

Supporting Information

Cyanophenyl spiro[acridine-9,9'-fluorene]s as simple structured hybridized local and charge-transfer-based ultra-deep blue emitters for highly efficient non-doped electroluminescent devices (CIE_y ≤ 0.05)

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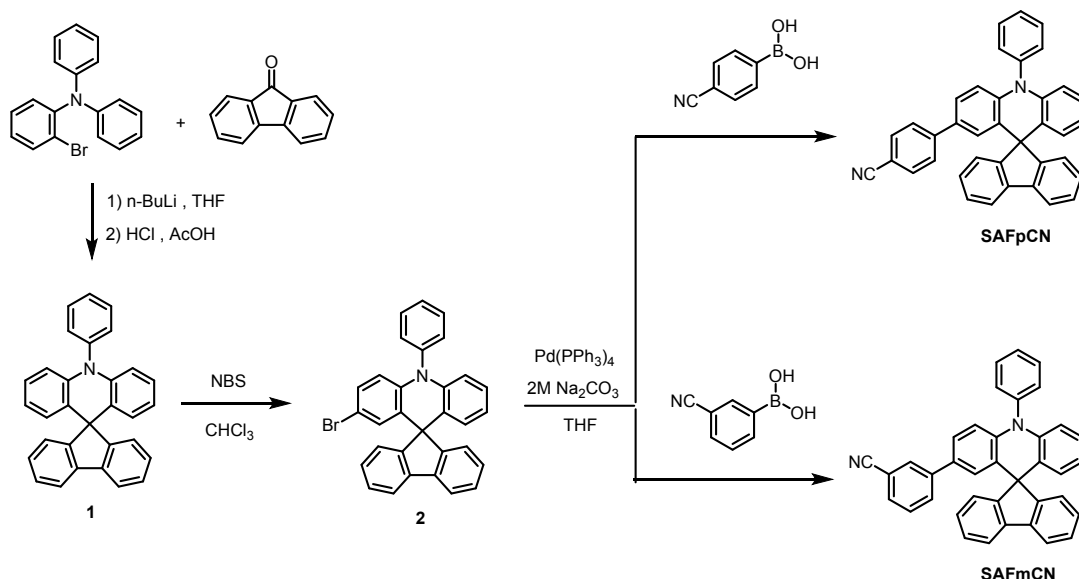
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1. Material Synthesis



Scheme S1

10-Phenyl-10H-spiro[acridine-9,9'-fluorene] (**1**)

A solution of 2-bromotriphenylamine (3.22 g, 9.95 mmol) in THF (80 ml) in 250 ml three-necked round bottom flask was degassed with N₂ for 5 min. The solution was cooled to -78 °C for 30 min, and then 1.6M n-Butyl lithium in hexane (9.40 ml, 14.9330 mmol) was added dropwise via syringe. The resulting mixture was allowed to stir at -78 °C for 1 h, and then a solution of 9-fluorenone (1.79 g, 9.95 mmol) in THF (80 ml) was slowly added via additional funnel for 30 min. After 1 h reaction at -78 °C, for 1 h, the reaction mixture was warmed up to room temperature and stirred overnight. Water (20 ml) was added to the reaction mixture and THF was evaporated by rotary evaporator. The resulting mixture was extracted with DCM, washed with water and brine solution, dried over

anhydrous Na₂SO₄ and removed organic solvent, respectively. The light yellow crude product was dissolved in acetic acid (50 ml) and 37% HCl (5 ml) and then refluxed for 4 h. After cooling to room temperature, the precipitate was filtrated and washed with hexane. The resulting solid was purified by silica gel column chromatography using hexane as eluent to obtain a white solid (2.70 g, 67%). ¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.56 (t, *J* = 7.3 Hz, 2H), 6.41 (d, *J* = 7.6 Hz, 2H), 6.36 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 156.62, 141.37, 141.17, 139.25, 131.24, 131.07, 128.45, 128.38, 127.76, 127.58, 127.19, 125.82, 124.85, 120.55, 119.88, 114.64, 56.89. MALDI-TOF *m/z* [M]⁺ calcd for C₃₁H₂₁N 407.1674, found 407.3410.

2-Bromo-10-phenyl-10H-spiro[acridine-9,9'-fluorene] (2)

A solution of N-bromosuccinimide (0.087 g, 0.49 mmol) in chloroform (10 ml) was added dropwise to a solution of **1** (0.20 g, 0.49 mmol) in chloroform (20 ml). The mixture was stirred at room temperature for 1 h and then water (50 ml) was added. The mixture was extracted with DCM, washed with water and brine, dried over anhydrous Na₂SO₄ and removed organic solvent, respectively. The crude product was purified by recrystallization from DCM/Methanol mixture solvent to give a white solid (0.21 g, 88%). ¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.72 (t, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.42 – 7.39 (m, 4H), 7.28 (td, *J* = 7.6, 0.9 Hz, 2H), 6.99 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.92 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 6.58 (td, *J* = 7.4, 1.0 Hz, 1H), 6.49 (d, *J* = 2.3 Hz, 1H), 6.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 6.24 (d, *J* = 8.9 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 155.84, 140.93, 140.74, 140.61, 139.18, 131.22, 130.96, 130.11, 130.06, 128.71, 128.52, 127.90, 127.65, 127.36, 127.01, 125.68, 124.66, 120.94, 120.10, 116.37, 114.73, 112.66, 56.64. MALDI-TOF *m/z* [M]⁺ calcd for C₃₁H₂₀BrN 485.0779, found 485.2946.

