

Supporting Information

Tunable Near-Infrared Piezochromic Luminescence by Effective Substitute Modification of D-A Structures

*Jianxun Liu,¹ Guoshuai Du,² Ning Liang,¹ Li Yang,¹ Yansong Feng,^{*1} Yabin Chen^{*2} and Chang-
Jiang Yao^{*1}*

¹ J. Liu, N Liang, L. Yang, Y. Feng, C.-J. Yao, State Key Laboratory of Explosion Science and
Technology, School of Mechatronical Engineering, Beijing Institute of Technology, Beijing,
100081, China.

E-mail: fengyansong@bit.edu.cn; cjyao@bit.edu.cn.

² G. Du, Y. Chen, School of Aerospace Engineering, Beijing Institute of Technology, Beijing,
100081, China.

E-mail: chyb0422@bit.edu.cn;

Contents:

1. Reagents.....	S2
2. Instruments.....	S2
3. Synthesis.....	S2
4. Selected spectra and data referred in the paper.....	S4
5. NMR spectra.....	S8
6. Crystallographic data.....	S13

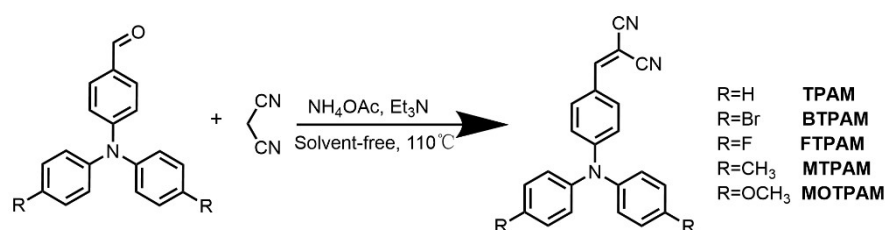
1. Reagents

Unless otherwise noted, all chemical reagents and solvents were commercially available and were used without further purification. TPA-4-aldehydes derivatives, malononitrile, ammonium acetate, and anhydrous sodium sulfate were purchased from Energy Chemical Co., Shanghai, China. Dichloromethane, alcohol, tetrahydrofuran and triethylamine were purchased from Beijing Tongguang Fine Chemical Company, All the other solvents were purchased from Tianjin Zhiyuan Chemical Reagent Co. LTD. Deionized water was used throughout all experiments.

2. Instruments

Unless otherwise noted, all the measurement experiments were performed at room temperature. Fluorescence spectra were obtained by using a F-380 spectrofluorimeter from Tianjin Gangdong Sci. & Tech. Development Co., Ltd. Absorption spectra were recorded by using a TU-1810DSPC spectrometer from Beijing Purkinje General Instrument Co., Ltd. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV400 NMR spectrometer operated at 400 MHz. DSC test was determined using a DSC 3 apparatus (METTLER TOLEDO, STARe system) under a nitrogen atmosphere at a flow rate of 50 mL·min⁻¹. Powder X-ray diffraction (PXRD) patterns were recorded with Ultima IV-185. The photos were taken by a SONY SEL 2870 camera. The crystallographic data were collected on a Rigaku Oxford Diffraction Supernova X-ray source diffractometer equipped with monochromatized Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The CCDC number of **TPAM**, **BTPAM**, **FTPAM** **MTPAM** and **MOTPAM** are 2220930, 2220931, 2220932, 2220933, 2220934, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Synthesis



Scheme S1. The synthetic routes of target compounds.

General synthetic procedure: TPA-4-aldehydes derivatives (2.0 mmol), and malononitrile (4.0 mmol, 0.26g), ammonium acetate (3 mmol, 0.23 g), and a catalytic amount of triethylamine (50 μ L) was heated with stirring at 110 °C for appropriate 2 h. The progress of the reaction was monitored by TLC. The reaction mixture was allowed to cool to room temperature after the reaction is complete. Next, CH₂Cl₂ (10 mL) and water (25 mL) were added to dissolve the mixture, and extracted with CH₂Cl₂ (25 mL \times 3), washed with water (25 mL \times 3), dried over anhydrous Na₂SO₄. The solvent was then removed under vacuum and the solid was purified by flash chromatography

(silica gel, PE/EA = 50:1).

TPAM: Orange crystalline. Yield is 75%. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 9.0$ Hz, 2H), 7.51 (s, 1H), 7.38 (t, $J = 7.8$ Hz, 4H), 7.24 - 7.15 (m, 6H), 6.94 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.96, 153.47, 145.13, 133.04, 129.98, 126.74, 126.15, 122.77, 118.48, 115.26, 114.14, 75.45.

BTPAM: Yellow crystalline. Yield is 70%. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 9.0$ Hz, 2H), 7.55 (s, 1H), 7.49 (d, $J = 8.7$ Hz, 4H), 7.04 (d, $J = 8.7$ Hz, 4H), 6.98 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.87, 152.44, 144.09, 133.22, 132.98, 127.88, 123.84, 119.52, 119.26, 114.84, 113.74, 77.15.

FTPAM: Orange crystalline. Yield is 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 9.0$ Hz, 2H), 7.52 (s, 1H), 7.17 (dd, $J = 9.0, 4.8$ Hz, 4H), 7.09 (t, $J = 8.5$ Hz, 4H), 6.87 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.89, 159.43, 157.94, 153.37, 140.96, 133.11, 128.49, 128.41, 122.83, 117.79, 117.19, 116.96, 115.10, 114.01, 75.96.

MTPAM: Red crystalline. Yield is 78%. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 9.0$ Hz, 1H), 7.48 (s, 1H), 7.18 (d, $J = 8.2$ Hz, 2H), 7.08 (d, $J = 8.3$ Hz, 2H), 6.88 (d, $J = 9.1$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.92, 153.79, 142.45, 136.18, 133.11, 130.66, 126.75, 122.16, 117.58, 115.50, 114.35, 74.49, 21.05.

MOTPAM: Yellow crystalline. Yield is 65%. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 9.0$ Hz, 2H), 7.47 (s, 1H), 7.13 (d, $J = 8.8$ Hz, 4H), 6.91 (d, $J = 8.9$ Hz, 4H), 6.80 (d, $J = 9.0$ Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.95, 157.81, 154.18, 137.79, 133.19, 128.17, 121.75, 116.64, 115.55, 115.25, 114.42, 74.09, 55.56.

