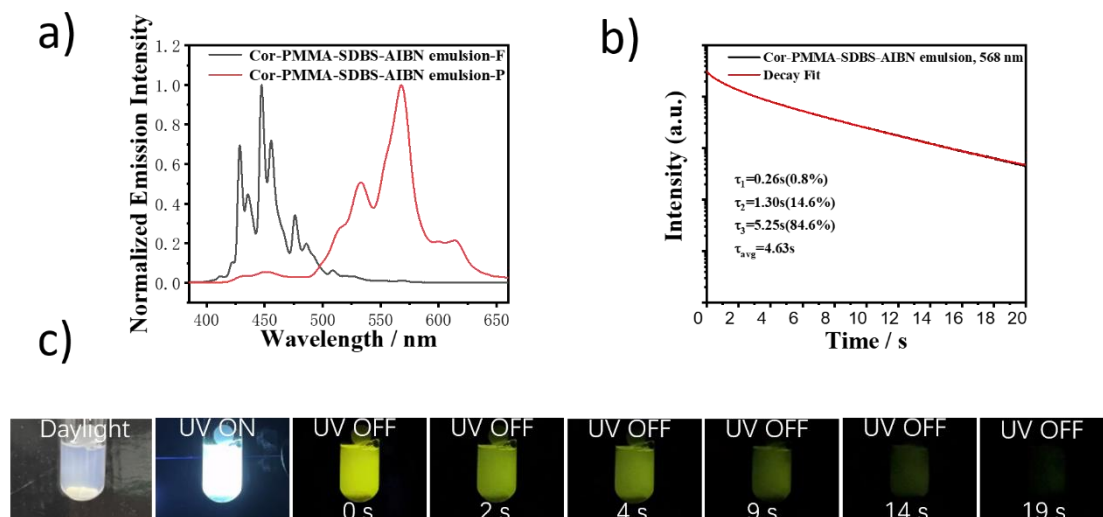


Figure S6. a) Room-temperature steady-state and delayed emission (1 ms delay) spectra of Cor-PMMA-SDBS-AIBN emulsions. b) Room-temperature emission decay profile of Cor-PMMA-SDBS-AIBN emulsions. c) Photographs of Cor-PMMA-SDBS-AIBN afterglow emulsions obtained under 365 nm UV and after switching-off the UV lamp at room temperature.

