Supplementary Information

Insights into Molecular Packing Effect on the Emission Properties of Fluorenone-based Molecules in the Aggregate State

Peigen Yao, Yixuan Wang, Weiguo Qiao, Xianglang Sun, Haiyan Peng, Xiaolin Xie, Zhong'an Li*

Key Laboratory for Material Chemistry of Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China. E-mail: lizha@hust.edu.cn

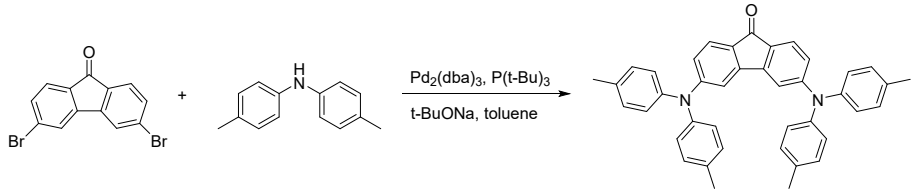
Instrumentations

^{1}H NMR and ^{13}C NMR spectra were measured using Bruker 400 and 600 MHz instrument spectrometers. High-resolution mass spectrometry was performed on a Bruker Daltonics instrument, SolariX 7.0T. Thermogravimetric analysis was performed on a NETZSCH STA 449 F3 Jupiter under nitrogen atmosphere with a heating rate of 10°C min^{-1}. The single crystal data was collected on the Rigaku Saturn diffractometer with CCD area detector. All calculations were performed using the SHELXL97 and crystal structure crystallographic software packages. UV-vis-NIR absorption spectra were recorded on a PerkinElmer LAMBDA 750 spectrophotometer. Photoluminescence spectra were recorded on an OmniFluo-960 fluorophotometer and a SHIMADZU RF-5301PC Spectrofluorophotometer. Absolute fluorescence quantum yield, photoluminescence lifetimes, radiative and nonradiative decay rates were measured by FLS1000 Photoluminescence Spectrometer. Powder X-ray diffraction was performed on a Rigaku SmartLab SE.

Materials

Toluene was dried with sodium and distilled under argon atmosphere. Most of reagents

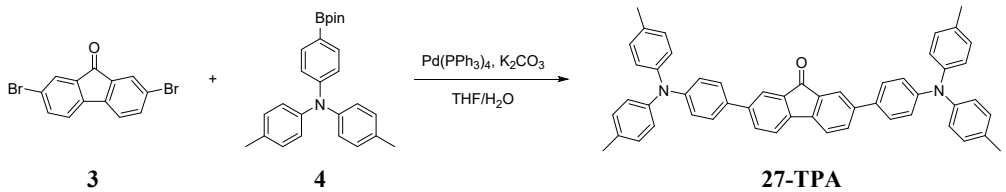
were purchased from Adamas (Titan Scientific, Shanghai) and used without further purification, except $Pd_2(dba)_3$ (Fluorochem), $P(t\text{-}Bu)_3$ (Energy Chemical, Shanghai). Compound **1**, **4** and **27-DPA** were synthesized according to previous literatures.[1-3]



1 **2** **36-DPA**

Synthesis of 36-DPA

A mixture of 3,6-dibromo-9-fluorenone (**1**, 0.50 g, 1.48 mmol), di-p-tolylamine (**2**, 0.73 g, 3.70 mmol), $Pd_2(dba)_3$ (0.07 g, 0.07 mmol), t-BuONa (0.20 g, 2.07 mmol), $P(t\text{-}Bu)_3$ (1.00 mL, 0.60 mmol) and dry toluene (20 mL) were added to a 100 mL Schlenk tube and then heated to reflux under argon overnight. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) three times. The combined organic layer was dried by anhydrous Na_2SO_4 and then concentrated. The crude product was first purified through column chromatography (SiO_2, petroleum ether/DCM, 1/1, V/V), followed by recrystallization from DCM and methanol to afford **36-DPA** (0.52 g, 62.4%) as bright orange solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 8H), 7.03 (d, *J* = 8.3 Hz, 8H), 6.98 (s, 2H), 6.71 (d, *J* = 10.2 Hz, 2H), 2.35 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.92, 153.63, 145.24, 144.24, 134.16, 130.21, 127.93, 125.68, 125.02, 120.15, 112.37, 20.91. HRMS (m/z): $[M+H]^+$ calculated for $C_{41}H_{35}ON_2$, 571.27; found, 571.2729.

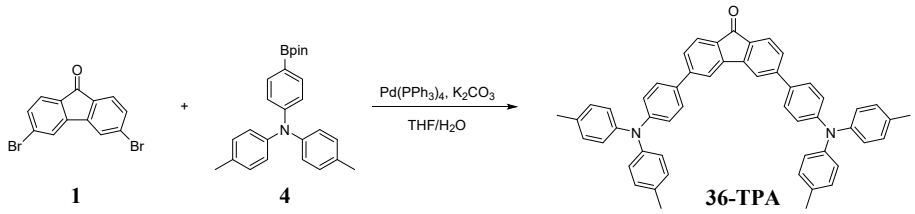


3 **4** **27-TPA**

Synthesis of 27-TPA

A mixture of 2,7-dibromo-9-fluorenone (**3**, 0.20 g, 0.59 mmol), compound **4** (0.59 g, 1.48

mmol), Pd (PPh_3)$_4$ (0.03 g, 0.03 mmol) and K_2CO_3 (0.25 g, 1.78 mmol), degassed THF (5 mL) and degassed H_2O (5 mL) were added to a 50 mL Schlenk tube and then then refluxed under argon overnight. After cooling to room temperature, the mixture was extracted with DCM for three times. The combined organic layer was dried by anhydrous Na_2SO_4 and then concentrated. The crude product was first purified by column chromatography (SiO_2, petroleum ether/DCM, 3/1, V/V), followed by recrystallization from DCM and methanol to afford **27-TPA** (0.34 g, 79.6%) as dark red solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (s, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 4H), 7.11 (t, *J* = 8.8 Hz, 12H), 7.06 (d, *J* = 8.4 Hz, 8H), 2.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.12, 148.20, 145.02, 142.49, 141.58, 135.23, 132.94, 132.45, 132.40, 130.00, 127.25, 124.94, 122.32, 122.25, 120.60, 20.87. HRMS (m/z): $[M+H]^+$ calculated for $C_{53}H_{43}ON_2$, 723.33; found, 723.3351.



Synthesis of 36-TPA

Following the same procedures as **27-TPA** and using 3,6-dibromo-9-fluorenone as the starting material afforded **36-TPA** as orange powder (0.28 g, 65.6%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 1.0 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 6.5 Hz, 4H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 12H), 7.08 (d, *J* = 8.4 Hz, 8H), 2.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.12, 148.73, 147.26, 144.93, 144.87, 133.18, 133.02, 132.50, 130.04, 127.78, 127.55, 127.04, 125.08, 124.86, 124.66, 121.93, 118.31, 20.89. HRMS (m/z): $[M+H]^+$ calculated for $C_{53}H_{43}ON_2$, 723.33; found, 723.3352.

Table S1. UV-Vis absorption and emission maxima of fluorenone-based molecules in different solvents (10^{-5} M).

solvent		**27-DPA**	**36-DPA**	**27-TPA**	**36-TPA**
n-hexane	λ_{abs} (nm)	379, 541	333, 387, 451	376, 466	411
	λ_{em} (nm)	638	510, 536	546, 578	486, 512
toluene	λ_{abs} (nm)	384, 559	339, 394, 465	378, 478	425
	λ_{em} (nm)	-	562	590	546
THF	λ_{abs} (nm)	381, 569	334, 397, 469	376, 479	424
	λ_{em} (nm)	-	572	616	614
EA	λ_{abs} (nm)	378, 559	333, 388, 464	376, 475	411
	λ_{em} (nm)	-	572	618	610
DCM	λ_{abs} (nm)	382, 570	337, 395, 479	377, 487	437
	λ_{em} (nm)	-	614	-	-
DMSO	λ_{abs} (nm)	381, 586	338, 387, 482	381, 491	443
	λ_{em} (nm)	-	-	-	-

λ_{abs}: maximum absorption wavelength. λ_{em}: maximum emission wavelength. Excitation wavelength: 380 nm for **27-DPA**; 340 nm for **36-DPA**; 376 nm for **27-TPA**; 398 nm for **36-TPA**.