2. Characterization data

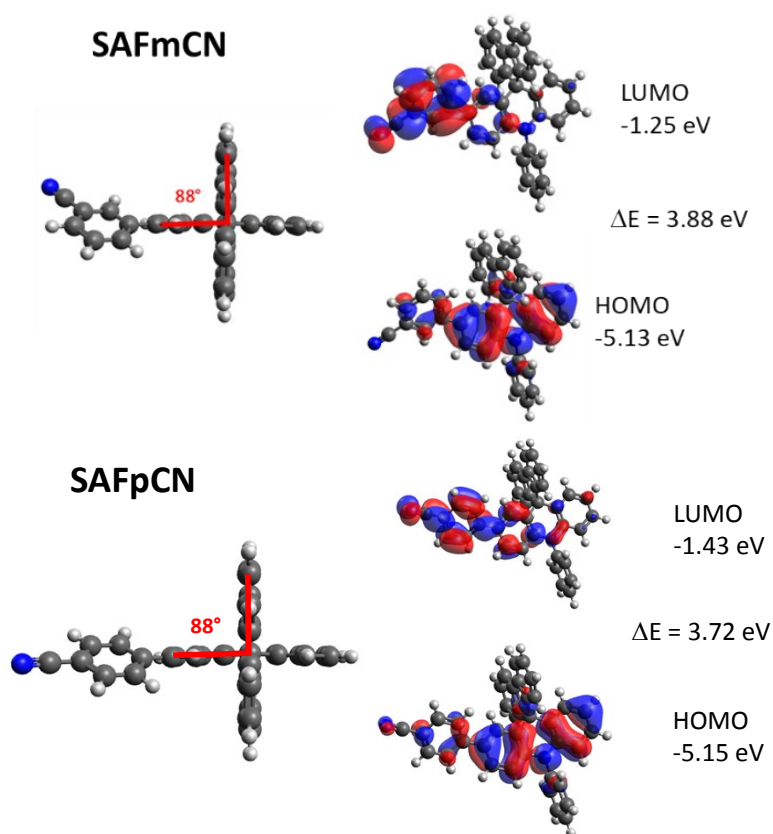


Fig. S1 Optimized structures, and molecular orbital energy level and HOMO-LUMO energy gaps calculated by B3LYP/6-31G(d,p) function.

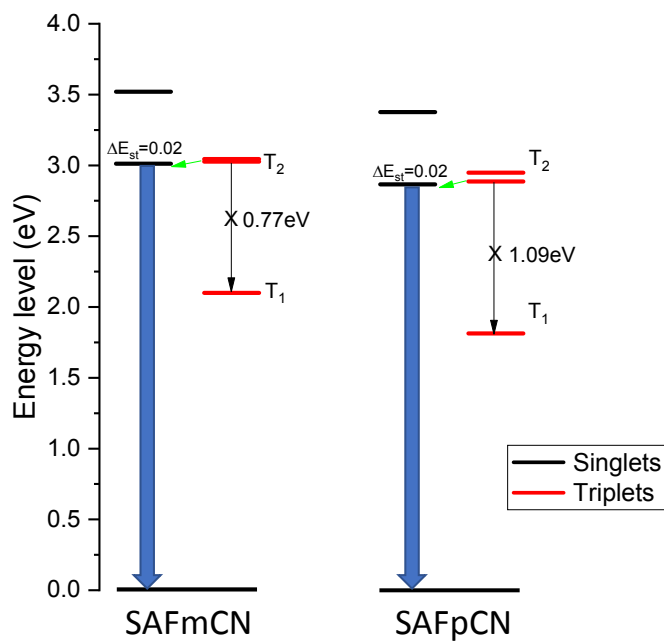


Fig. S2 The energy diagram of singlet and triplet excited states of the compounds from TD-B3LYP/6-31G(d,p) calculations.