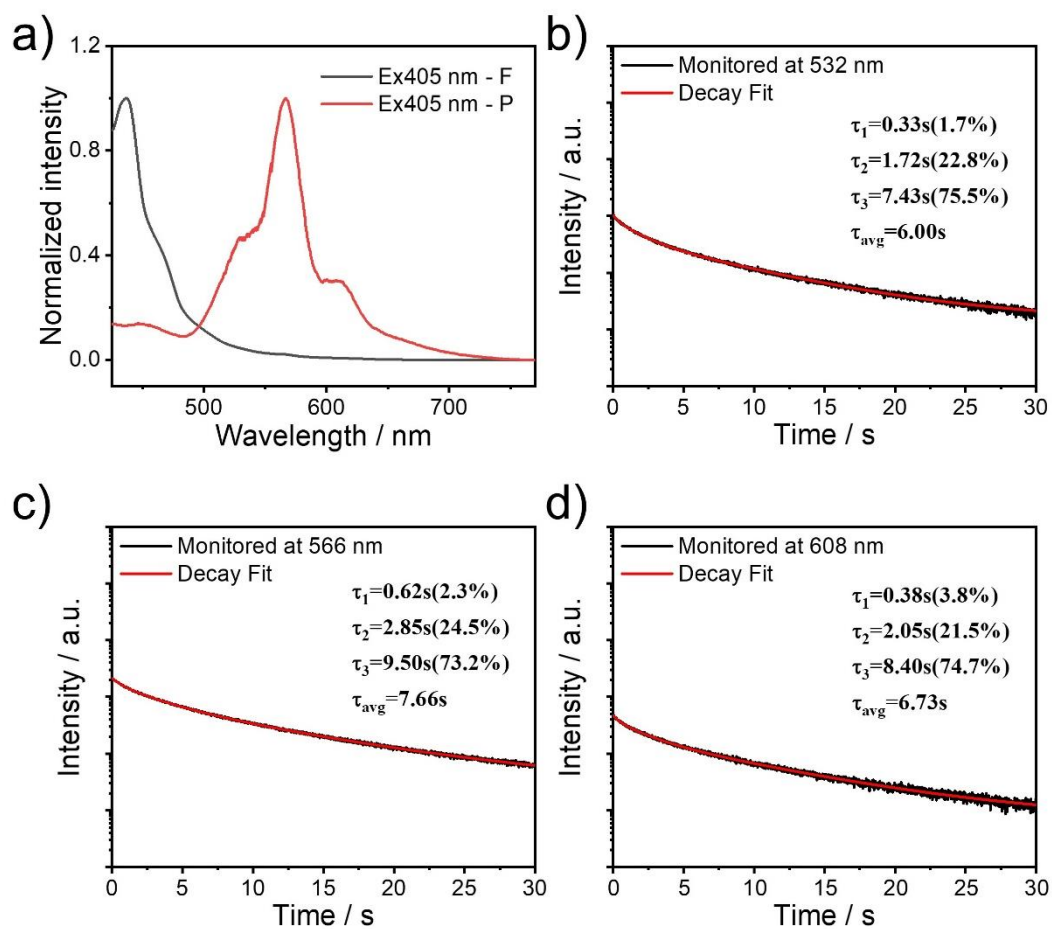


Figure S7. a) Room-temperature steady-state and delayed emission (1 ms delay) spectra of D-Cor-PMMA emulsion ($\lambda_{\text{ex}} = 405\text{ nm}$). Room-temperature emission decay profile of D-Cor-PMMA emulsion monitored at b) 532 nm, c) 566 nm, and d) 608 nm, respectively.

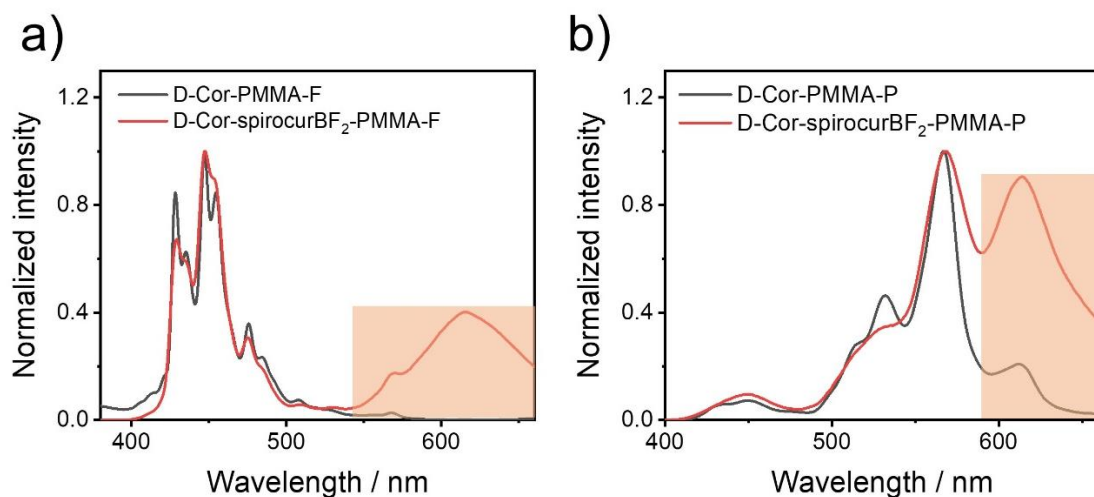


Figure S8. a) Room-temperature steady-state and b) delayed emission (1 ms delay) spectra of D-Cor-PMMA and D-Cor-SpirocurBF₂-PMMA emulsions ($\lambda_{\text{ex}} = 340$ nm).