Table S2. Photoluminescence lifetimes, radiative and nonradiative decay rates of fluorenone-based molecules.

compounds	τ_{agg} [a] (ns)	$k_{r,\,agg}$ [b] (10^7 s^{-1})	$k_{nr,\,agg}$ [c] (10^8 s^{-1})	τ_{solid} [d] (ns)	$k_{r,\,solid}$ [e] (10^7 s^{-1})	$k_{nr,\,solid}$ [f] (10^8 s^{-1})
27-DPA	- [g]	-	-	- [g]	-	-
36-DPA	4.68	4.71	1.66	8.28	5.82	0.63
27-TPA	1.90	1.95	5.07	1.84	4.45	4.99
36-TPA	8.83	1.44	0.99	5.1	3.57	1.60

[a] Photoluminescence lifetime measured in DMSO/H_2O mixed solvents (aggregated states). [b] Radiative decay rate of aggregated state. [c] Nonradiative decay rate of aggregated state. [d] Photoluminescence lifetime of solid powders. [e] Radiative decay rate of solid powders. [f] Nonradiative decay rate of solid powders. [g] Data of **27-DPA** was unable to be collected because of its quenched fluorescence. Excitation wavelength: 375 nm for solution and 450 nm for powders. Note that due to the quenched emission, the data for all molecules in DMSO solutions was also not obtained.

Table S3. Crystal data and structure refinement for **27-DPA**.

Identification code	27-DPA
Empirical formula	C41H34N2O
Formula weight	570.70
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.0273(2)
b/Å	11.8821(3)
c/Å	13.1597(2)
α/°	78.351(2)
β/°	89.587(2)
γ/°	65.611(2)
Volume/Å3	1532.45(6)
Z	2
ρ_{calc}g/cm3	1.237
μ/mm-1	0.569
F(000)	604.0
Crystal size/mm3	0.25 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.884 to 147.674
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	35471
Independent reflections	6047 [Rint = 0.0312, Rsigma = 0.0171]
Data/restraints/parameters	6047/0/402
Goodness-of-fit on F2	1.054
Final R indexes [I>=2σ (I)]	R1 = 0.0375, wR2 = 0.0973
Final R indexes [all data]	R1 = 0.0389, wR2 = 0.0983
Largest diff. peak/hole / e Å-3	0.27/-0.19

Table S4. Crystal data and structure refinement for **36-DPA**.

Identification code	36-DPA
Empirical formula	C86H76N4O3
Formula weight	1213.50
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.08710(10)
b/Å	17.4149(2)
c/Å	22.2469(2)
α/°	70.5830(10)
β/°	82.2510(10)
γ/°	85.9270(10)
Volume/Å3	3288.74(6)
Z	2
ρcalcg/cm3	1.225
μ/mm-1	0.571
F(000)	1288.0
Crystal size/mm3	0.35 × 0.2 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.242 to 147.936
Index ranges	-11 ≤ h ≤ 11, -21 ≤ k ≤ 20, -23 ≤ l ≤ 27
Reflections collected	42535
Independent reflections	12931 [Rint = 0.0626, Rsigma = 0.0512]
Data/restraints/parameters	12931/0/847
Goodness-of-fit on F2	1.072
Final R indexes [I>=2σ (I)]	R1 = 0.0493, wR2 = 0.1368
Final R indexes [all data]	R1 = 0.0549, wR2 = 0.1409
Largest diff. peak/hole / e Å-3	0.32/-0.29

Table S5. Crystal data and structure refinement for **36-TPA** O-crystal.

Identification code	36-TPA O-crystal
Empirical formula	C61H58N2O3
Formula weight	867.09
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0514(2)
b/Å	15.5876(5)
c/Å	17.7580(6)
α/°	69.435(3)
β/°	88.203(2)
γ/°	83.972(2)
Volume/Å3	2332.80(13)
Z	2
ρcalcg/cm3	1.234
μ/mm-1	0.581
F(000)	924.0
Crystal size/mm3	0.5 × 0.1 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.316 to 147.974
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected	55501
Independent reflections	9207 [Rint = 0.0710, Rsigma = 0.0438]
Data/restraints/parameters	9207/0/599
Goodness-of-fit on F2	1.051
Final R indexes [I>=2σ (I)]	R1 = 0.0576, wR2 = 0.1478
Final R indexes [all data]	R1 = 0.0668, wR2 = 0.1540
Largest diff. peak/hole / e Å-3	0.61/-0.44

Table S6. Crystal data and structure refinement for **36-TPA** R-crystal.

Identification code	36-TPA R-crystal
Empirical formula	C54H43Cl3N2O
Formula weight	842.25
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.16790(10)
b/Å	13.54080(10)
c/Å	17.3270(2)
α/°	71.2180(10)
β/°	85.7300(10)
γ/°	86.0060(10)
Volume/Å3	2249.67(4)
Z	2
ρcalcg/cm3	1.243
μ/mm-1	2.156
F(000)	880.0
Crystal size/mm3	0.3 × 0.2 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.396 to 147.782
Index ranges	-11 ≤ h ≤ 12, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	54466
Independent reflections	8900 [Rint = 0.0414, Rsigma = 0.0261]
Data/restraints/parameters	8900/0/545
Goodness-of-fit on F2	1.074
Final R indexes [I>=2σ (I)]	R1 = 0.0515, wR2 = 0.1520
Final R indexes [all data]	R1 = 0.0556, wR2 = 0.1558
Largest diff. peak/hole / e Å-3	0.58/-0.90

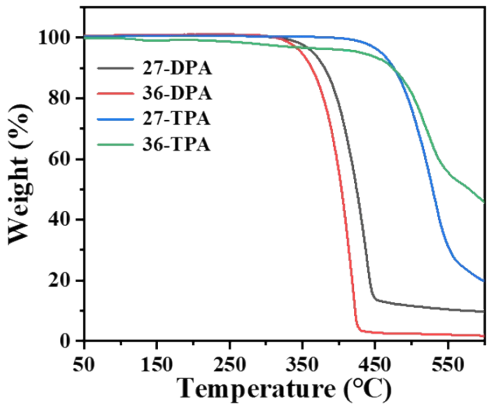


Figure S1. TGA curves of fluorenone-based molecules.

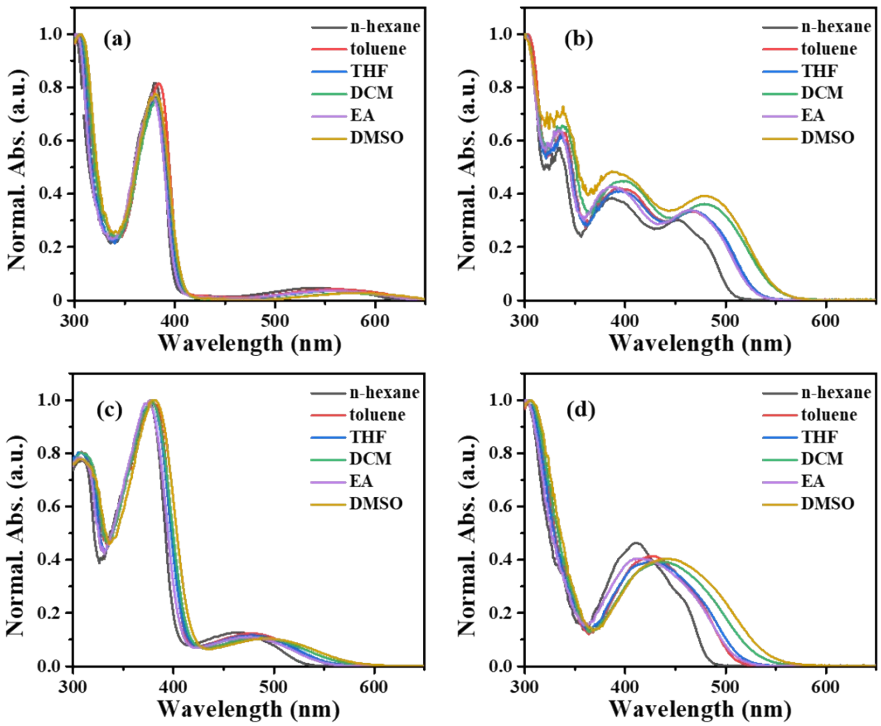


Figure S2. UV-Vis absorption spectra in different solvents (10^{-5} M) of (a) **27-DPA**, (b) **36-DPA**, (c) **27-TPA** and (d) **36-TPA**.