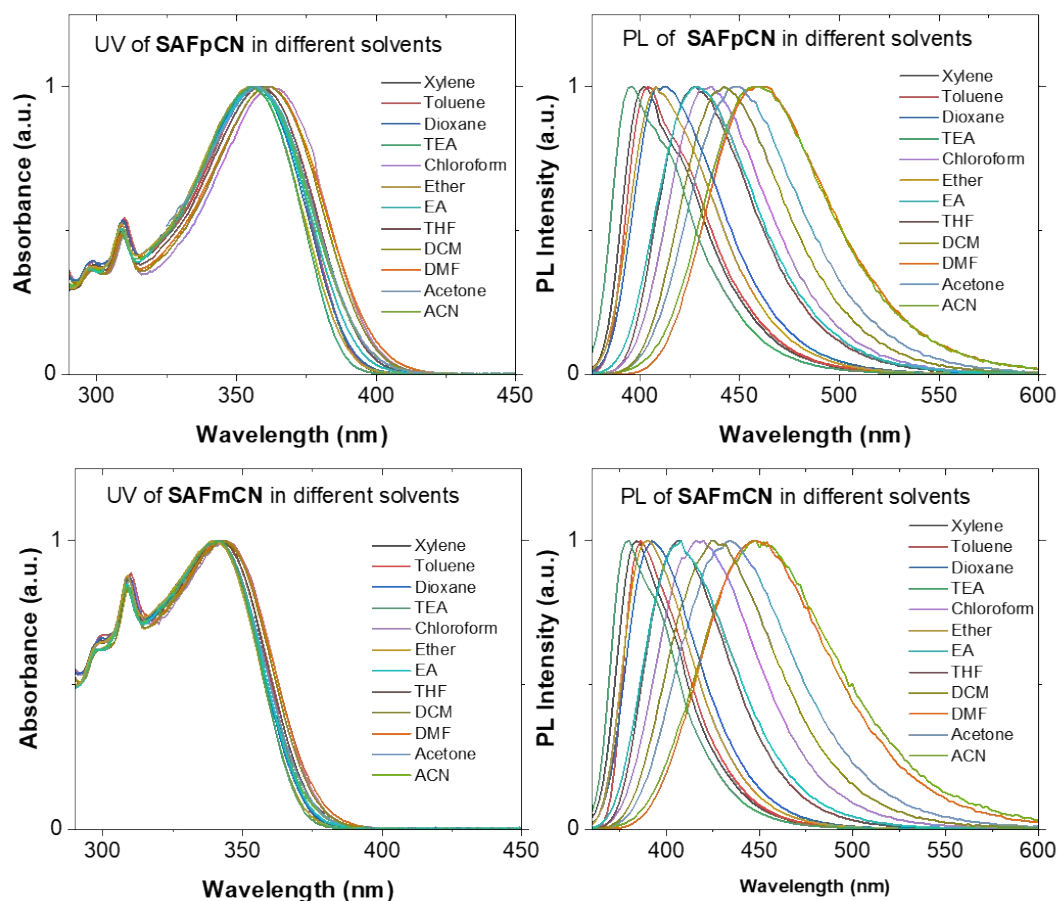


Fig. S3 UV-vis absorption and PL spectra in different solvents.

Table S1 Detail of the optical data in different solvents.

Solvents	ϵ	n	$f(\epsilon, n)$	SAFpCN			SAFmCN		
				λ_a (nm)	λ_f (nm)	$\nu_a - \nu_f$ (cm ⁻¹)	λ_a (nm)	λ_f (nm)	$\nu_a - \nu_f$ (cm ⁻¹)
Xylene	2.57	1.496	0.003	358	402	3057	343	384	3113
Toluene	2.38	1.494	0.015	357	404	3259	343	386	3248
Dioxane	2.22	1.422	0.021	356	410	3700	340	394	4031
Triethylamine	2.42	1.401	0.048	355	396	2916	341	378	2870
Chloroform	4.81	1.446	0.148	363	434	4507	344	418	5146
Ethyl ether	4.34	1.352	0.167	355	408	3659	340	390	3771
Ethyl acetate	6.02	1.372	0.200	356	428	4725	340	408	4902
Tetrahydrofuran	7.58	1.407	0.210	359	428	4491	341	406	4695
Dichloromethane	8.93	1.424	0.217	361	442	5076	343	427	5735
Dimethyl formamide	37.0	1.427	0.274	361	460	5962	342	448	6918
Acetone	20.7	1.359	0.284	357	448	5690	340	434	6370
Acetonitrile	37.5	1.344	0.305	356	458	6256	340	450	7190

The dipole moment of ground state μ_g can be estimated by DFT calculation, and the dipole moment of excited state are determined from the slope of linear fitted Stokes' shift ($\nu_a - \nu_f$) against orientation polarizability $f(\epsilon, n)$ in different solvents according to Lippert-Mataga equation.¹

$$hc(\nu_a - \nu_f) = hc(\nu_a^0 - \nu_f^0) + \frac{2(\mu_e - \mu_g)^2}{a_0^3} f(\epsilon, n),$$

$$f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} + \frac{n^2 - 1}{2n^2 + 1},$$

Among which ϵ and n are dielectric constant and refractive index of solvent respectively, and a_0 is the solvent cavity radius

$$a_0 = \left(\frac{3M}{4N\pi d}\right)^{1/3},$$

where N is Avogadro number, M is molecular weight, and d is density. Two-region trends found in **mTAHPI**, **pTAHPI** and **pTAPI** are steady slopes of 4774, 5099, and 4854 for low-polar solvents and sharp slopes of 21838, 23295, and 23477 for high-polar solvents.

