Electronic Supplementary Information (ESI)

Cyanobenzene-containing tetraphenylethene derivatives with aggregation-induced emission and self-recovering mechanofluorochromic characteristics

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1. Experimental Section

Materials and measurements

General: All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. The starting materials diphenylmethane, (4-bromophenyl)(phenyl)methanone and *p*-toluenesulfonic acid purchased from Alfa Aesar were used as received. All other starting materials and reagents were obtained as analytical-grade from commercial suppliers and used without further purification. Compound **1-1**[1] and Compound **1-2**[1] were prepared by procedures described in the corresponding literatures. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ^{1}H NMR spectra are reported as followed: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constant (Hz). ^{13}C NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. EI-MS was obtained using Thermo scientific DSQ Ⅱ. Elemental analyses (C, H, N) were carried out with a PE CHN 2400 analyzer. Fluorescence spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer. XRD studies were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered and graphite-monochromated Cu Kα radiation (λ = 1.54 Å, 40 kV, 30 mA).

The N, N-dimethyl formamide (DMF)/water mixtures with various water fractions were prepared by slowly adding ultra-pure water into the DMF solution of samples. Absolute luminescence quantum yields were measured by HAMAMATSU ABSOLUTE PL QUANTUM YIELD SPECTROMETER C11347. The X-ray crystal-structure determinations of compounds **1** and **2** were obtained on a Bruker APEX DUO CCD system. The aggregate behaviors of **1** and **2** were investigated by scanning electron microscopy (SEM, Zeiss, Sigma). Column chromatographic separations were carried out on silica gel (200-300 mesh). TLC was performed by using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm.
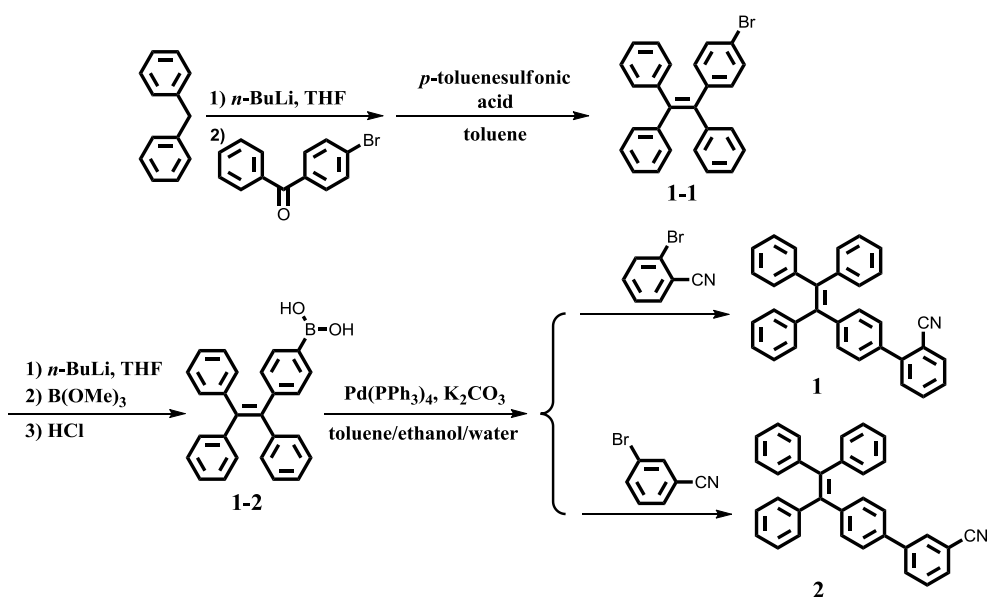
Scheme S1. Synthesis of the compounds **1** and **2**.