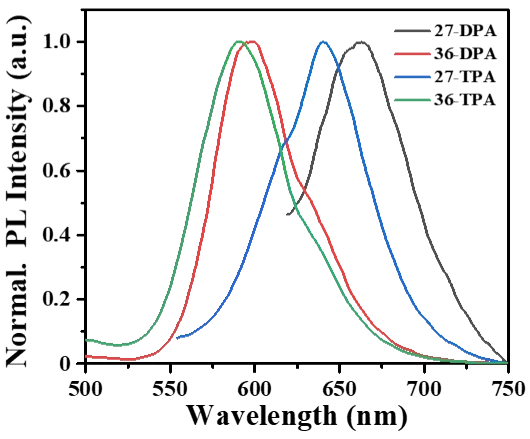


Figure S3. PL spectra of fluorenone-based molecules in powder state excited at 470 nm.

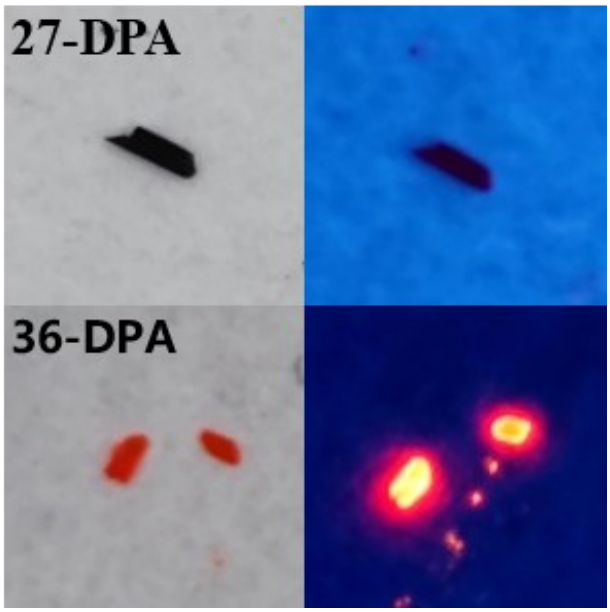


Figure S4. Photographs of single-crystals of **27-DPA** and **36-DPA** (left: under ambient light; right: under 365 nm UV excitation).

.

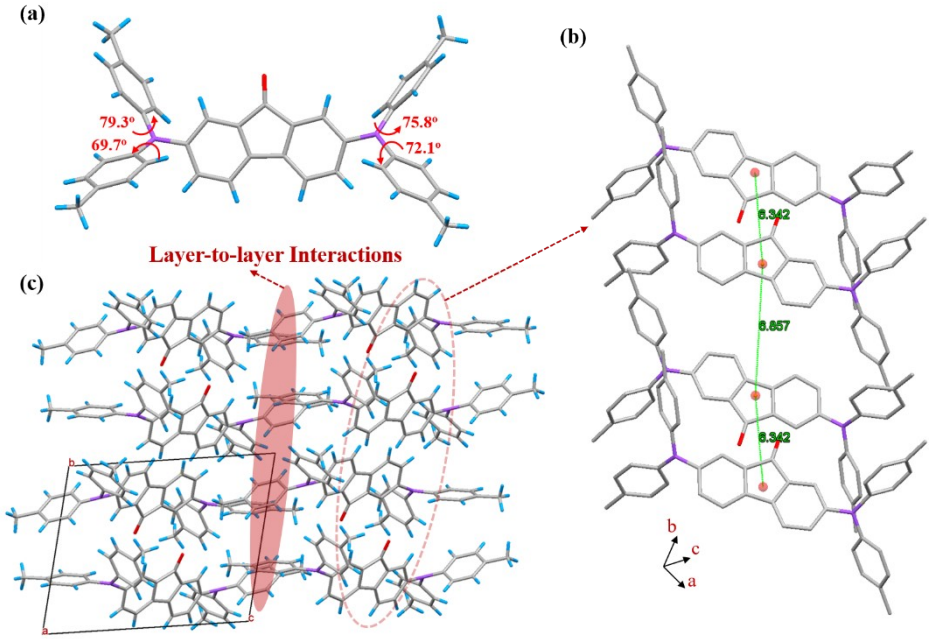


Figure S5. Single crystal structure of **27-DPA**: (a) Conformation with dihedral angles noted; (b) Molecular packing viewed along a-axis; (c) Anti-parallel molecular packing with center to center distances ($d_{c\text{-}c}$s) between the adjacent fluorenones noted. The nitrogen atoms are marked in purple, oxygen atoms in red, carbon atoms in grey and hydrogen atoms in light blue.

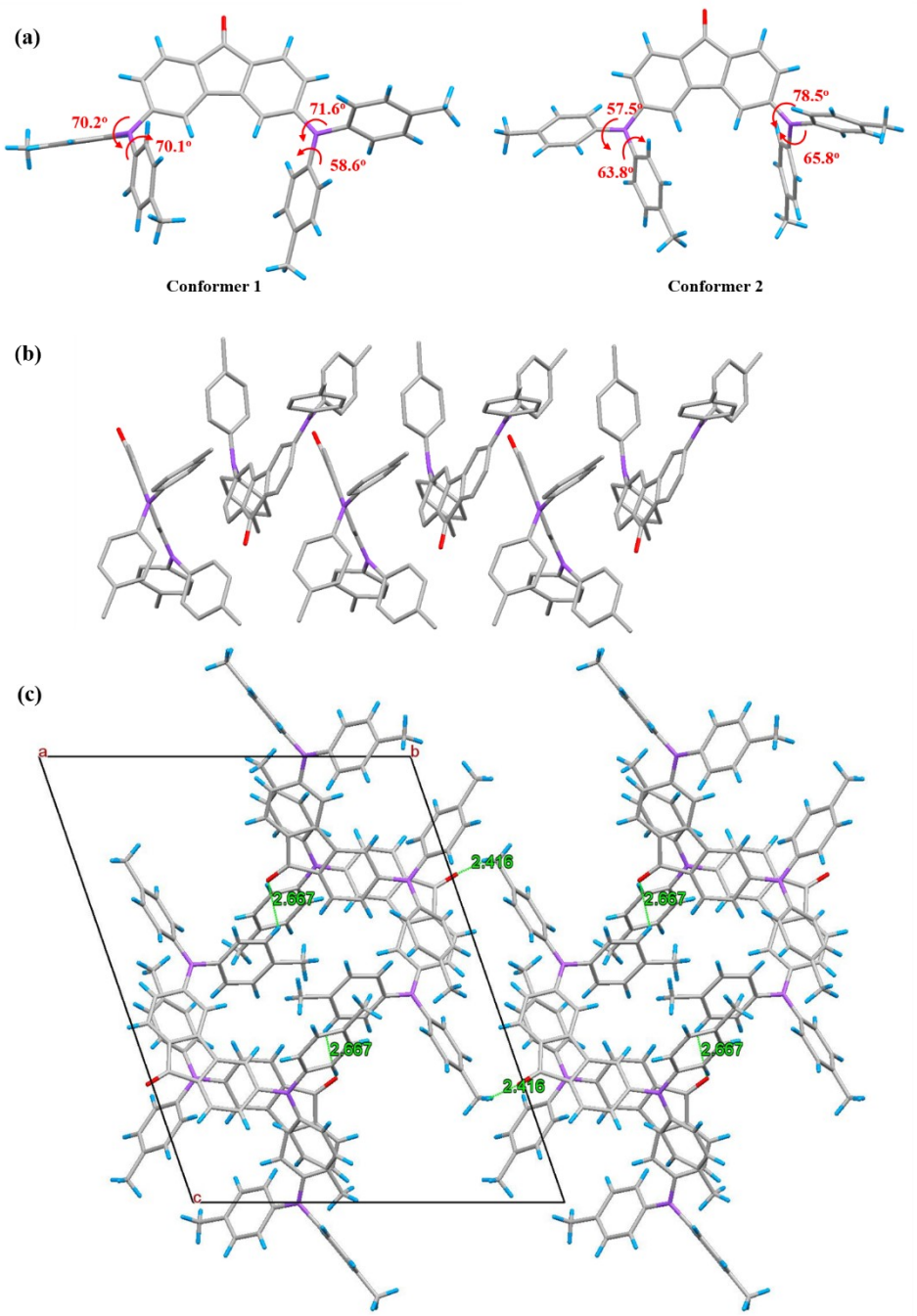


Figure S6. Single crystal structure of **36-DPA**: (a) Two conformation isomers with dihedral angles noted; (b) Extended dimeric packing between two isomers (c) Molecular packing viewed along a-axis with H-bonding distances noted. The nitrogen atoms are marked in purple, oxygen atoms in red, carbon atoms in grey and hydrogen atoms in light blue.