4. Selected spectra and data referred in the paper

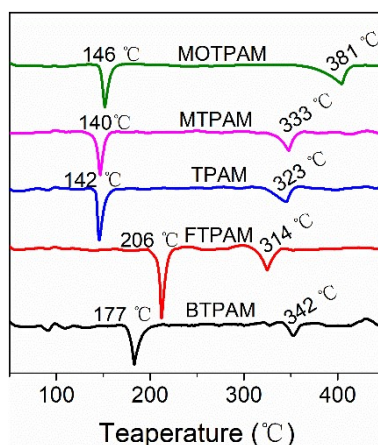


Figure S1. The DSC thermograms of five AIEgens. Left numbers are the melting temperatures (T_m) and right numbers are the sublimation temperatures (T_s).

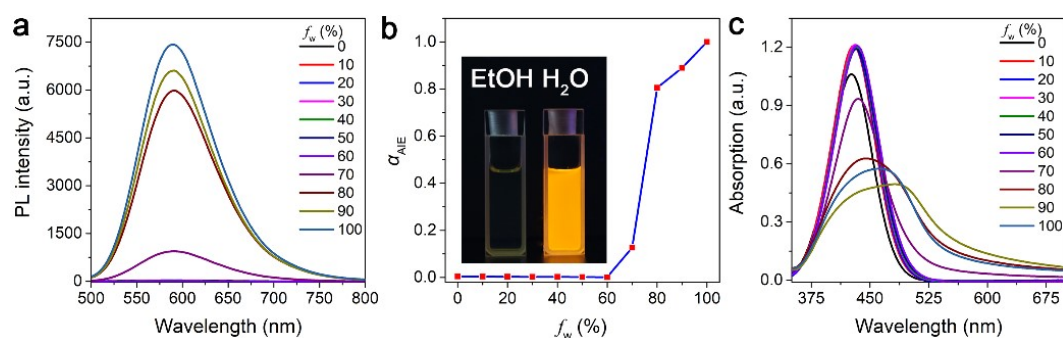


Figure S2. a) Fluorescence spectra of FTPAM in water/ethanol mixtures with different f_w ; b) α_{AIE} values of FTPAM as a function of f_w ; c) Absorption spectra of FTPAM in water/ethanol mixtures with f_w from 0% to 100%. Inset: A photograph of FTPAM in water/ethanol mixtures with f_w of 0% and 100% under UV light irradiation.

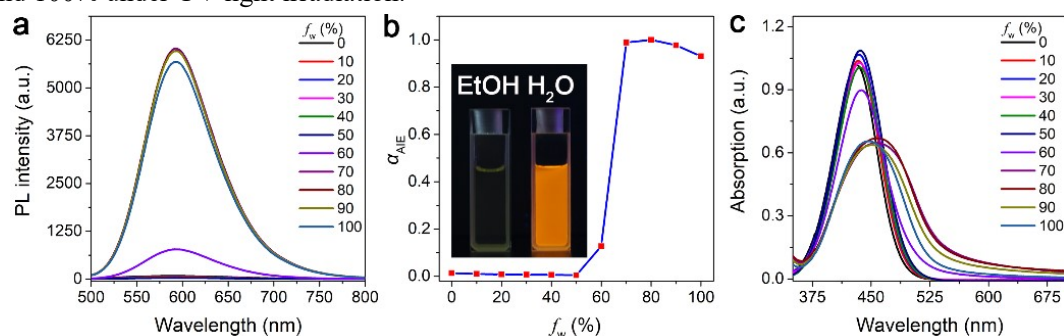


Figure S3. a) Fluorescence spectra of BTPAM in water/ethanol mixtures with different f_w ; b) α_{AIE} values of BTPAM as a function of f_w ; c) Absorption spectra of BTPAM in water/ethanol mixtures with f_w from 0% to 100%. Inset: A photograph of BTPAM in water/ethanol mixtures with f_w of 0% and 100% under UV light irradiation.

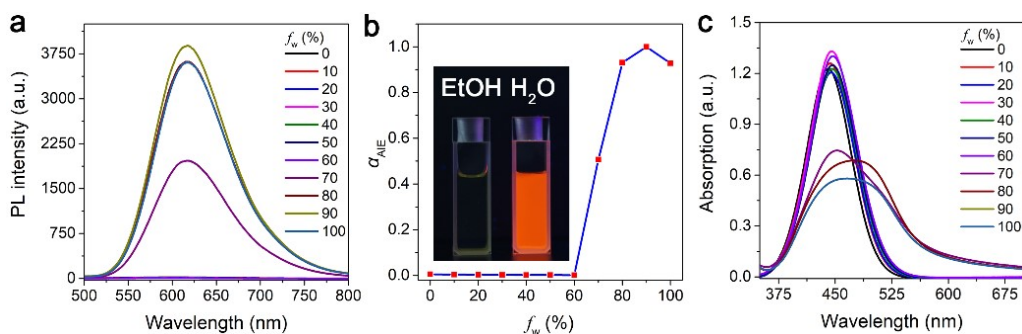


Figure S4. a) Fluorescence spectra of MTPAM in water/ethanol mixtures with different f_w ; b) α_{AIE} values of MTPAM as a function of f_w ; c) Absorption spectra of MTPAM in water/ethanol mixtures with f_w from 0% to 100%. Inset: A photograph of MTPAM in water/ethanol mixtures with f_w of 0% and 100% under UV light irradiation.

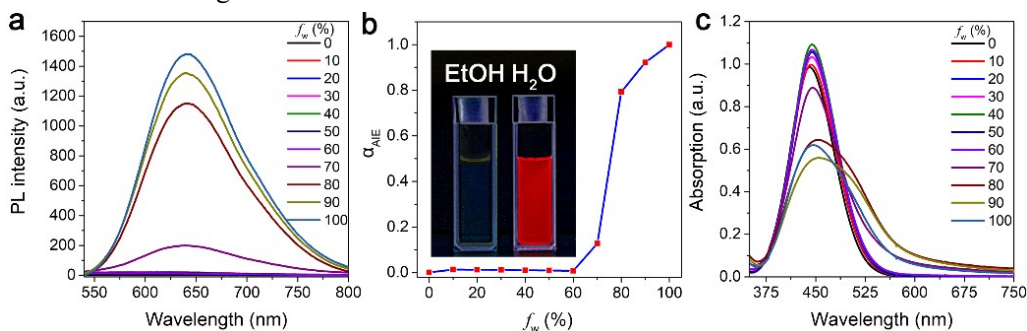


Figure S5. a) Fluorescence spectra of MOTPAM in water/ethanol mixtures with different f_w ; b) α_{AIE} values of MOTPAM as a function of f_w ; c) Absorption spectra of MOTPAM in water/ethanol mixtures with f_w from 0% to 100%. Inset: A photograph of MOTPAM in water/ethanol mixtures with f_w of 0% and 100% under UV light irradiation.