General procedure for the synthesis

Synthesis of **1**: A mixture of compounds **1-2** (0.95 mmol, 0.357 g)，

2-bromobenzonitrile (0.86 mmol), K_2CO_3 (3.6 mmol), $Pd(PPh_3)_4$ (0.09 mmol) were stirred in toluene (50 ml), ethanol (50 ml) and H_2O (5 ml) for 16 h under an argon atmosphere at 80℃. After completion of present reaction, the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 73.7%. **1**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.73 (d, J = 8 Hz, 1H), 7.60 (t, J = 8 Hz, 1H), 7.47 (d, J = 8 Hz, 1H), 7.40 (t, J = 6 Hz, 1H), 7.32-7.30 (m, 2H), 7.15-7.04 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 145.1, 144.2, 143.5, 143.4, 143.3, 141.8, 140.1, 136.0, 133.7, 132.6, 131.6, 131.3, 131.3, 129.9, 128.0, 127.8, 127.6, 127.3, 126.6, 126.5, 126.5, 118.5, 111.1. EI-MS: m/z = 433.32[M]$^+$. Anal. Calcd. for $C_{33}H_{23}N$: C, 91.42; H, 5.35; N, 3.23. Found: C, 91.49; H, 5.41; N, 3.15.

Synthesis of **2**: A mixture of compounds **1-2** (0.95 mmol, 0.357 g)，3-bromobenzonitrile (0.86 mmol), K_2CO_3 (3.6 mmol), $Pd(PPh_3)_4$ (0.09 mmol) were stirred in toluene (50 ml), ethanol (50 ml) and H_2O (5 ml) for 16 h under an argon atmosphere at 80℃. After completion of present reaction, the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of

78.2%. **2:** ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.82 (s, 1H), 7.76 (d, J = 8 Hz, 1H), 7.58 (d, J = 8 Hz, 1H), 7.49 (t, J = 8 Hz, 1H), 7.31 (d, J = 8 Hz, 2H), 7.14-7.10 (m, 12H), 7.08-7.03 (m, 5H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 144.0, 143.4, 143.4, 141.8, 141.6, 140.0, 136.4, 132.0, 131.3, 131.2, 131.1, 130.4, 130.4, 129.4, 127.8, 127.7, 127.6, 126.6, 126.5, 126.5, 126.1, 118.7, 112.8. EI-MS: m/z = 433.33[M]$^+$. Anal. Calcd. for C$_{33}$H$_{23}$N: C, 91.42; H, 5.35; N, 3.23. Found: C, 91.46; H, 5.39; N, 3.18.

Crystallographic Details

Single crystals of compounds **1** and **2** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of dichloromethane. A crystal of **1** or **2** with appropriate dimensions was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97)[2] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97)[3]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Detailed crystal data are summarized in Table S1 and Table S2. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC

1553506 (compound **1**) and CCDC 1553507 (compound **2**).

2. References

1. Z. Zhao, C. Y. K. Chan, S. Chen, C. Deng, J. W. Y. Lam, C. K. W. Jim, Y. Hong, P. Lu, Z. Chang, X. Chen, P. Lu, H. S. Kwok, H. Qiu and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 4527-4534.

2. G. M. Sheldrick, SHELXS-97: Program for crystal structure solution, University of Götingen, Götingen, Germany, **1997**.
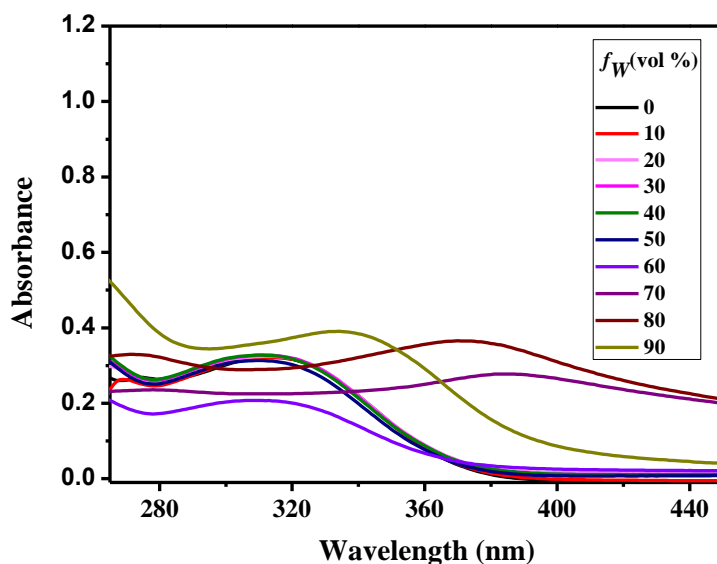
3. G. M. Sheldrick, SHELXL-97: Program for crystal structure refinement, University of Götingen, Götingen, Germany, **1997**.