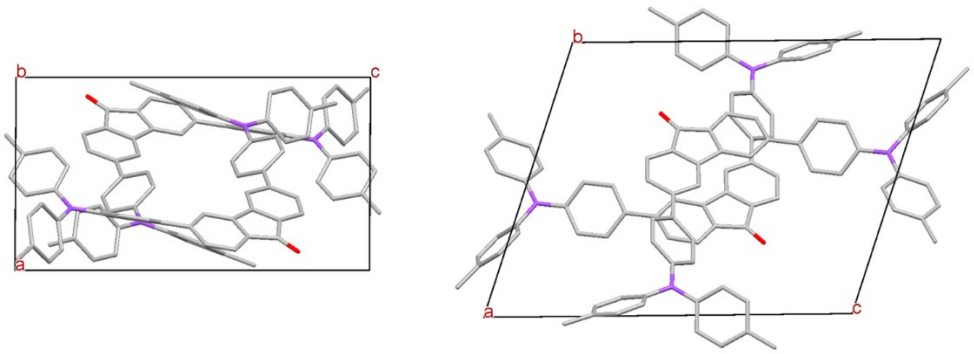


Figure S7. Dimeric packing made in one unit cell of O-crystal (left) and R-crystal (right) of **36-TPA** viewed along b-axis and a-axis, respectively. The nitrogen atoms are marked in purple, oxygen atoms in red and carbon atoms in grey.

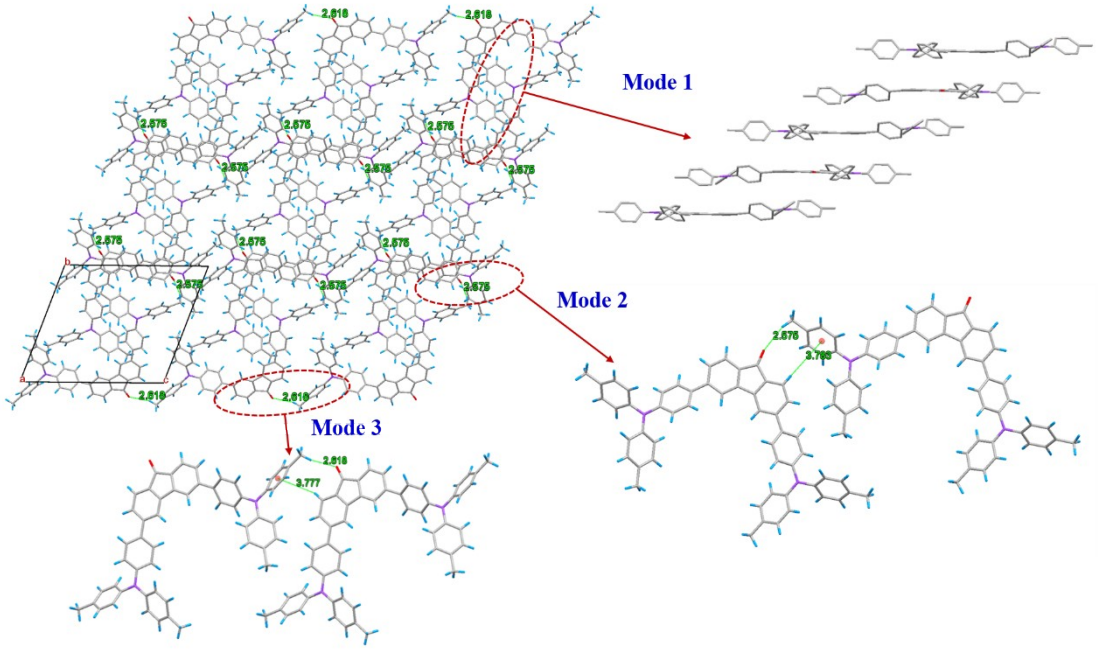


Figure S8. Three-dimensional molecular packing network found in the O-crystal of **36-TPA**, with three packing modes noted. The nitrogen atoms are marked in purple, oxygen atoms in red, carbon atoms in grey and hydrogen atoms in light blue.

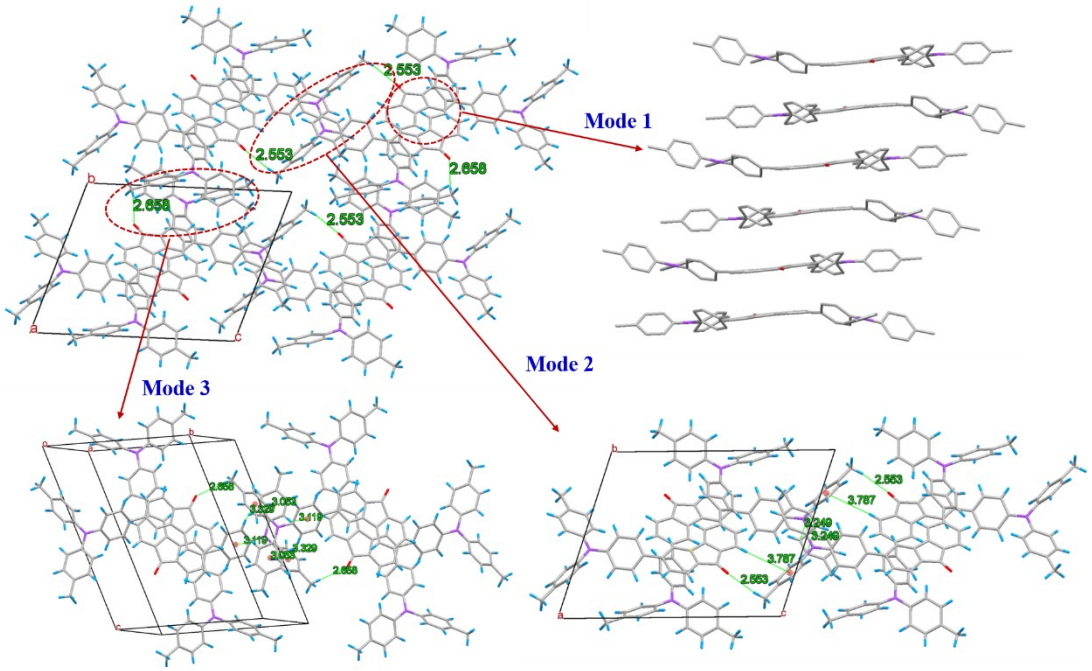


Figure S9. Three-dimensional molecular packing network found in the R-crystal of **36-TPA**, with three packing modes noted. The nitrogen atoms are marked in purple, oxygen atoms in red, carbon atoms in grey and hydrogen atoms in light blue.

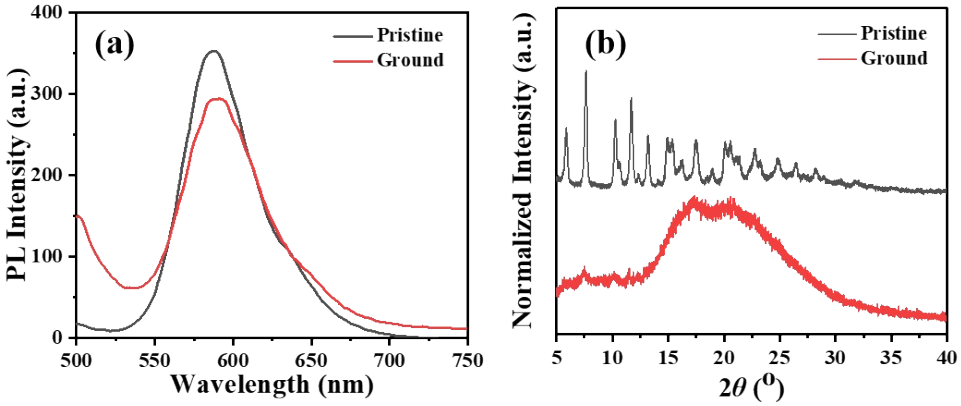


Figure S10. Emission spectra (a) and XRD patterns (b) of pristine and ground **36-DPA** powders.