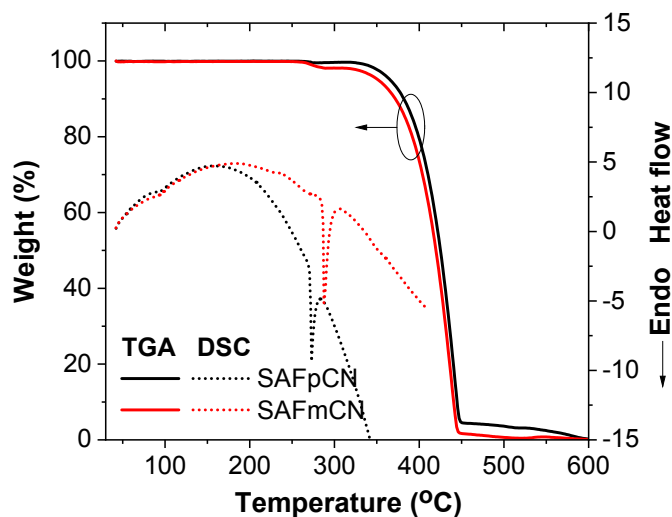


Fig. S4 TGA and DSC (2nd heating scan) thermograms measured at heating rate of 10 °C min⁻¹ under N₂ flow.

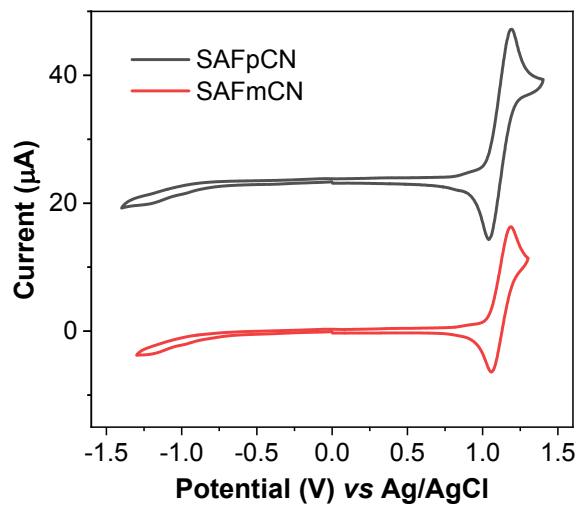


Fig. S5 CV traces measured in CH_2Cl_2 containing $n\text{-Bu}_4\text{NPF}_6$ as a supporting electrolyte at a scan rate of 50 mV s^{-1} under Ar atmosphere.

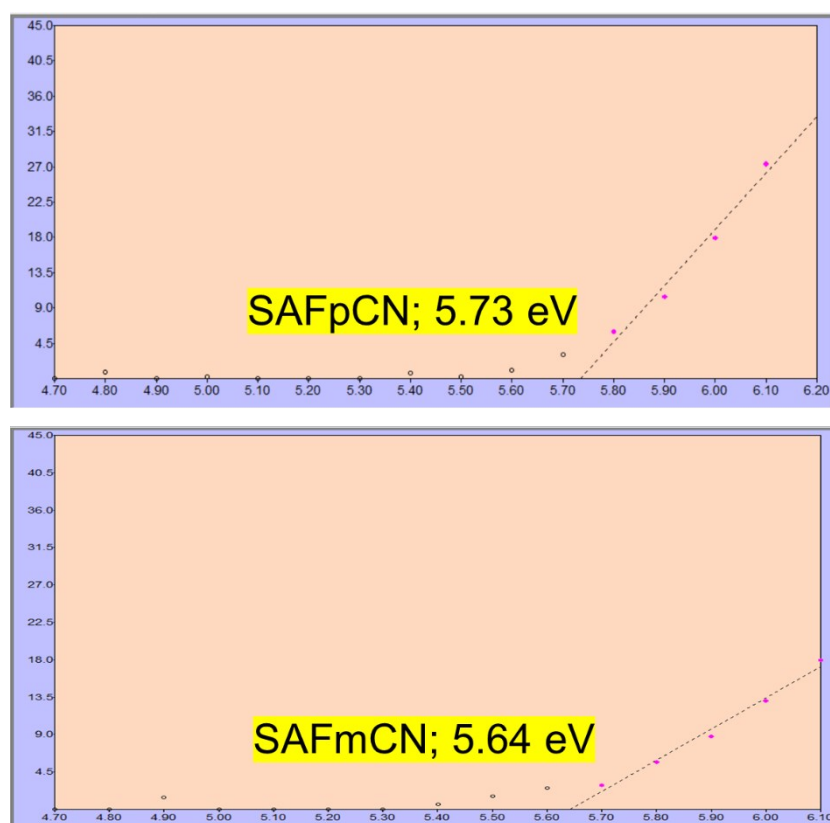


Fig. S6 Photoemission yield spectroscopy in air (PYS) spectra.