3. Figs. S1-S5

Fig. S1 UV-Vis absorption spectra of **1** in DMF-water mixtures with different volume fractions of water (0-90%).
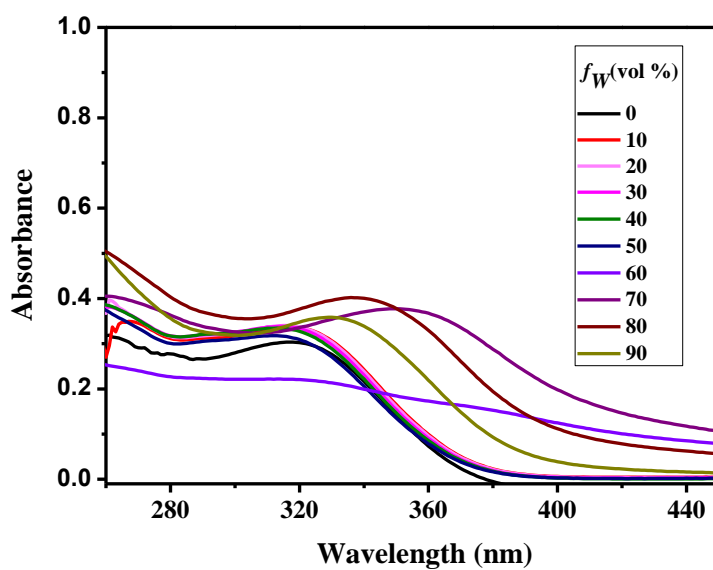
Fig. S2 UV-Vis absorption spectra of **2** in DMF-water mixtures with different volume fractions of water (0-90%).
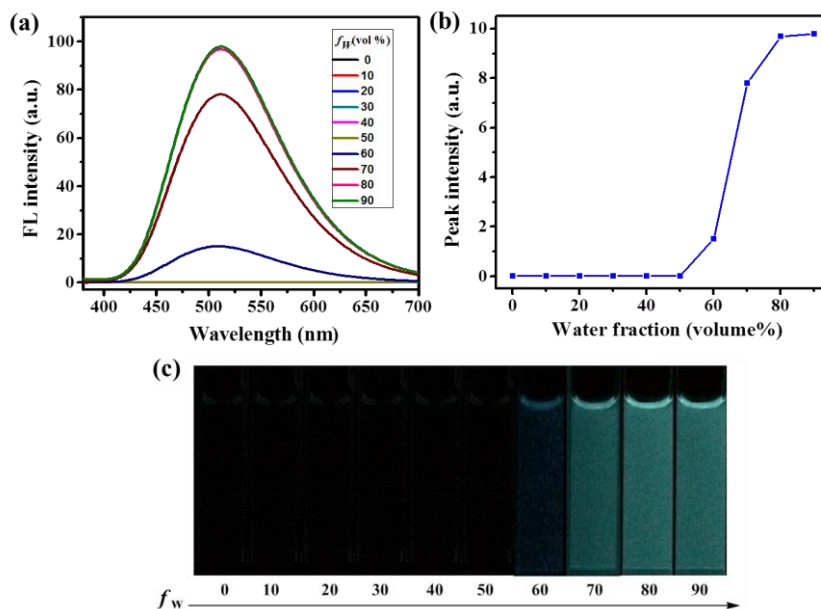

Fig. S3 (a) PL spectra of the dilute solutions of compound **2** (2.0×10^{-5} mol L^{-1}) in DMF-water mixtures with different water content (0-90%). Excitation wavelength = 365 nm. (b) Changes in the emission intensity of compound **2** at 511 nm in