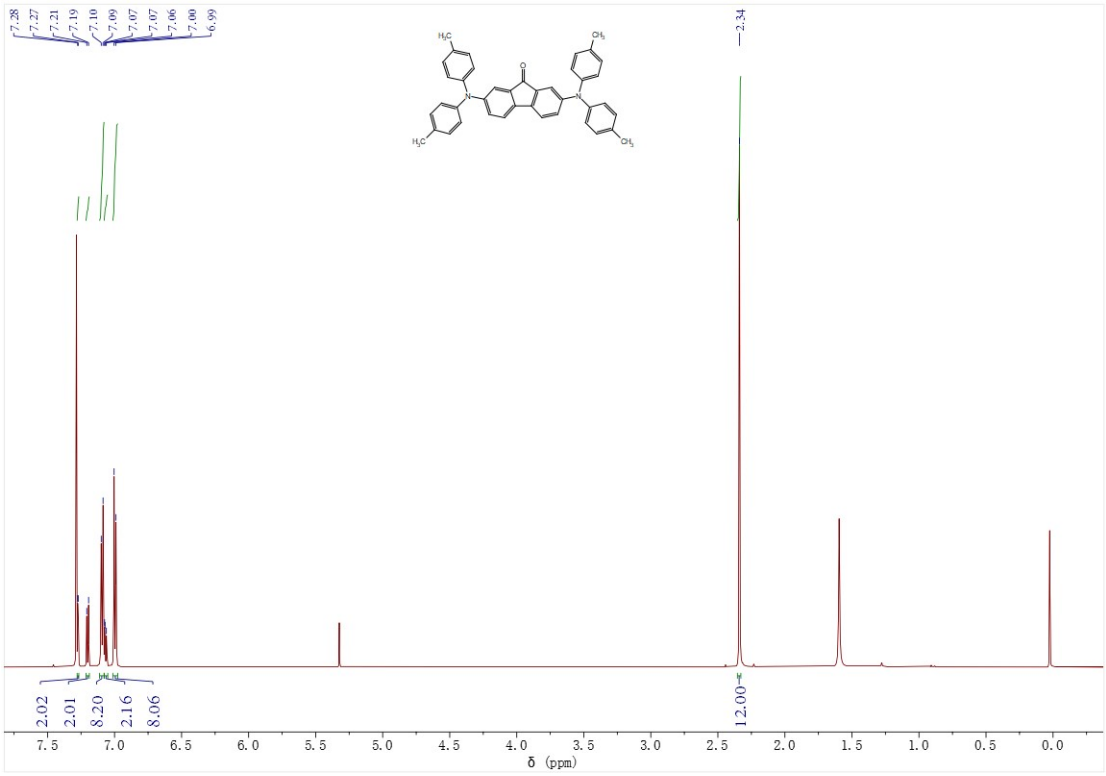


Figure S7. ^{1}H NMR spectrum of **27-DPA**.

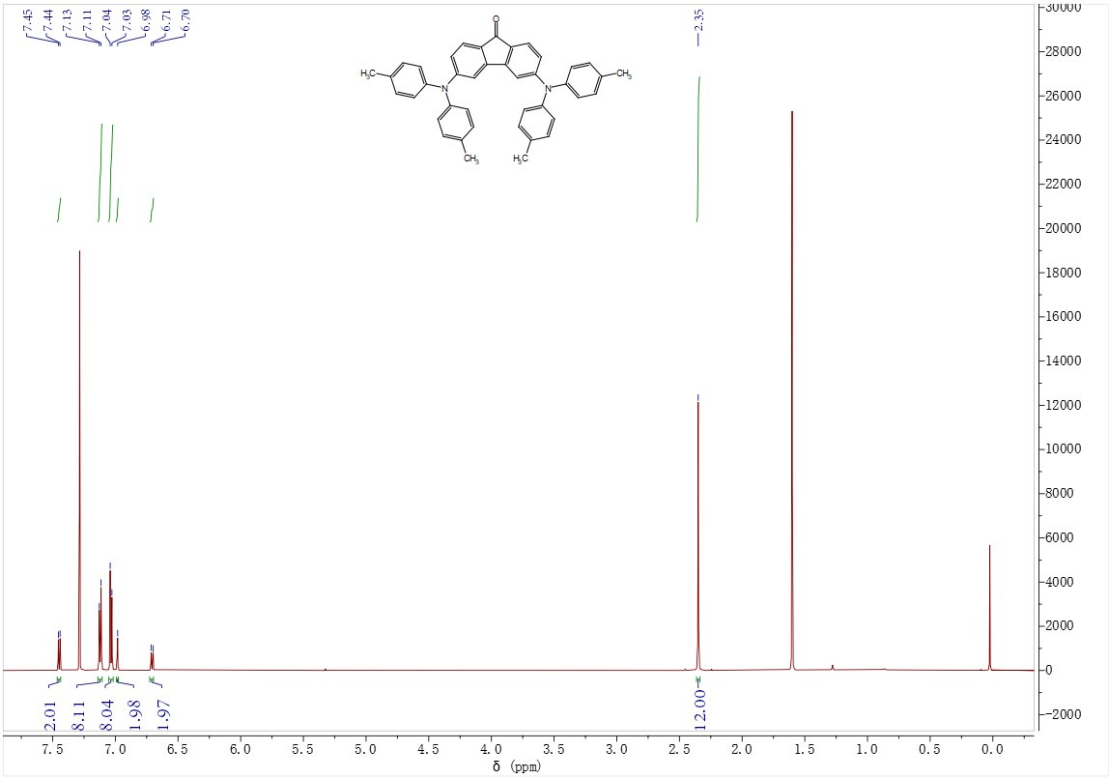


Figure S8. ^{1}H NMR spectrum of **36-DPA**.

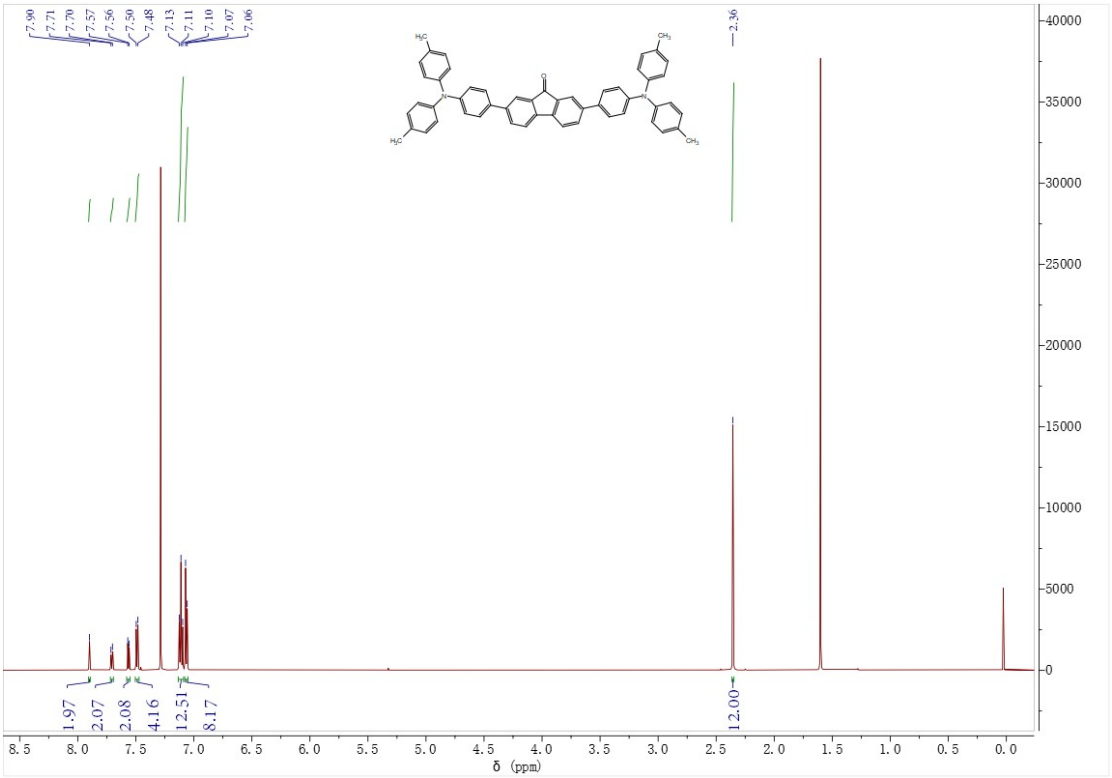


Figure S9. ^{1}H NMR spectrum of **27-TPA**.