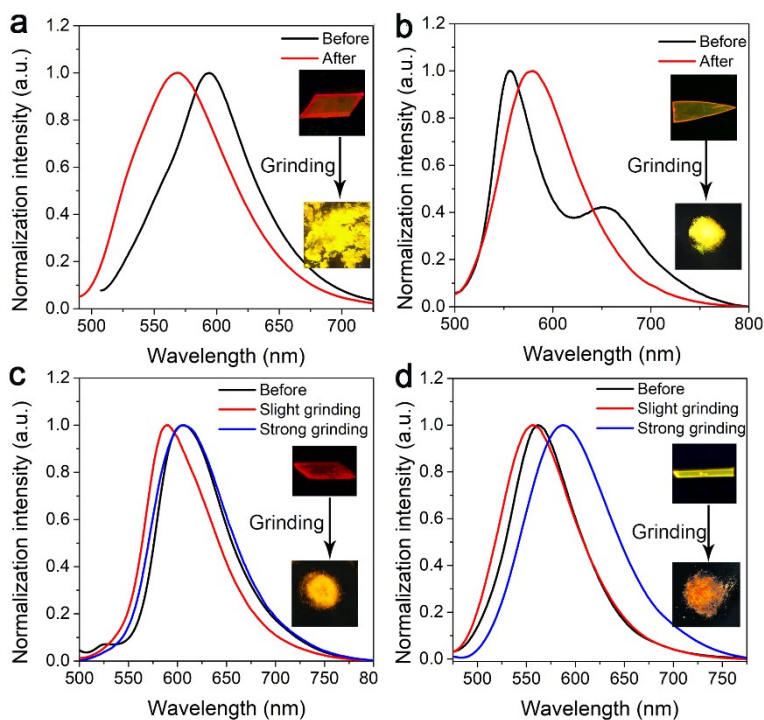


Figure S6. Fluorescence spectra of a) FTPAM; b) BTPAM; c) MTPAM and d) MOTPAM before and after grinding. Inset: The photograph before and after grinding under UV light irradiation.

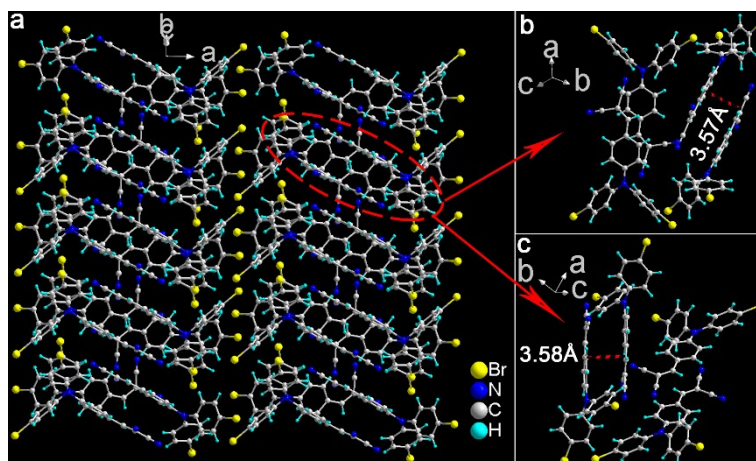


Figure S7. Crystal structure of BTPAM viewed from different directions.

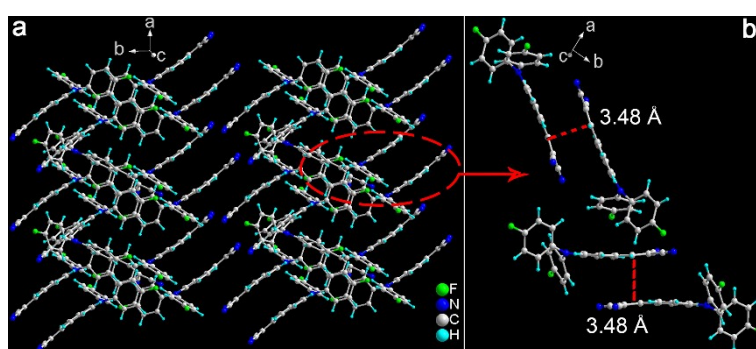


Figure S8. Crystal structure of FTPAM viewed from different directions.

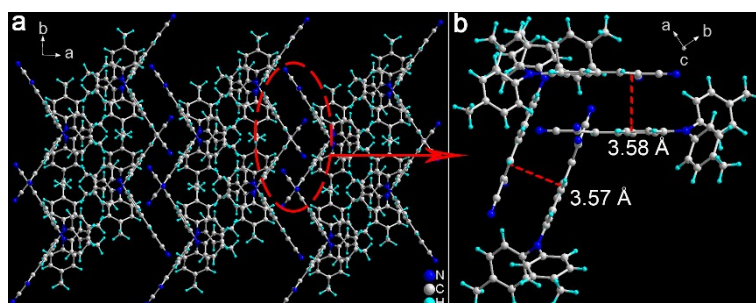


Figure S9. Crystal structure of MTPAM viewed from different directions.

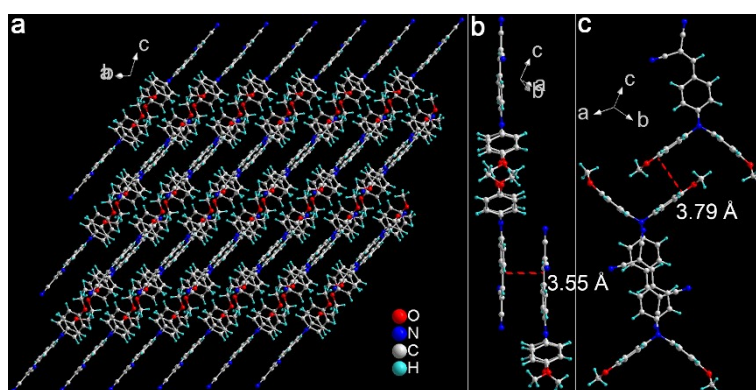


Figure S10. Crystal structure of MOTPAM viewed from different directions.