DMF-water mixtures with various volume fractions of water (0-90%). (c) PL images of compound **2** (2.0×10^{-5} mol L^{-1}) in various DMF-water mixtures with diverse f_w values (0-90%) under 365 nm UV light.
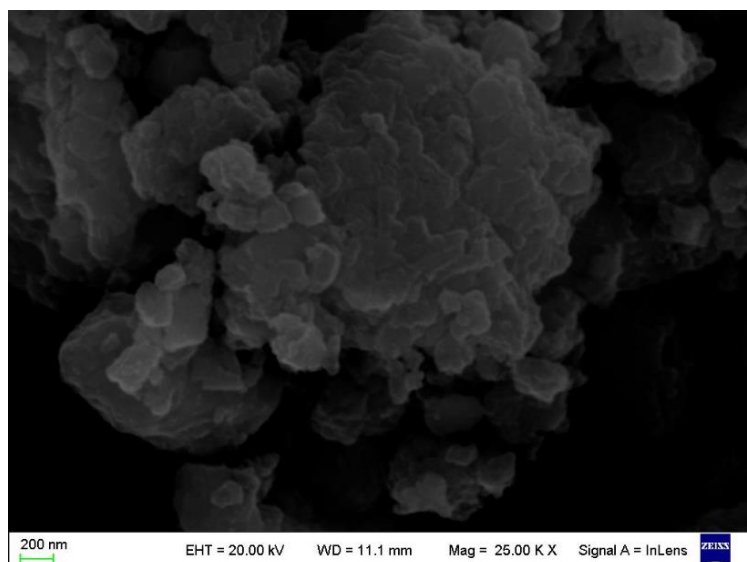

Fig. S4 SEM image of compound **2** (2.0×10^{-5} mol L^{-1}) formed from DMF/water mixture ($f_w = 90\%$).
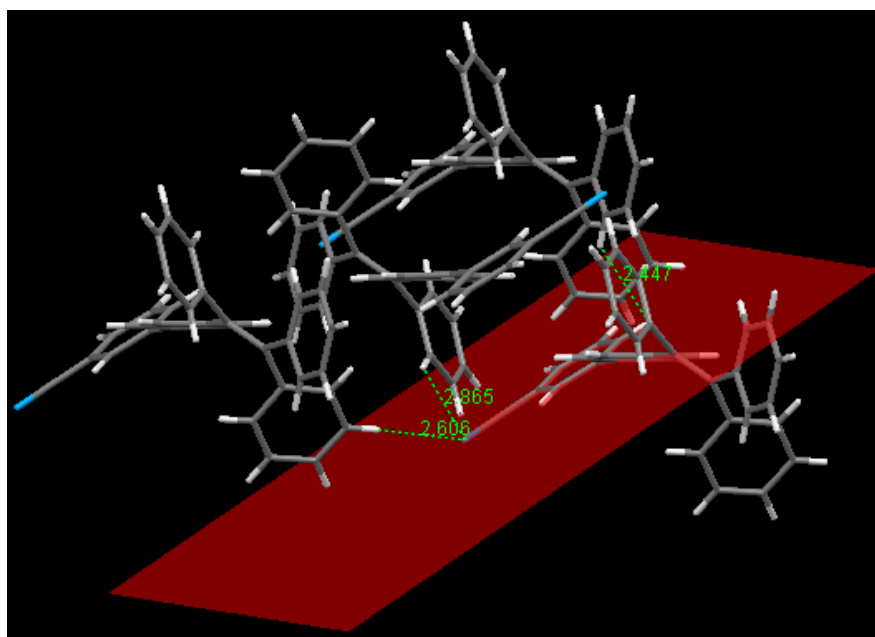

Fig. S5 The structural organization of compound **2**.