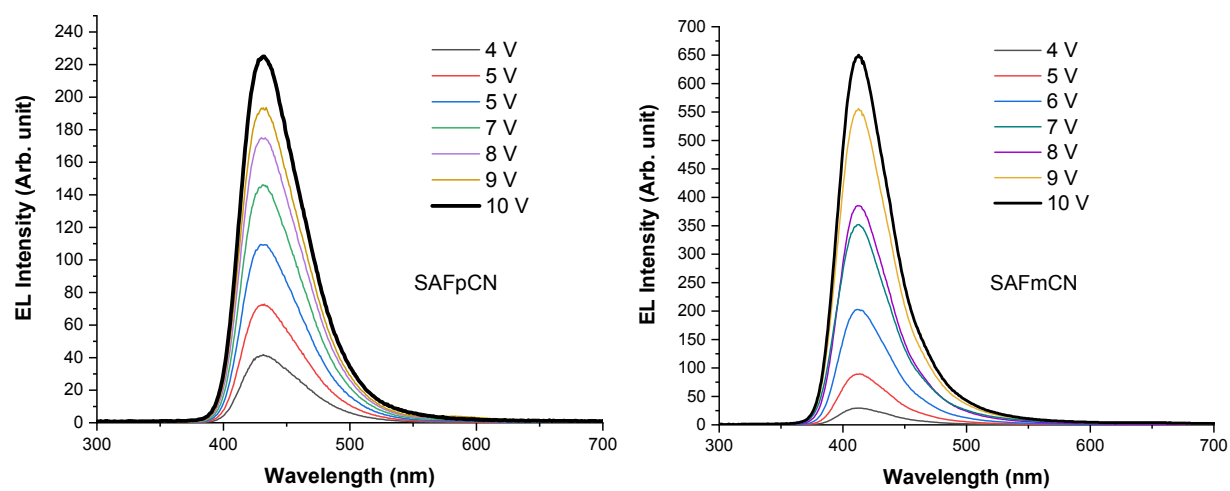
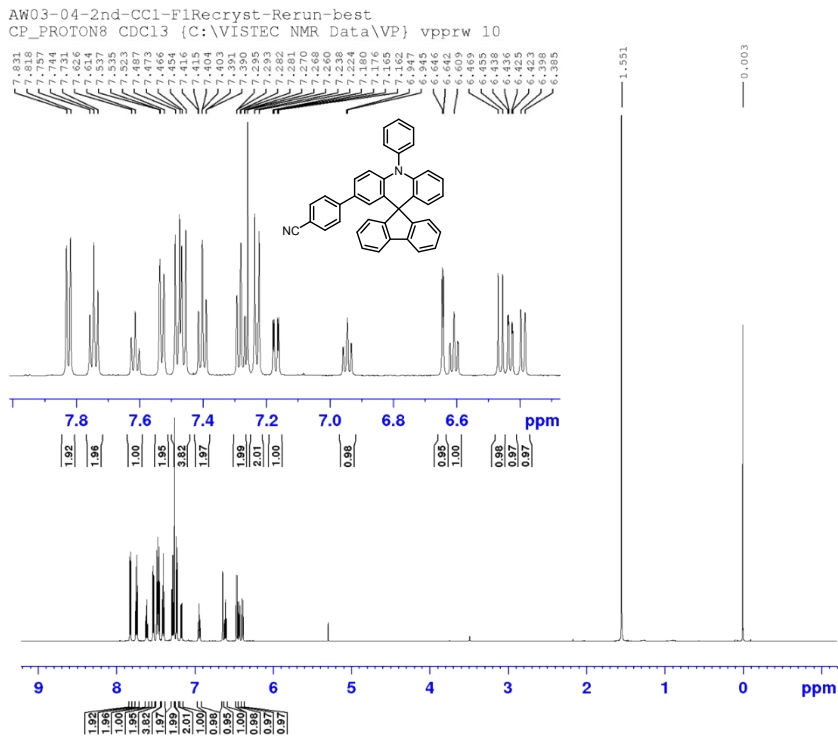


Fig. S7 EL spectra of the fabricated OLEDs at different applied voltages.

Reference

- 1) C. Feng, J. Li, X. Han, X. He, L. Liu, X. Li, X. Sun, P. Lu and Y. Ma, *Faraday Discuss.* 2017, **196**, 163-176.