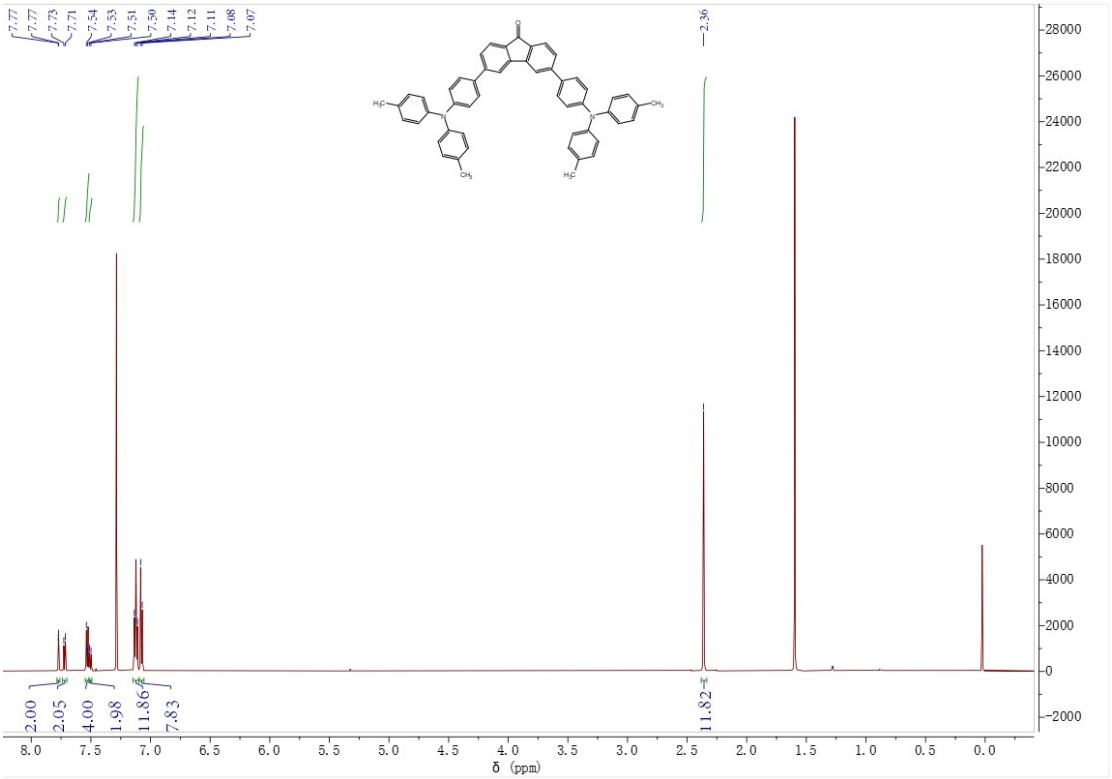


Figure S10. ^{1}H NMR spectrum of **36-TPA**.

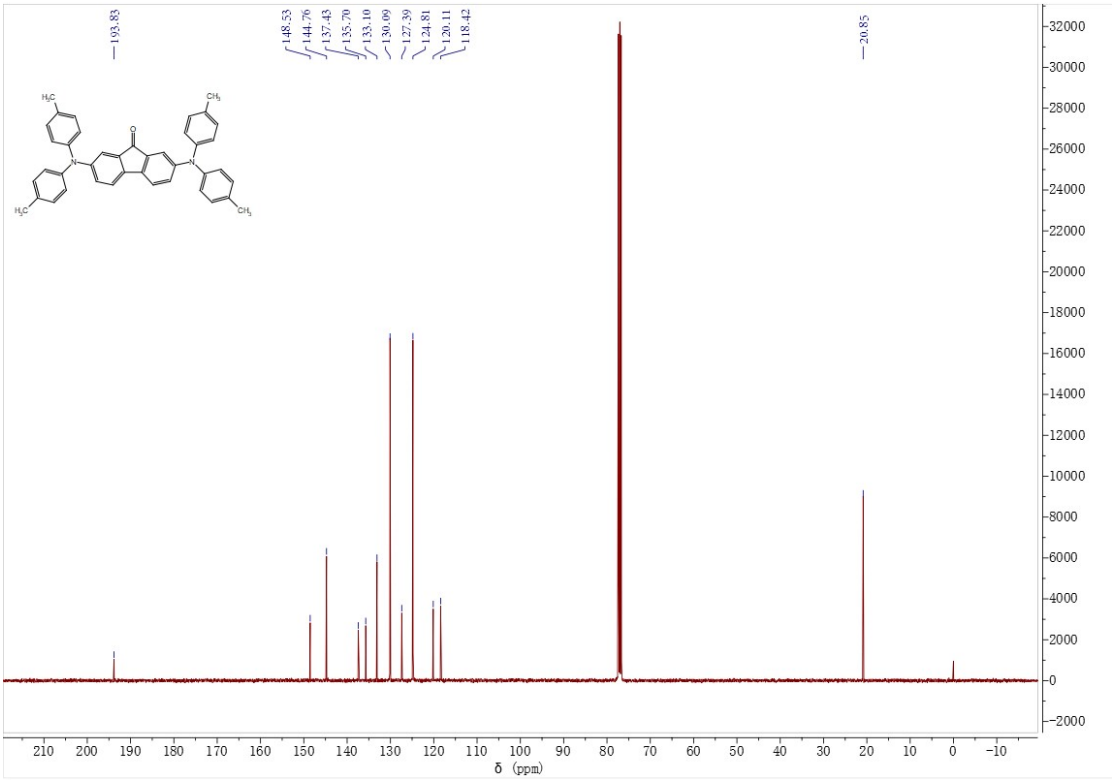


Figure S11. ^{13}C NMR spectrum of **27-DPA**.

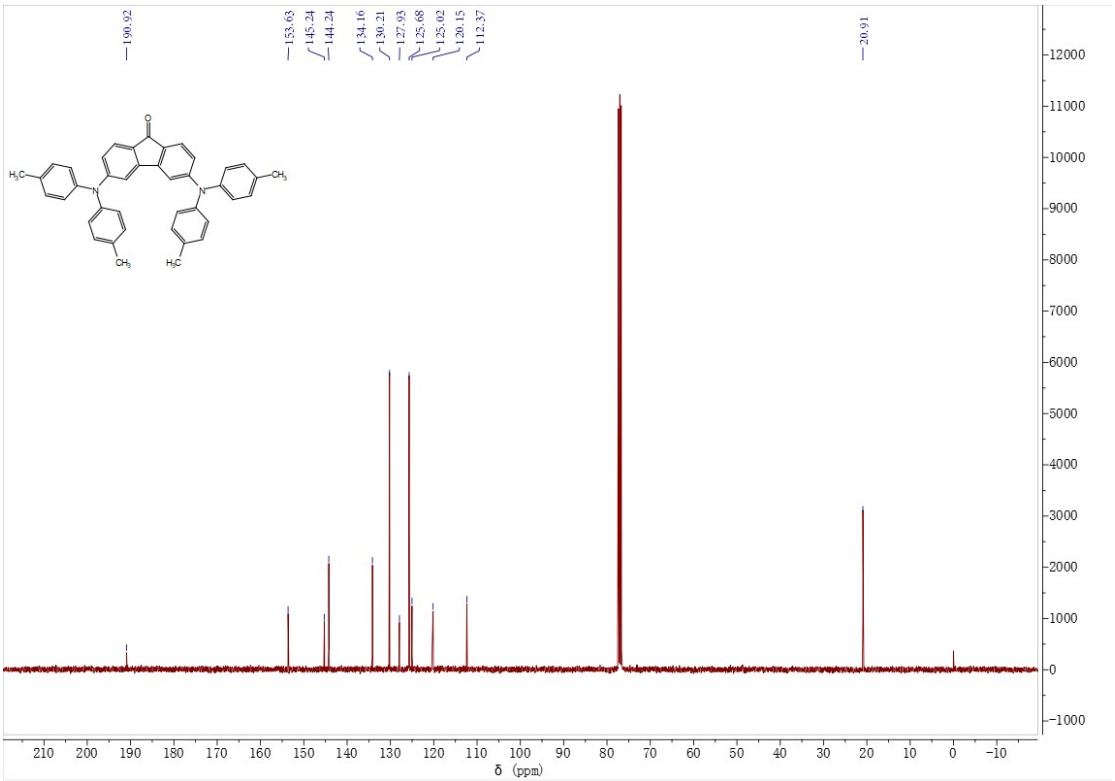


Figure S12. ^{13}C NMR spectrum of **36-DPA**.