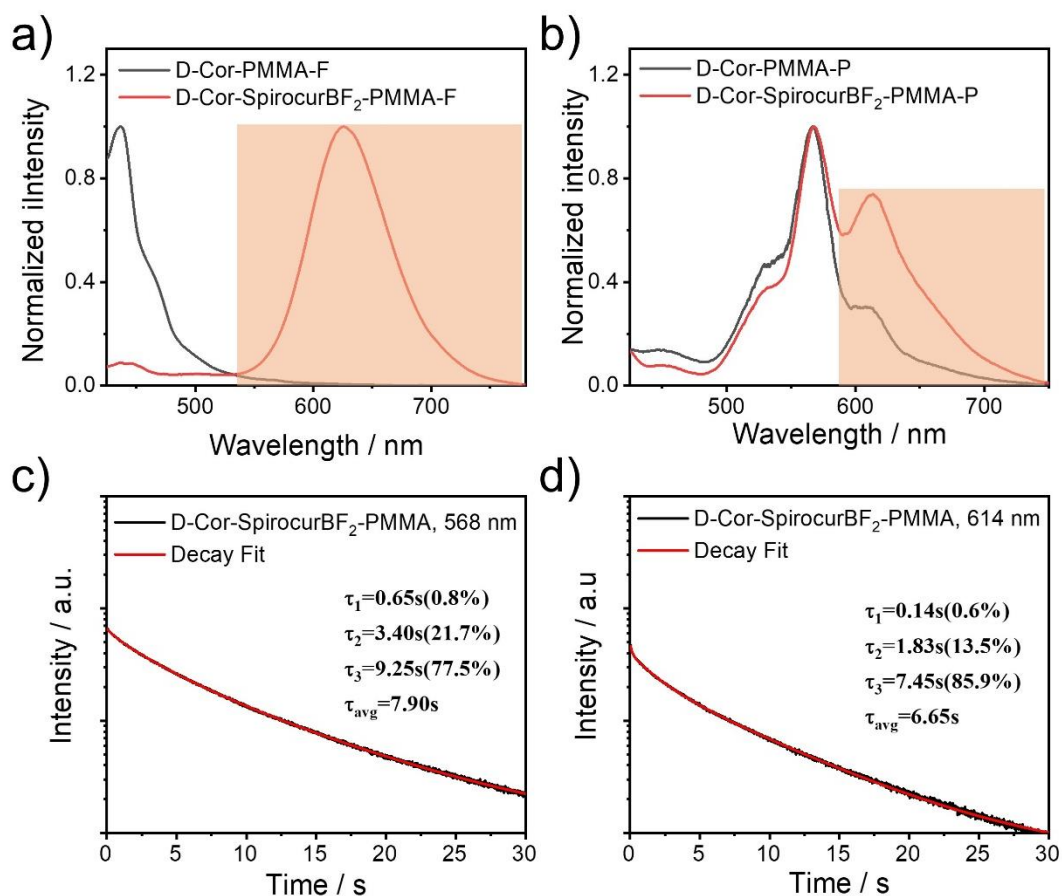


Figure S9. a) Room-temperature steady-state and b) delayed emission (1 ms delay) spectra of D-Cor-PMMA and D-Cor-SpirocurBF₂-PMMA emulsions ($\lambda_{\text{ex}} = 405$ nm). Room-temperature emission decay profile of D-Cor-SpirocurBF₂-PMMA emulsion monitored at c) 568 nm, and d) 614 nm, respectively.