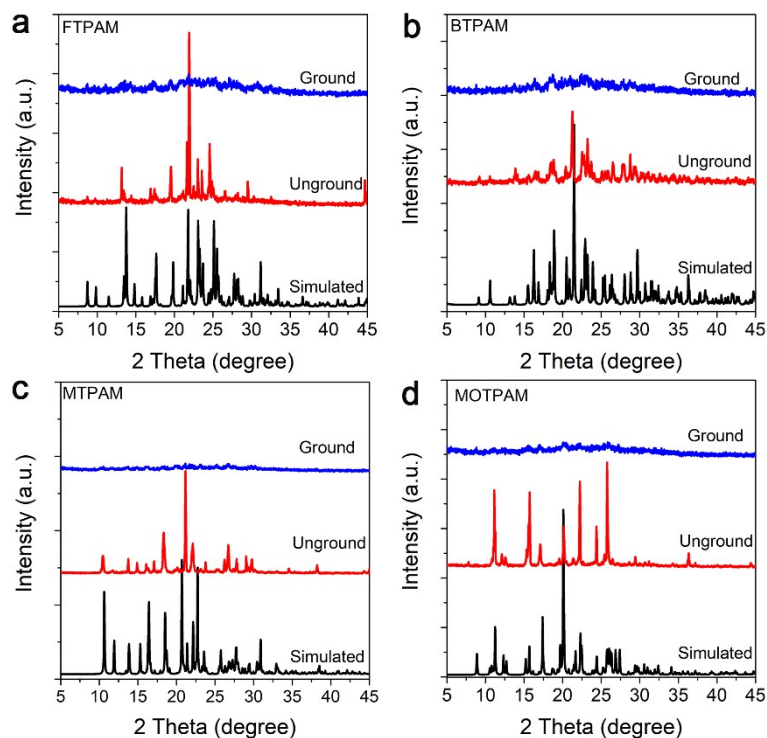


Figure S11. PXRD spectra of a) FTPAM; b) BTPAM; c) MTPAM and d) MOTPAM in different states.

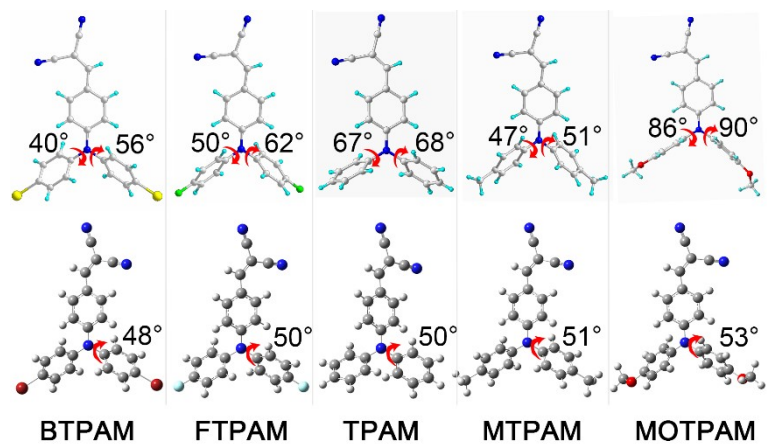


Figure S12. The molecular conformations of crystalline (up) and calculation (down).

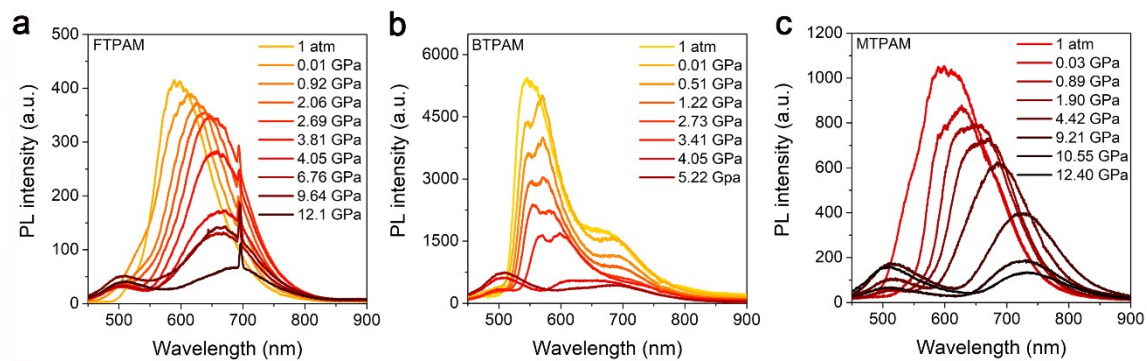


Figure S13. Fluorescence spectra of a) FTPAM; b) BTPAM; c) MTPAM under different pressure.

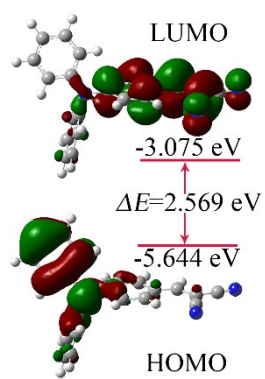


Figure S14. The frontier molecular orbitals of TPAM obtained *via* DFT calculations.

5. NMR spectra

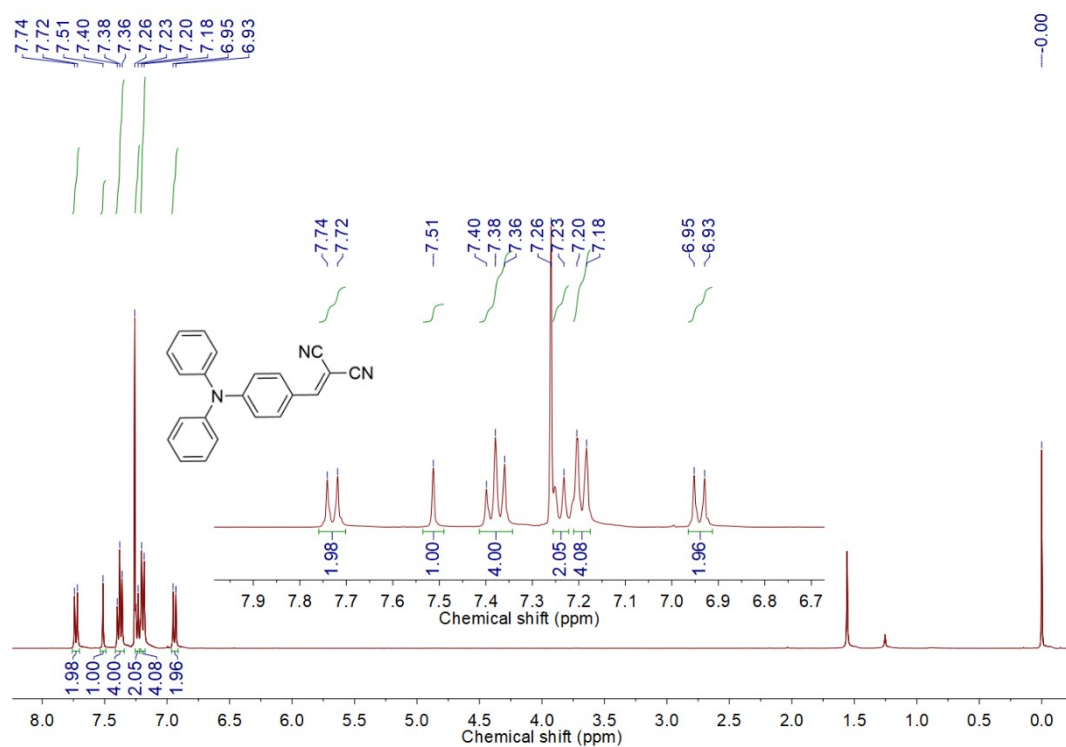


Figure S15. ¹H NMR spectra of TPAM.