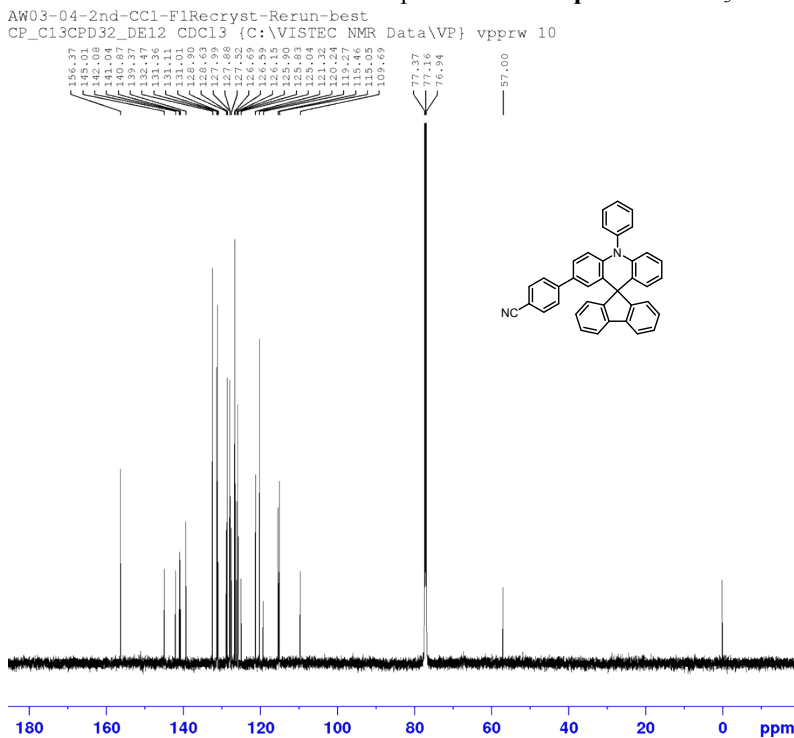


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PROCNO   1

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DS        2
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DE        40.00 usec
TE        303.2 K
D1        1.00000000 sec
TEC
SFO1     600.137058 MHz
NUC1      1H
P2        3.47 usec
P1        11.00 usec
P1M1     19.9979919 W
P1M2
P1M3

F2 - Processing parameters
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SSB       0
LB        0.30 Hz
GB        0
PC        1.00
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The ¹H NMR spectrum of SAFpCN in CDCl₃ solution.