4. Table S1-S2

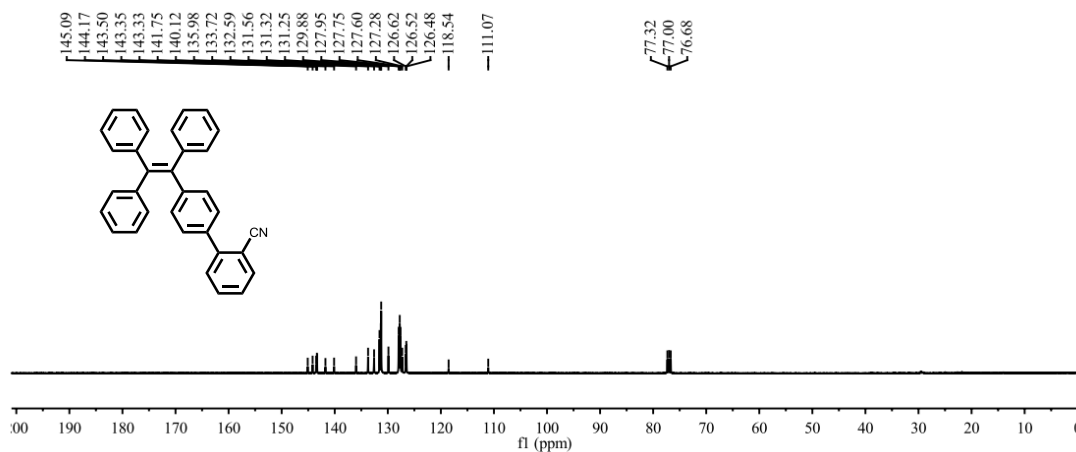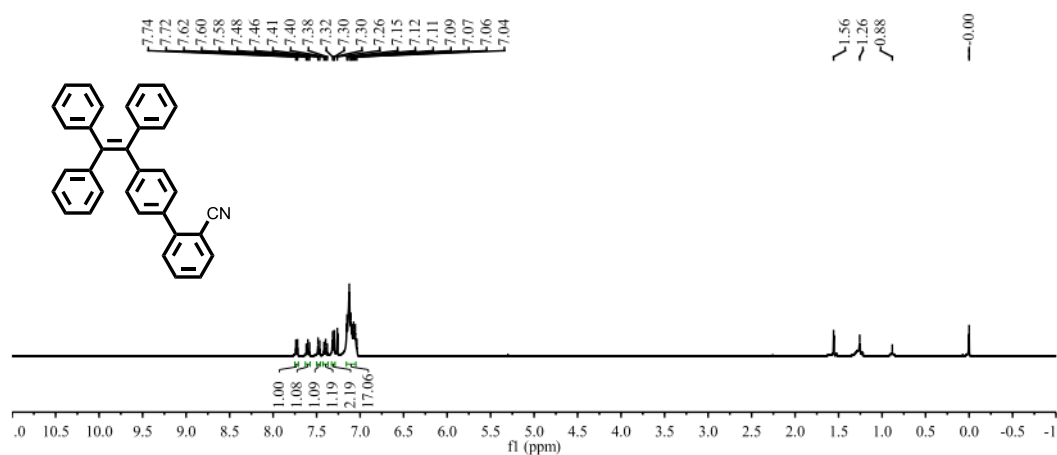**Table S1**. Structure determination summary for the compound **1**.

Empirical formula	$C_{33} H_{23} N$
Formula weight	433.52
Temperature (K)	296(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	10.6406(19)
b (Å)	14.908(3)
c (Å)	15.474(3)
α (deg)	90.00
β (deg)	94.207(2)
γ (deg)	90.00
V (Å^3)	2448.0(7)
Z	4
Absorption coefficient (mm^{-1})	0.068
F (000)	912
Theta range for data collection (deg)	1.90 to 26.00
Index ranges	-13<=h<=13, -18<=k<=18, -18<=l<=19