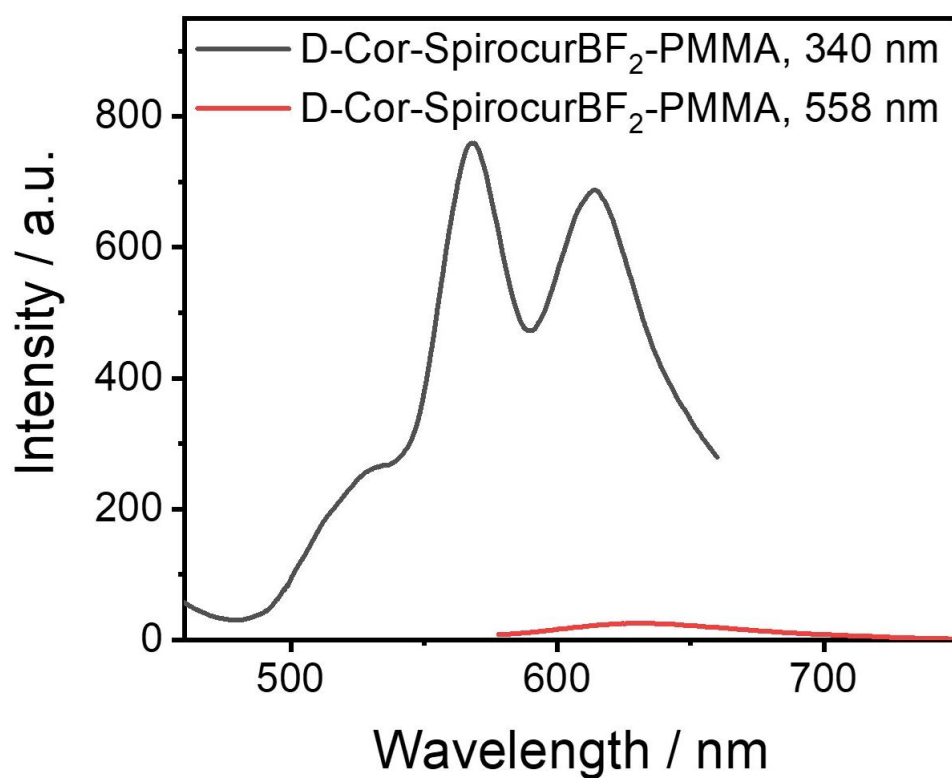


Figure S10. Room-temperature delayed emission (1 ms delay) spectra of D-Cor-SpirocurBF₂-PMMA emulsions excited at 340 nm and 558 nm, respectively.



Figure S11. a) Photographs of PMMA and b) SpirocurBF₂-PMMA emulsions obtained under 365 nm UV and after switching-off the UV lamp at room temperature.