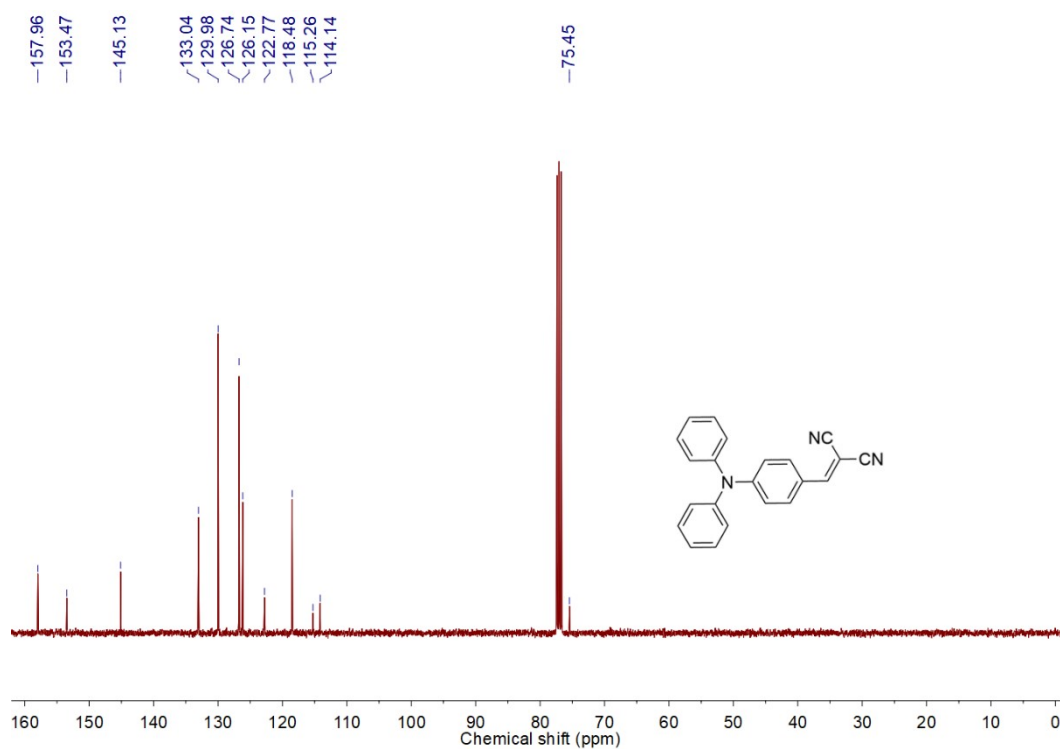


Figure S16. ¹³C NMR spectra of TPAM.

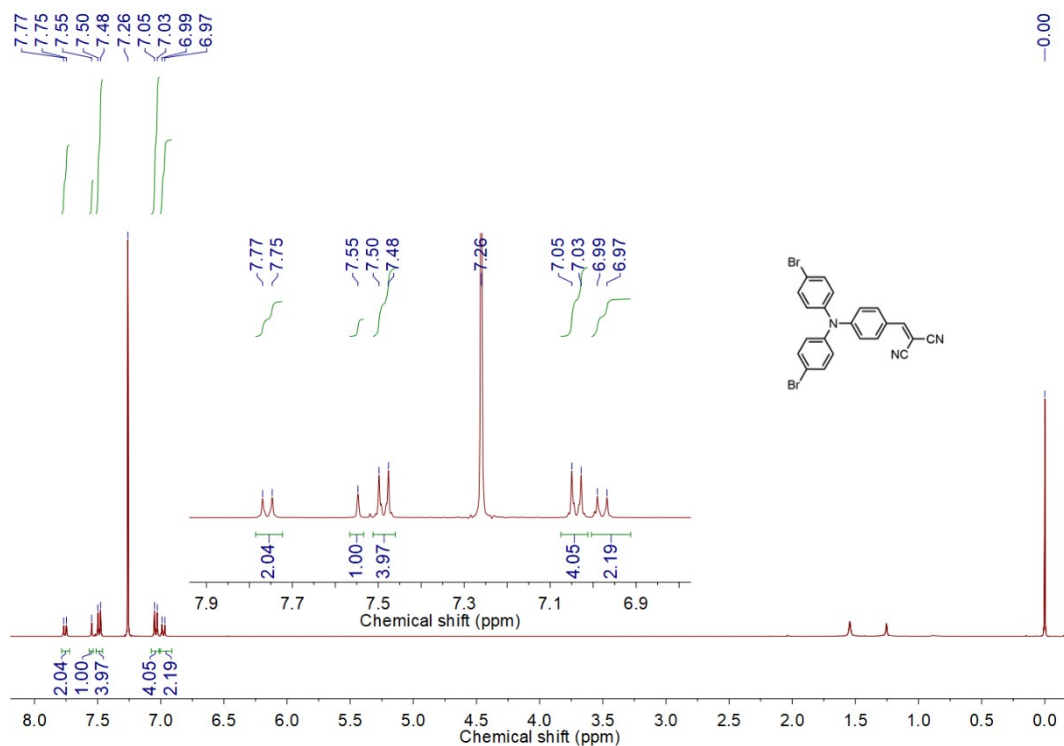


Figure S17. ^1H NMR spectra of BTPAM.