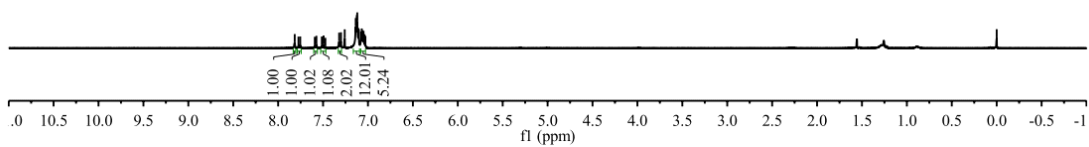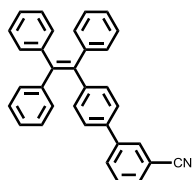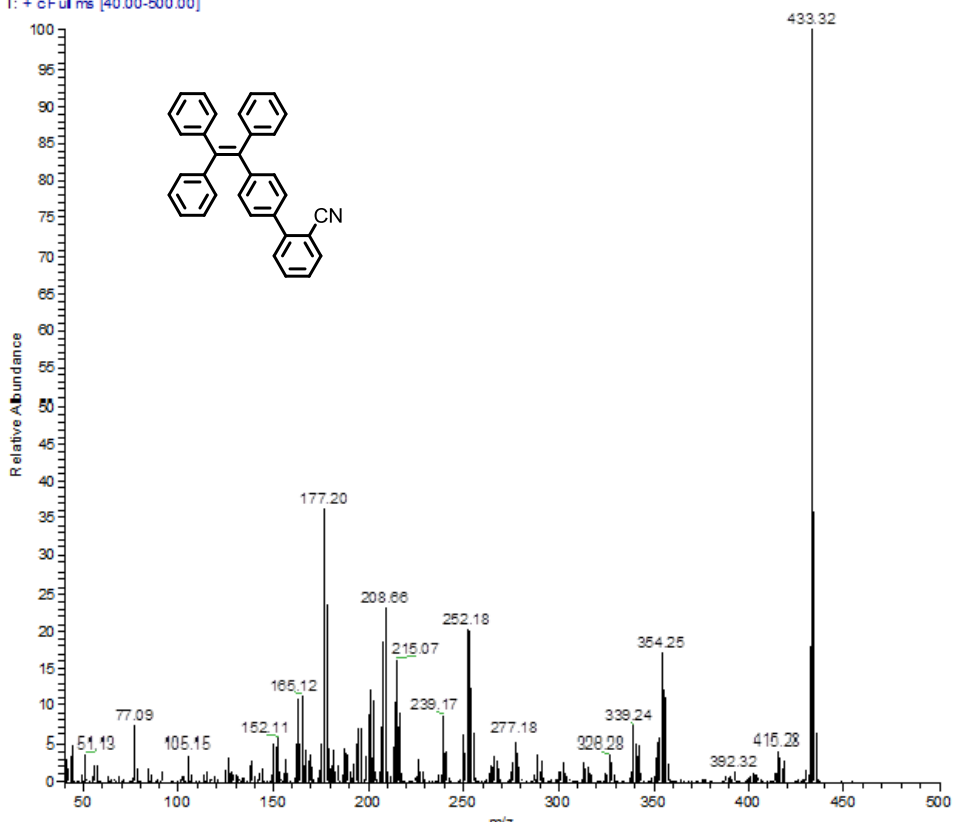**Table S2**. Structure determination summary for the compound **2**.

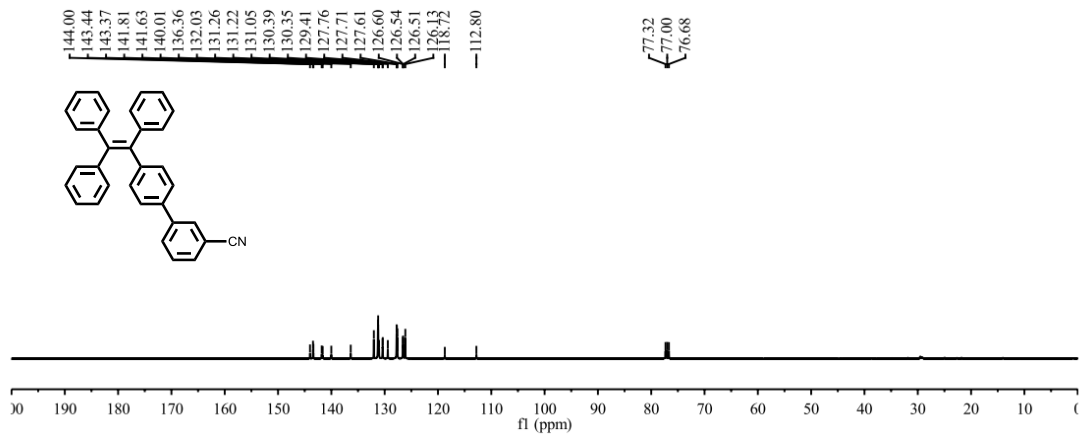|	
Empirical formula	$C_{33} H_{23} N$
Formula weight	433.52
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	P -1
a (Å)	10.5396(17)
b (Å)	10.8992(17)
c (Å)	11.6905(18)
α (deg)	75.586(2)
β (deg)	72.924(2)
γ (deg)	75.975(2)
V (Å^3)	1222.4(3)
Z	2
Absorption coefficient (mm^{-1})	0.068

F (000)	456
Theta range for data collection (deg)	2.570 to 25.994
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14

5. Copies of NMR spectra and Mass spectra

144.00
143.44
143.37
141.81
141.63
140.01
136.36
132.03
131.26
131.22
131.05
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130.35
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77.00
76.68

fl (ppm)

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CN

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T: + c Ful ms [40.00-500.00]

433.33

Relative Abundance

CN

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77.10
115.09
126.11
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165.13
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216.75
239.18
253.20
278.20
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354.26
392.27
418.30

m/z

50 100 150 200 250 300 350 400 450 500