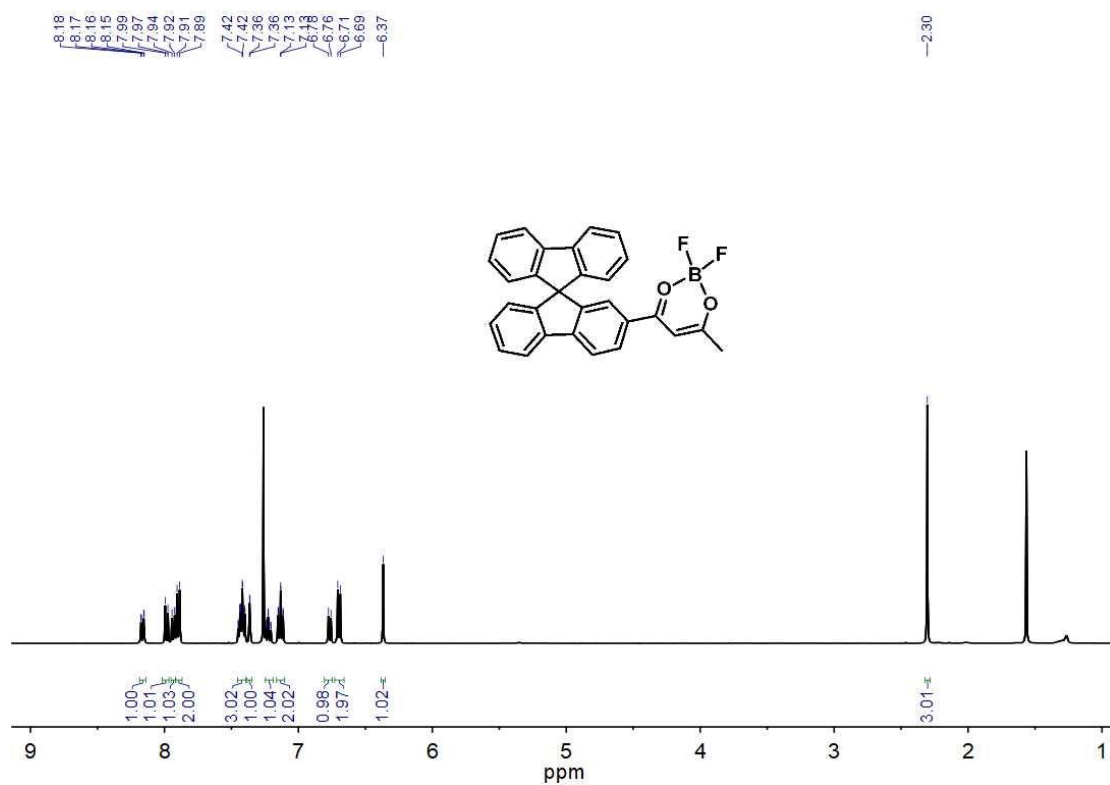


Figure S12. ¹H NMR spectrum of SpiroBF₂ (CDCl₃, 298 K, 400 MHz).

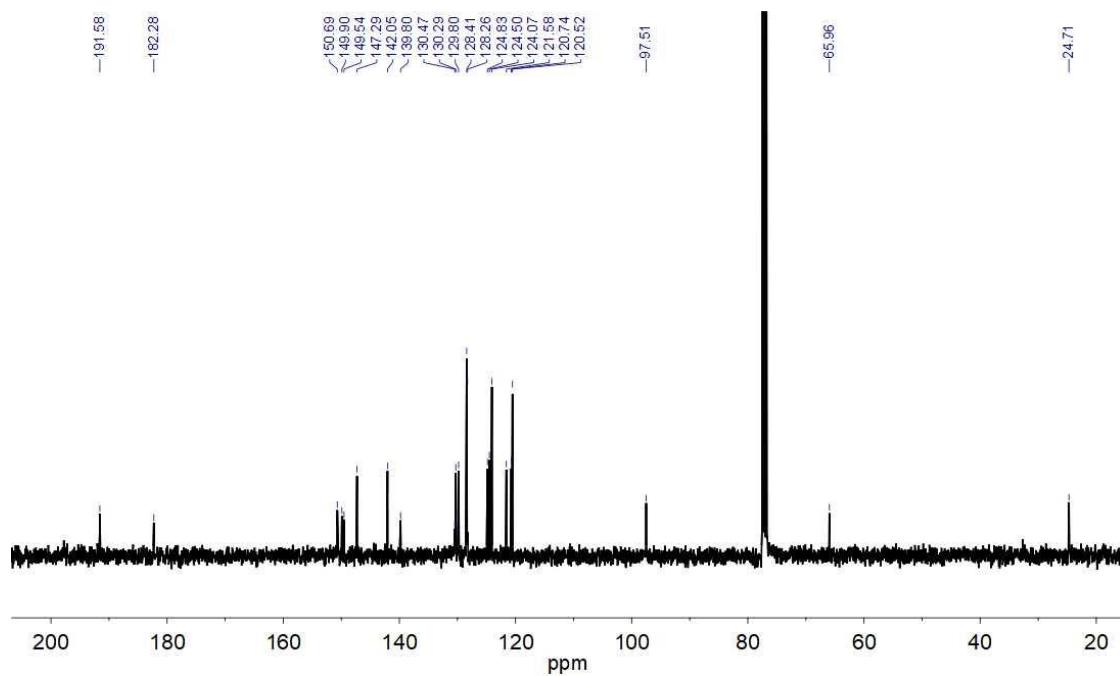


Figure S13. ¹³C NMR spectrum of SpiroBF₂ (CDCl₃, 298 K, 101 MHz).