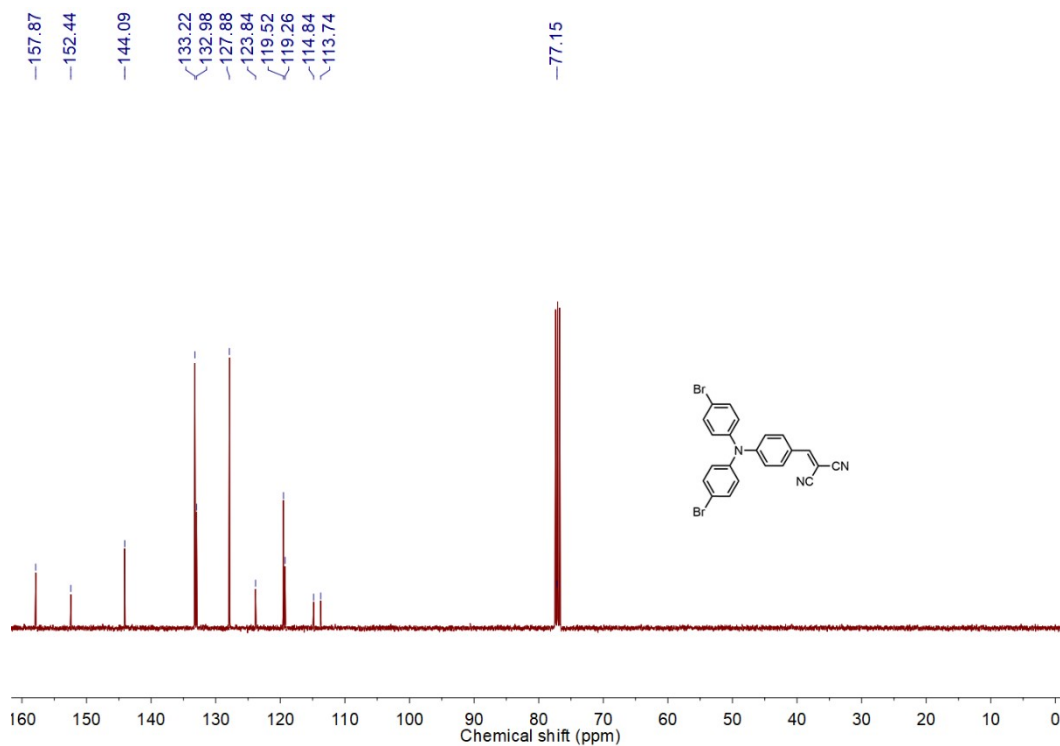


Figure S18. ^{13}C NMR spectra of BTPAM.

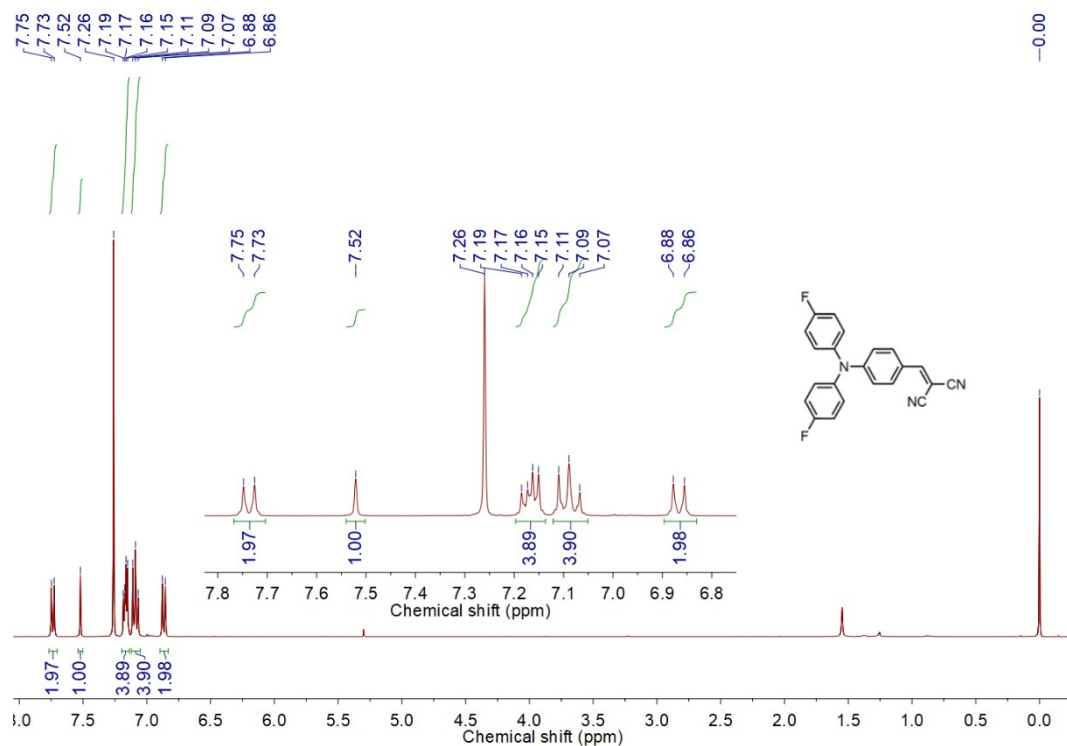


Figure S19. ^1H NMR spectra of FTPAM.

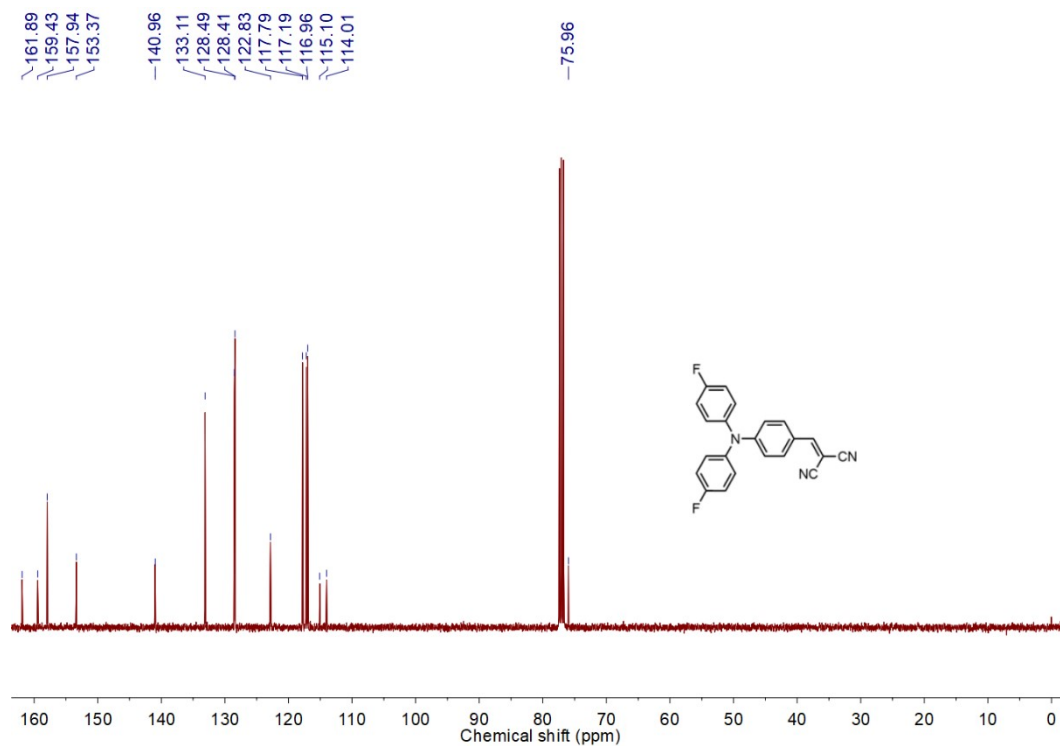


Figure S20. ^{13}C NMR spectra of FTPAM.