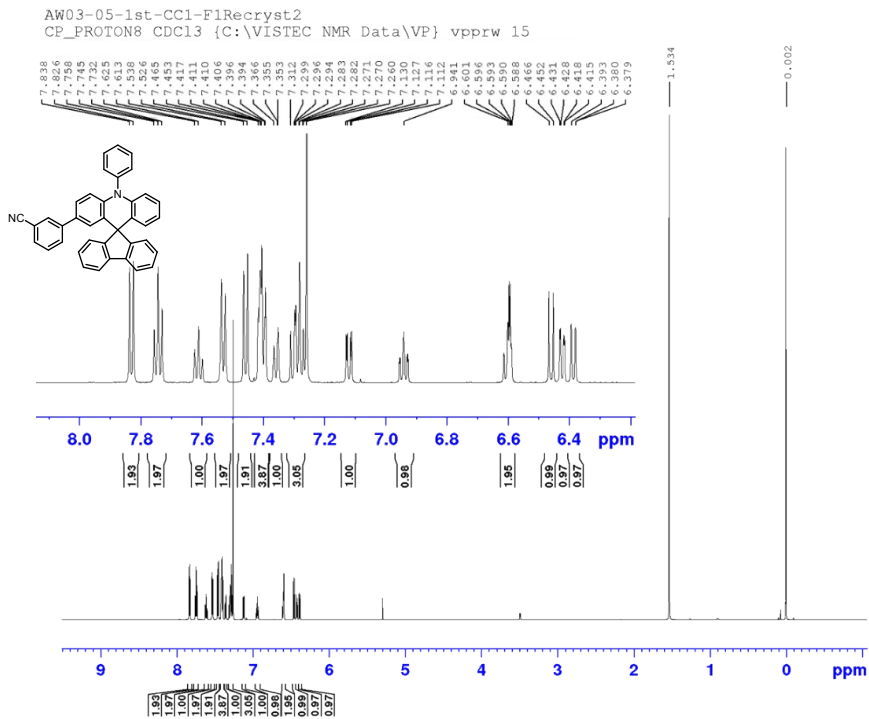


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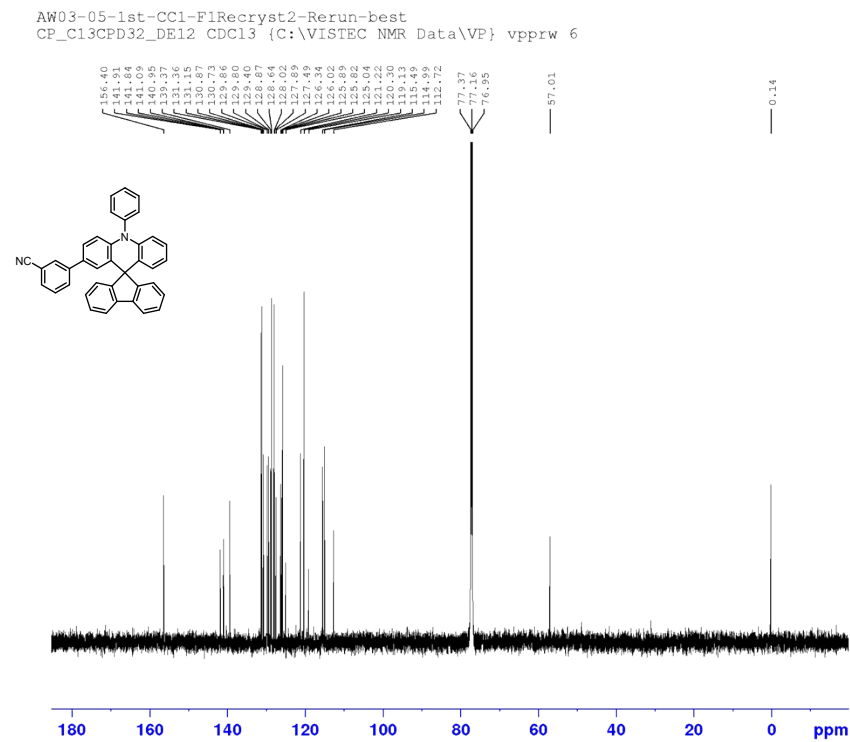
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P1        11.20 usec
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P1M2     600.1324000 MHz
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F2 - Processing parameters
SI        32768
SF        150.9027860 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
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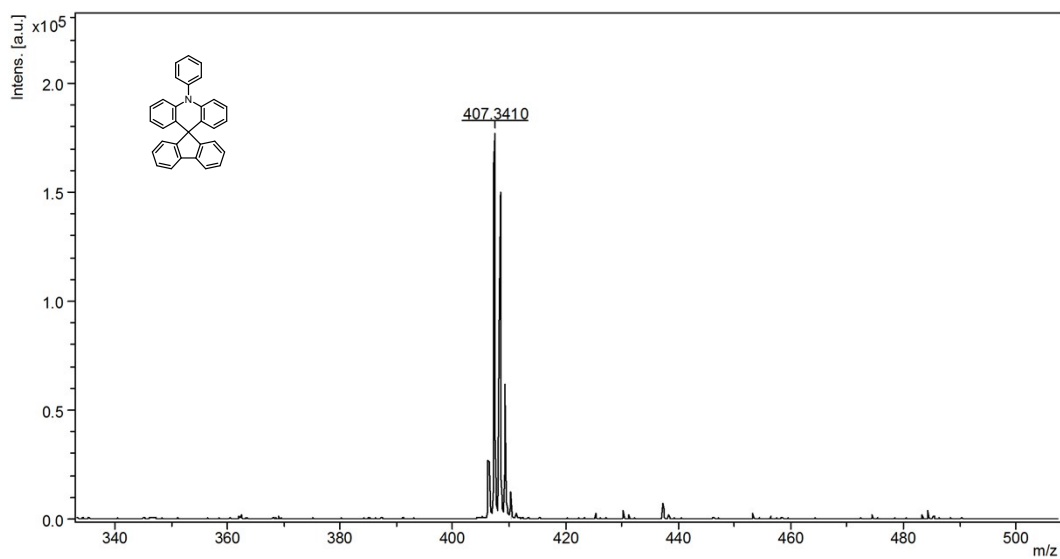
The ¹³C NMR spectrum of SAFpCN in CDCl₃ solution.



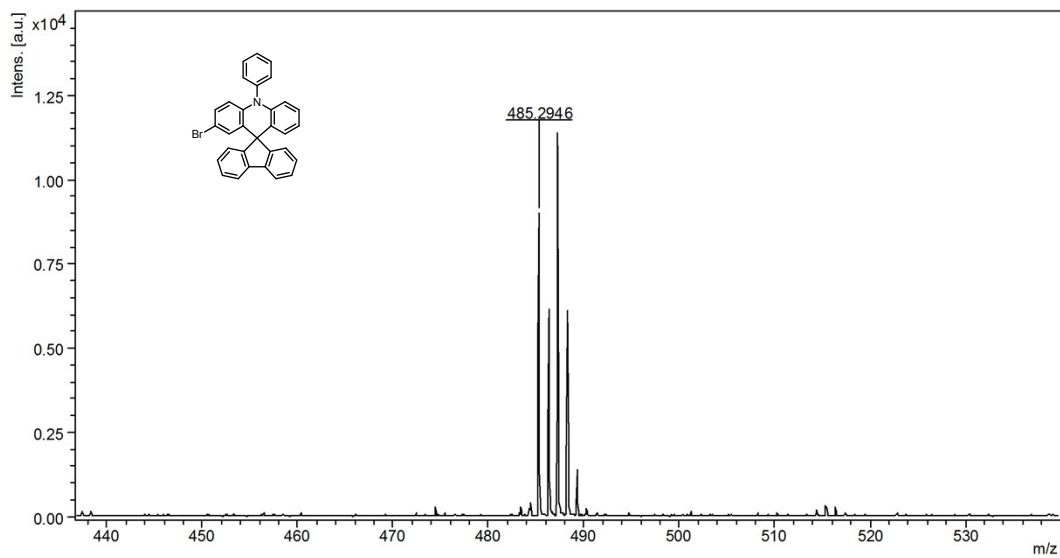
The ¹H NMR spectrum of SAFmCN in CDCl₃ solution.