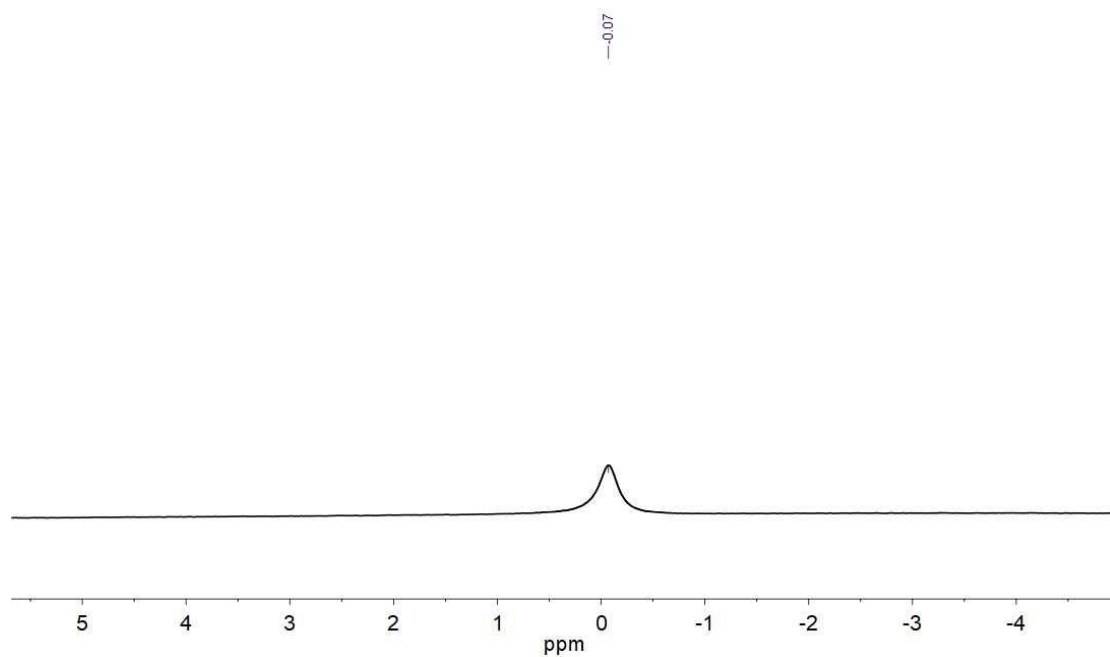


Figure S14. ^{11}B NMR spectrum of SpiroBF₂ (CDCl₃, 298 K, 128 MHz).