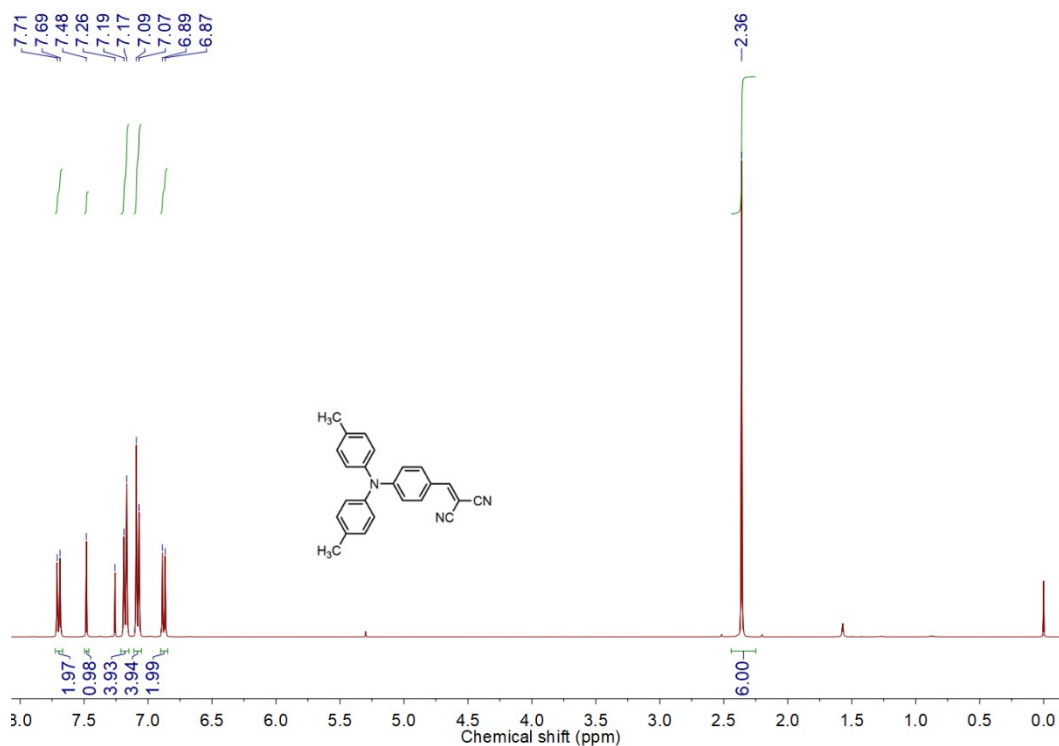


Figure S21. ¹H NMR spectra of MTPAM.

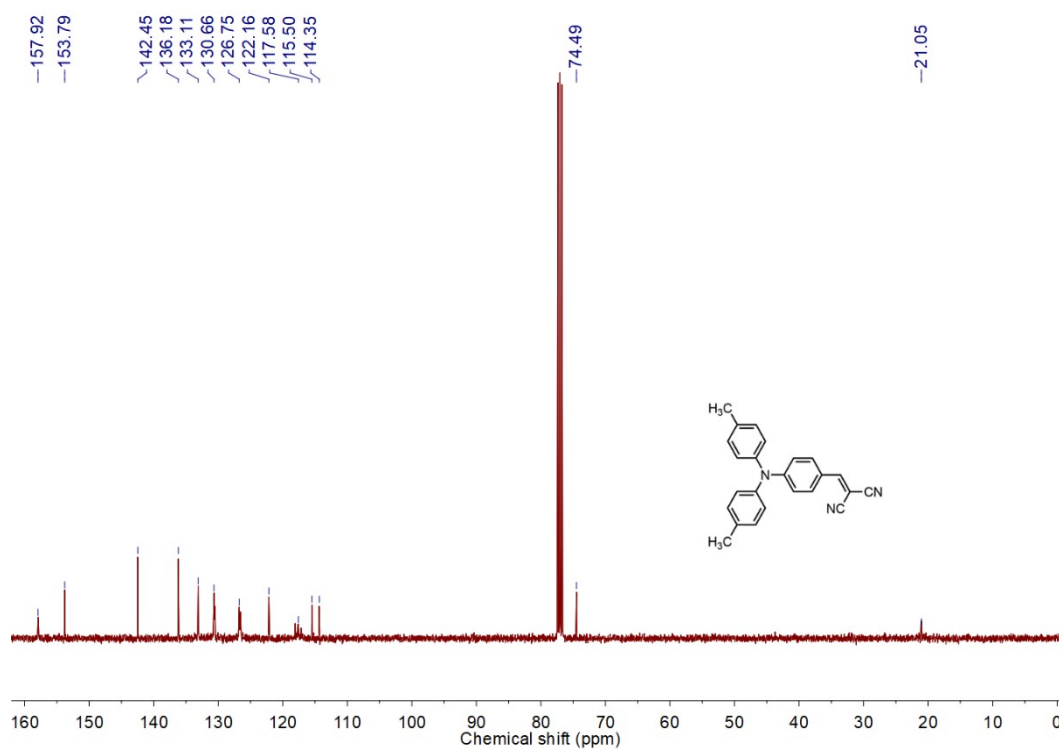


Figure S22. ¹³C NMR spectra of MTPAM.