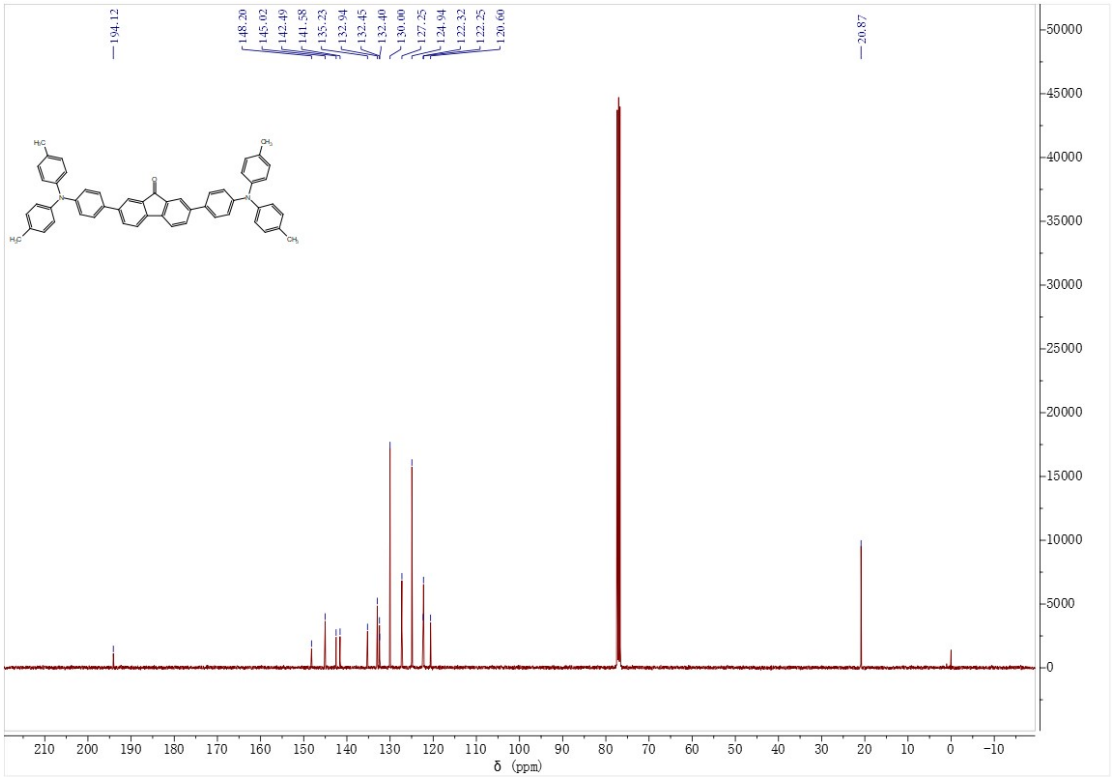


Figure S13. ^{13}C NMR spectrum of **27-TPA**.

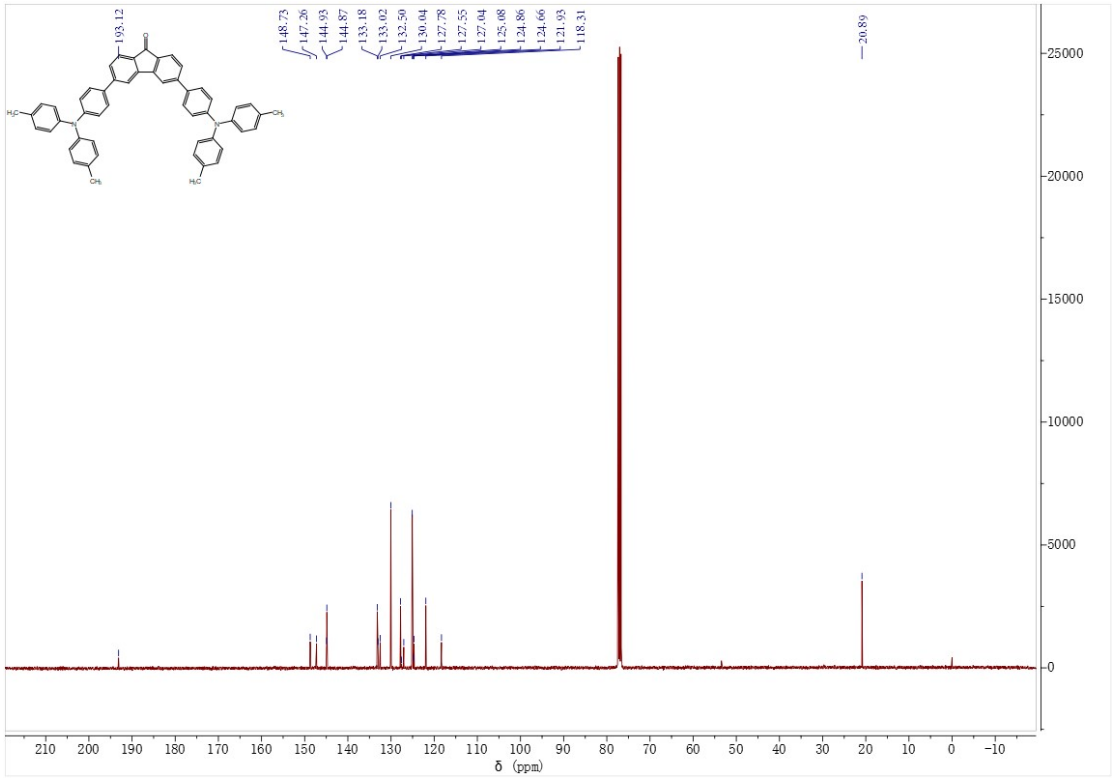


Figure S14. ^{13}C NMR spectrum of **36-TPA**.

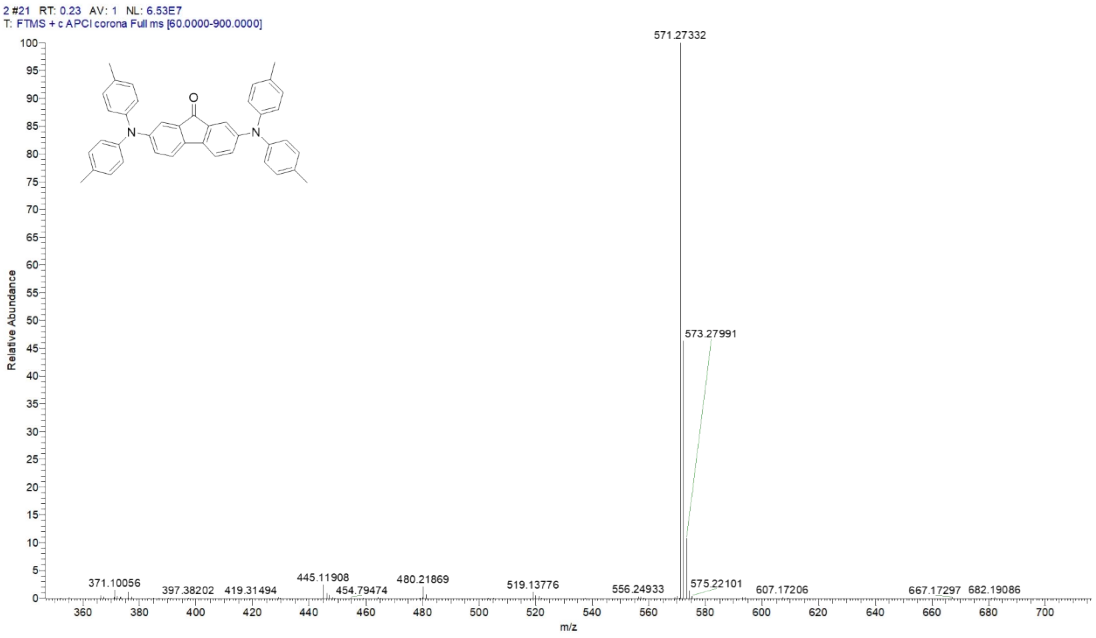


Figure S15. HR-Mass spectrum of **27-DPA**.