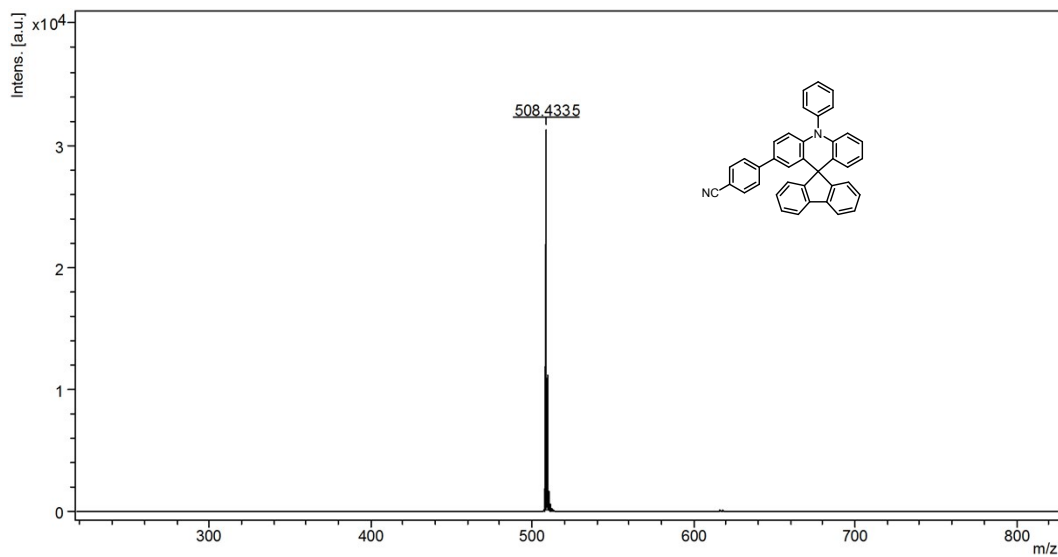
The ¹³C NMR spectrum of SAFmCN in CDCl₃ solution.



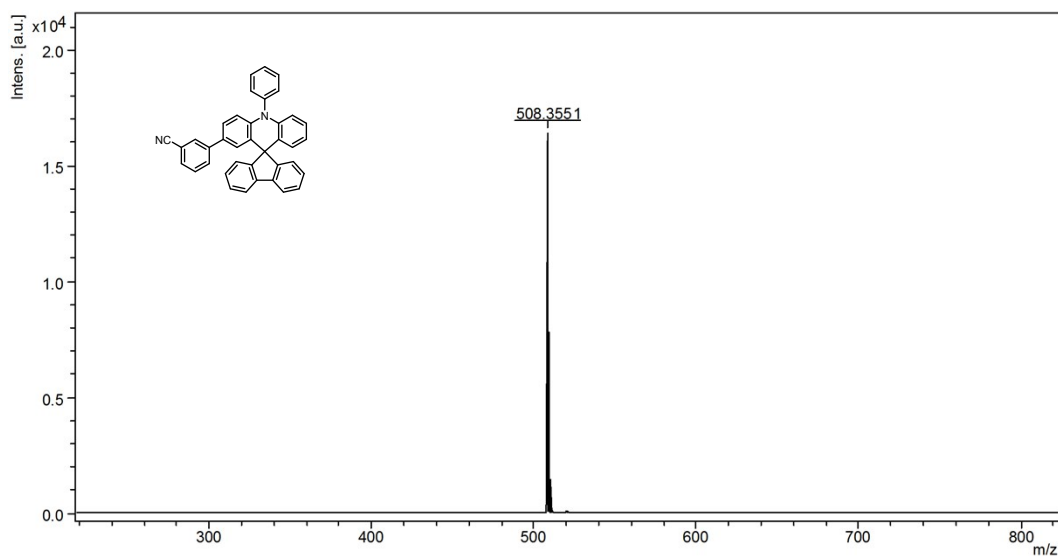
The MALDI-TOF spectra of **1**.



The MALDI-TOF spectrum of **2**.



The MALDI-TOF spectrum of SAFpCN



The MALDI-TOF spectrum of SAFmCN