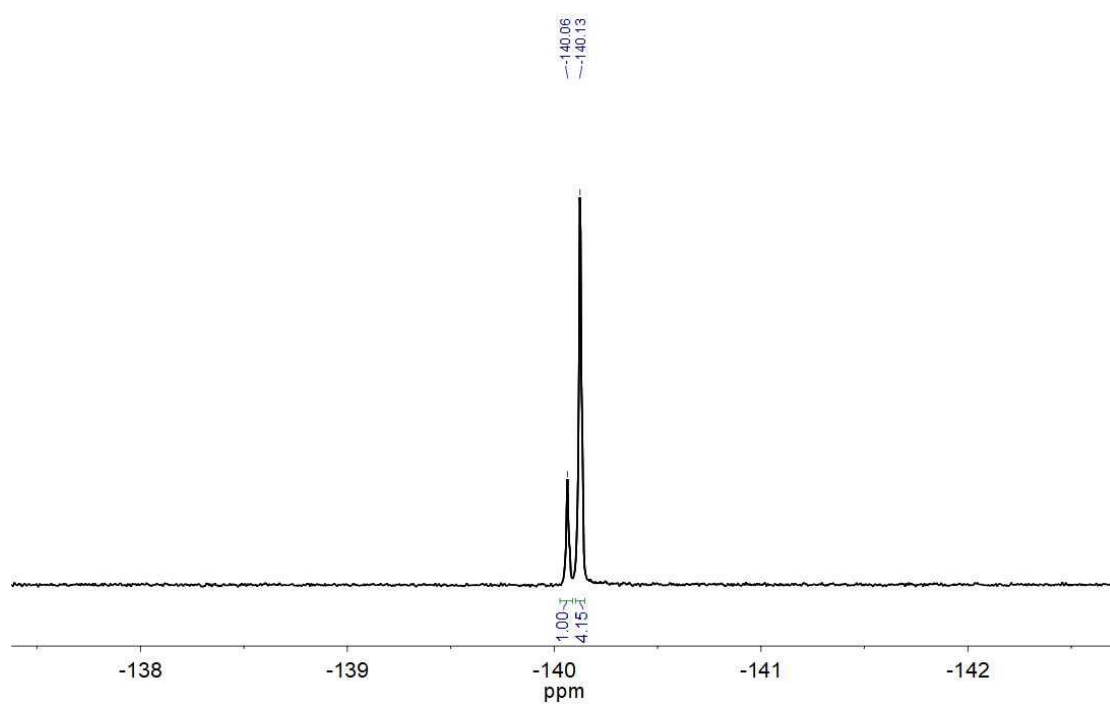


Figure S15. ^{19}F NMR spectrum of SpiroBF₂ (CDCl₃, 298 K, 376 MHz).

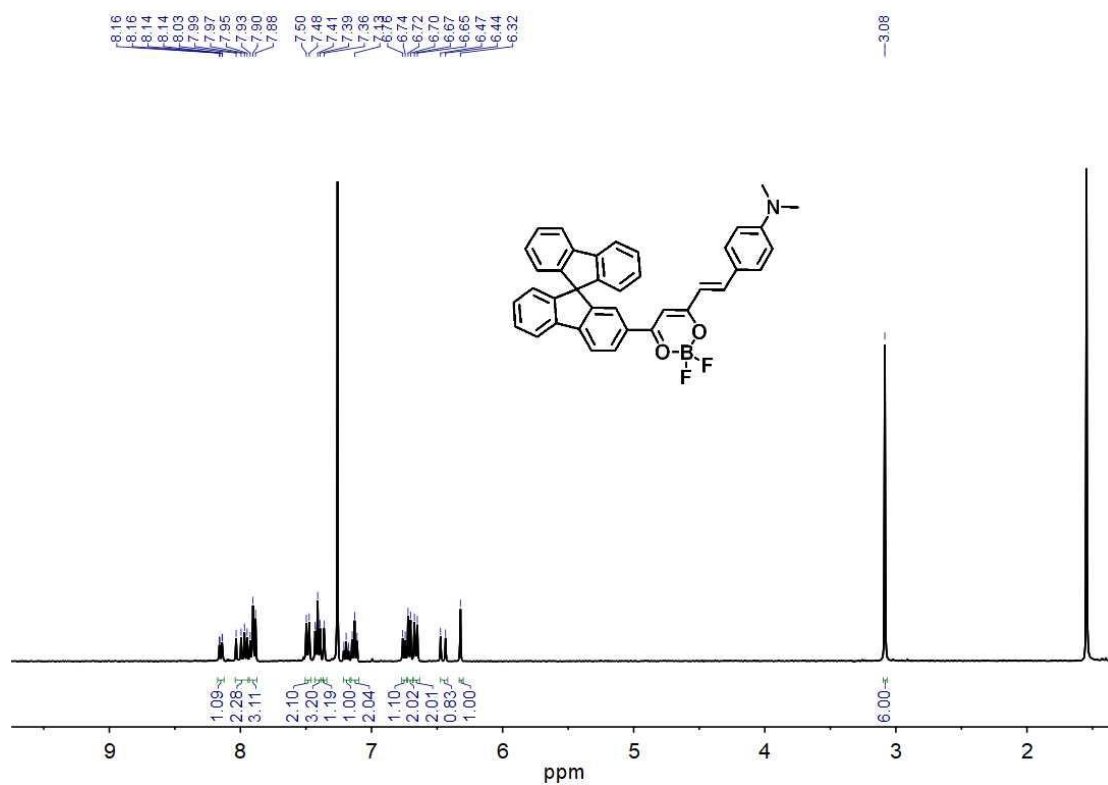


Figure S16. ¹H NMR spectrum of SpirocurBF₂ (CDCl₃, 298 K, 400 MHz).