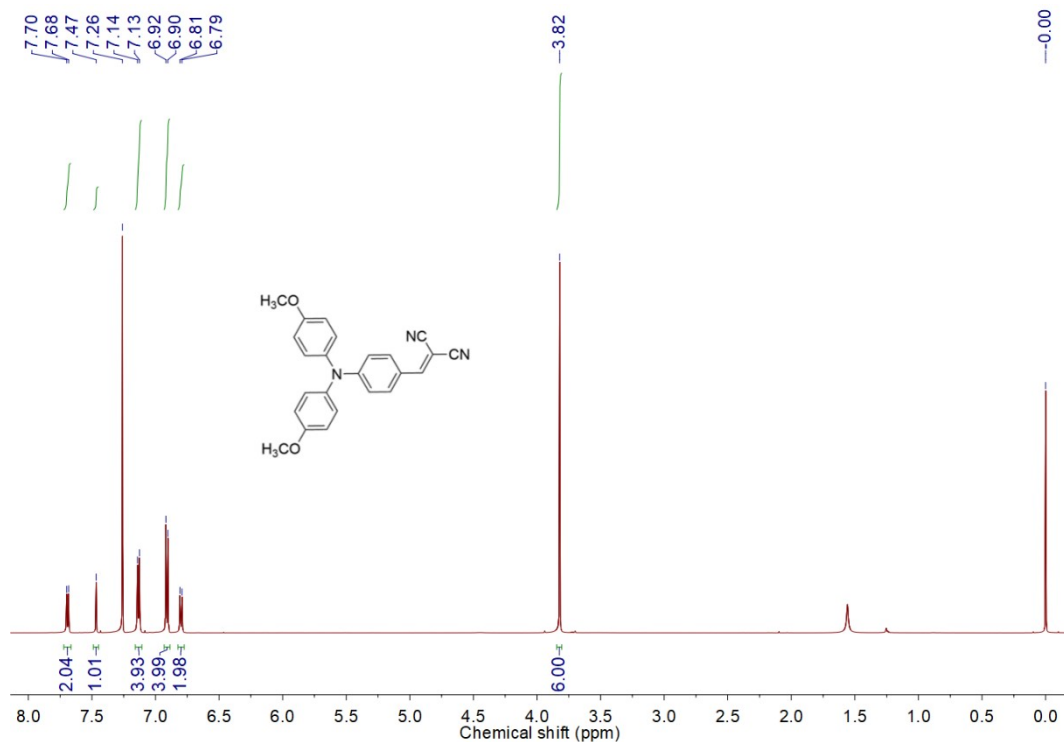


Figure S23. ¹H NMR spectra of MOTPAM.

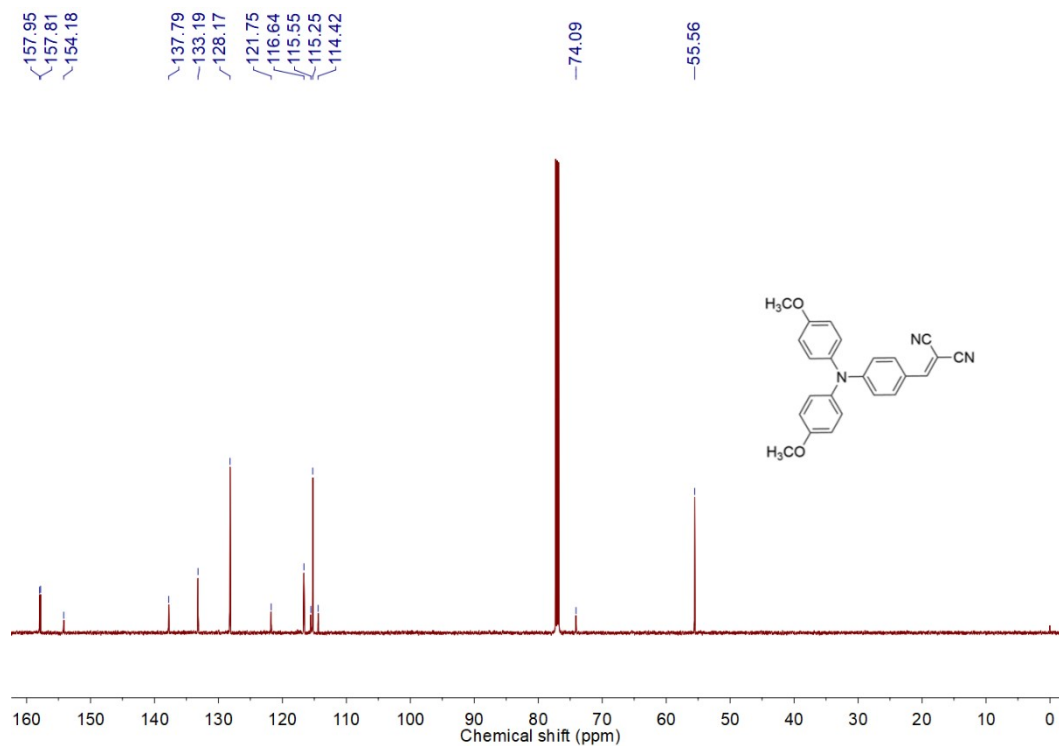


Figure S24. ¹³C NMR spectra of MOTPAM.

6. Crystallographic data

Table S1. Crystallographic data and structure refinement details for five compounds.

Compound	TPAM	BTPAM	FTPAM	MTPAM	MOTPAM
CCDC	2220930	2220931	2220932	2220933	2220934
Formula	C ₂₂ H ₁₅ N ₃	C ₂₂ H ₁₃ Br ₂ N ₃	C ₂₂ H ₁₃ F ₂ N ₃	C ₂₄ H ₁₉ N ₃	C ₂₄ H ₁₉ N ₃ O ₂
<i>F_w</i>	321.37	479.15	357.35	349.42	381.42
Temp.(K)	170 K	100	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	6.9351(1)	18.9668(3)	8.4263(1)	14.2958(19)	9.1712(2)
<i>b</i> (Å)	15.7313(2)	9.0817(1)	20.2390(3)	10.3262(14)	10.3056(19)
<i>c</i> (Å)	16.1037(2)	11.2527(2)	10.1663(1)	13.0988(17)	11.8241(3)
α (°)	90	90	90	90	91.7175
β (°)	95.163	90.605	98.855	102.503	108.187
γ (°)	90	90	90	90	108.5272
<i>V</i> (Å ³)	1749.76(4)	1938.18(5)	1713.10(4)	1887.82(4)	996.31(4)
<i>Z</i>	4	4	4	4	2
<i>D_c</i> (g·cm ⁻³)	1.220	1.642	1.386	1.229	1.271
μ (mm ⁻¹)	0.573	0.588	0.818	0.570	0.662
<i>F</i> (000)	672.0	944.0	736.0	736.0	400.0
GOF on <i>F</i> ²	1.090	1.084	1.029	1.069	1.043
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0405	0.0398	0.0431	0.0451	0.0349
<i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.1040	0.1097	0.1220	0.1237	0.0903

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.