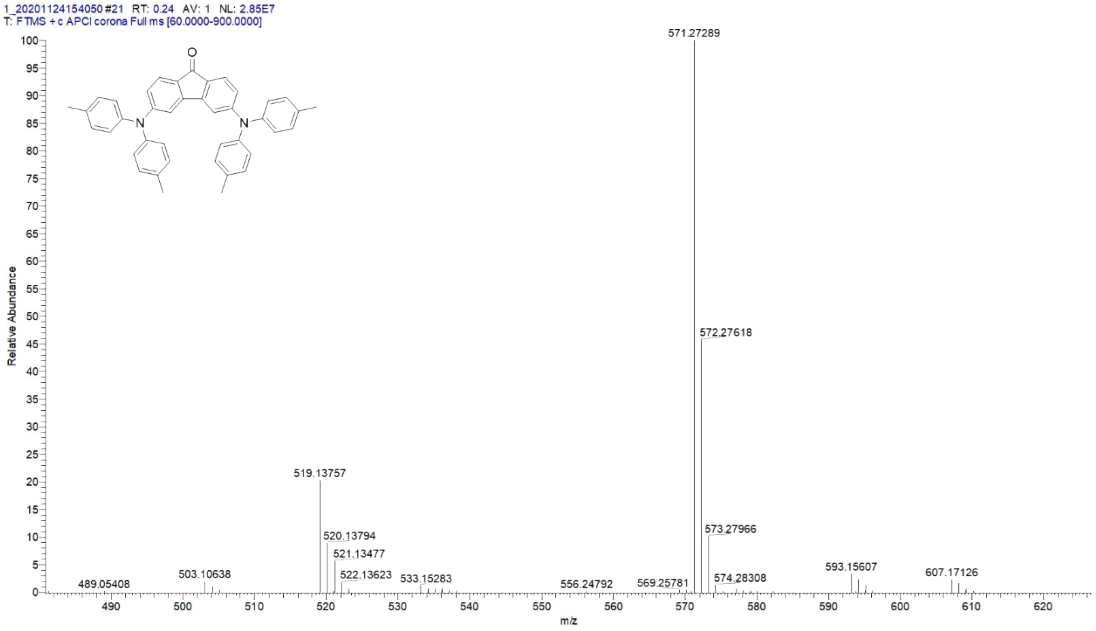


Figure S16. HR-Mass spectrum of **36-DPA**.

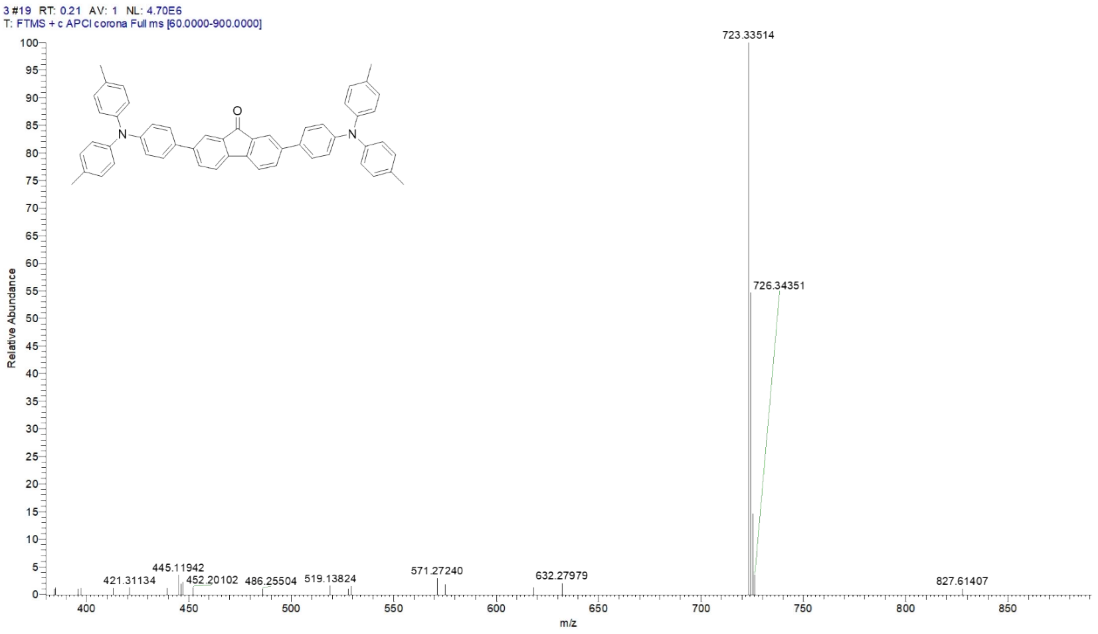


Figure S17. HR-Mass spectrum of **27-TPA**.

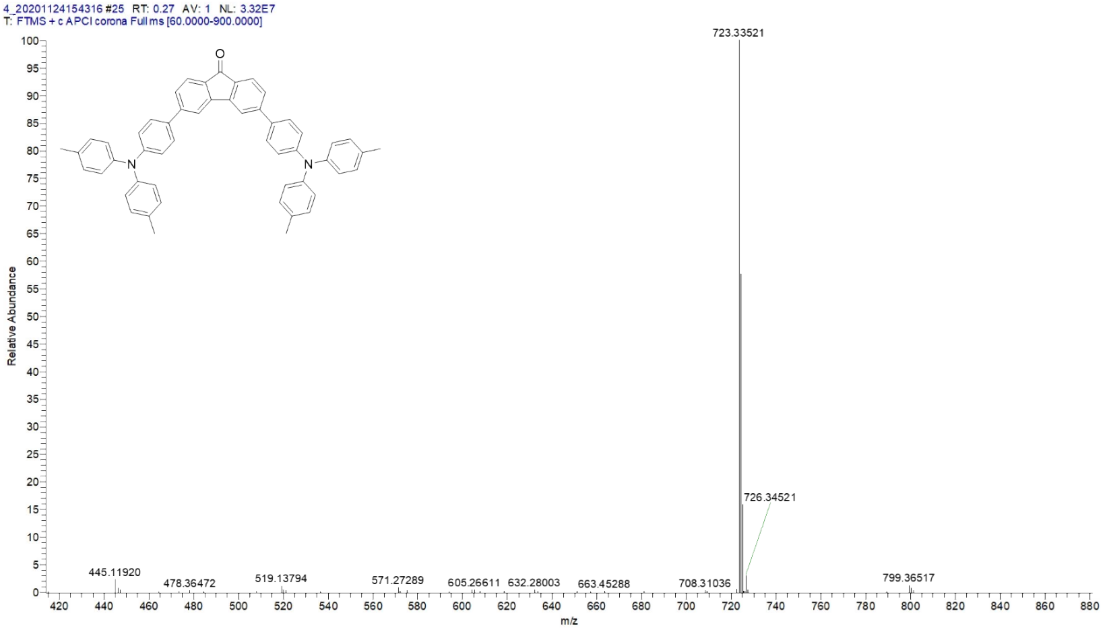


Figure S18. HR-Mass spectrum of **36-TPA**.

References

1. Z. Li, M. Siklos, N. Pucher, K. Cicha, A. Ajami, W. Husinsky, A. Rosspeintner, E. Vauthey, G. Gescheidt, J. Stampfl and R. Liska, *J. Polym. Sci.Part A: Polym. Chem.*, 2011, **49**, 3688-3699.

2. R. Anémian, D. C. Cupertino, P. R. Mackie and S. G. Yeates, *Tetra. Lett.*, 2005, **46**, 6717-6721.

3. X. Sun, Q. Xue, Z. Zhu, Q. Xiao, K. Jiang, H.-L. Yip, H. Yan and Z. a. Li, *Chem. Sci.*, 2018, **9**, 2698-2704.