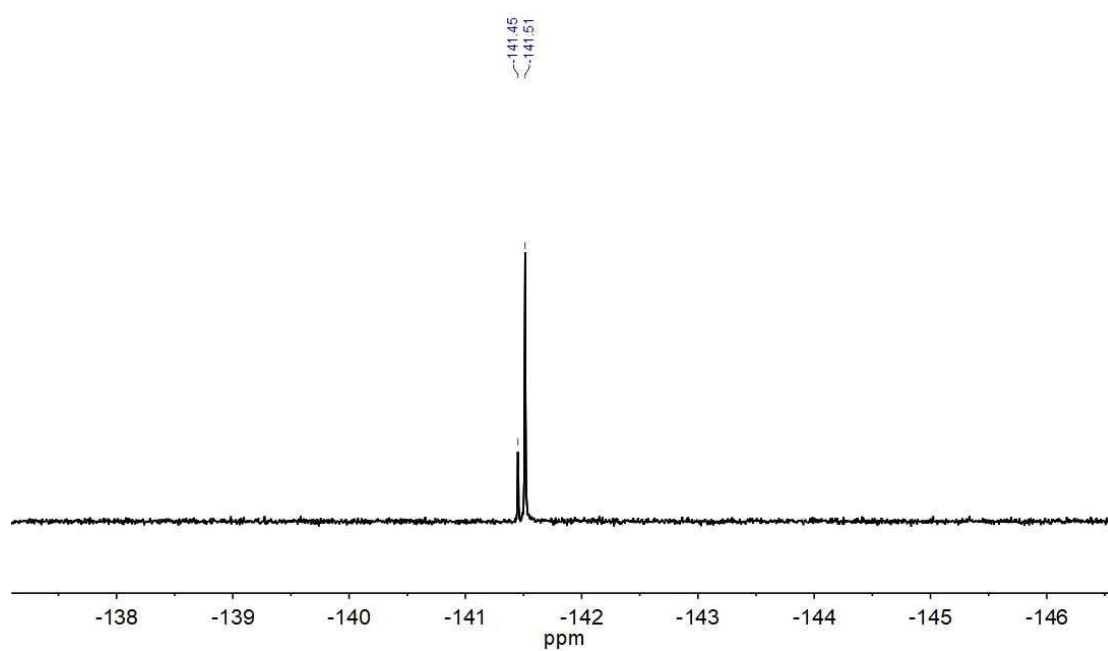


Figure S17. ¹⁹F NMR spectrum of SpirocurBF₂ (CDCl₃, 298 K, 376 MHz).

References

- 1 M. Wu, X. Wang, Y. Pan, J. Li, X. Li, Y. Sun, Y. Zou, H. Zhang, K. Zhang, *J. Phys. Chem. C* 2021, **125**, 26986.
- 2 Y. Sun, G. Wang, X. Li, B. Zhou, K. Zhang, *Adv. Opt. Mater.* 2021, **9**, 2100353.
- 3 X. Deng, J. Huang, J. Li, G. Wang, K. Zhang, *Adv. Funct. Mater.* 2023, **33**, 2214960
- 4 X. Zhen, Y. Tao, Z. An, P. Chen, C. Xu, R. Chen, W. Huang, K. Pu, *Adv. Mater.* 2017, **29**, 1606665.
- 5 X. Wang, W. Guo, H. Xiao, Q. Yang, B. Chen, Y. Chen, C. Tung, L. Wu, *Adv. Funct. Mater.* 2020, **30**, 1907282
- 6 X. F. Wang, H. Xiao, P. Z. Chen, Q. Z. Yang, B. Chen, C. H. Tung, Y. Z. Chen, L. Z. Wu, *J. Am. Chem. Soc.* 2019, **141**, 5045.