Electronic Supplementary Information (ESI)

Isomeric intramolecular charge-transfer complexes: the effect of relative positions of donor and acceptor on photophysical and mechanochromic properties

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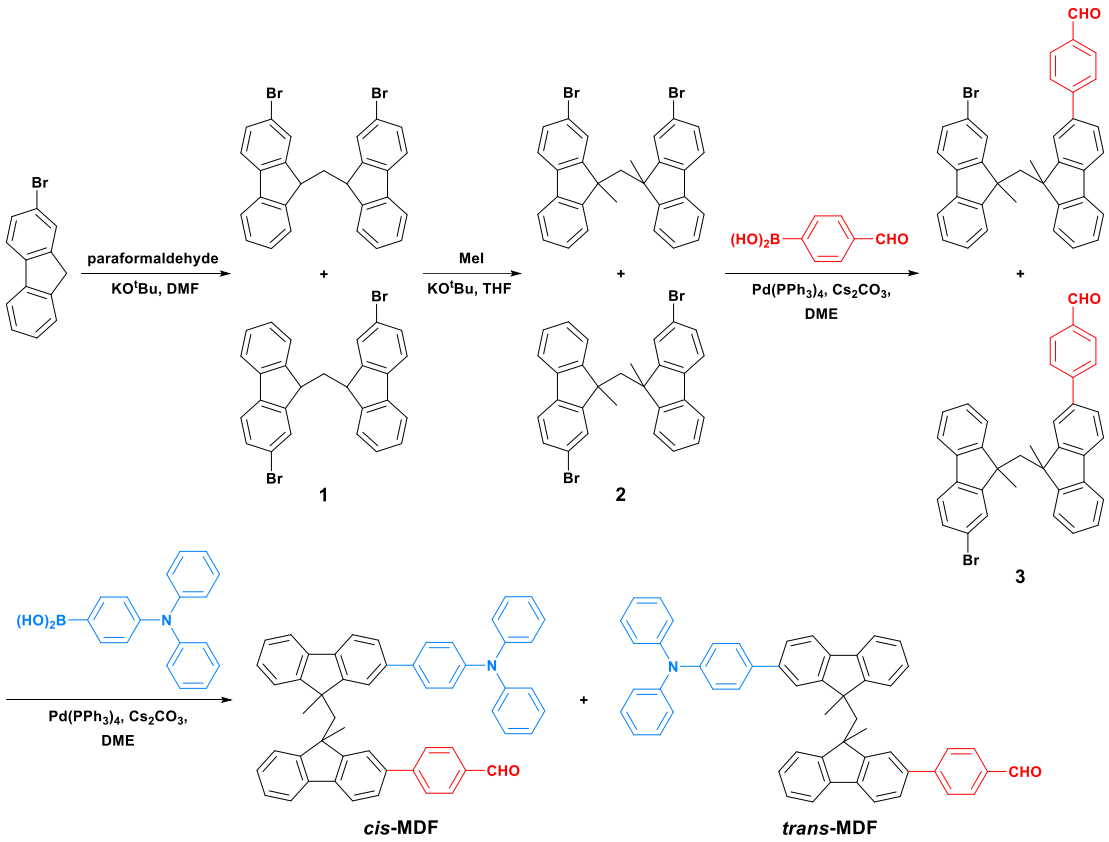
1. Experimental Section

1.1 General information

All reagents and solvents were obtained from commercial supplies and used directly without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AC 400 spectrometer using $CDCl_3$ as the solvent. IR spectra were recorded on a Shimadzu instrument (affinity-1S). High-resolution mass spectra (HRMS) were performed on a Bruker Daltonics micrOTOF-Q II instrument (ESI). Single-crystal diffraction data were collected using a Rigaku MM007-Saturn70 diffractometer. Density functional theory (DFT) calculations were implemented with the Gaussian 09 program package,[S1] at the RWB97XD/6-31G (d, p) level. UV-vis spectra were carried out on a Shimadzu UV2700 spectrophotometer (solution samples) and a Hitachi UH5700 spectrophotometer (solid samples). Cyclic voltammetry was performed on a CHI660E electrochemistry workstation in CH_2Cl_2 solution containing 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate, with Pt electrode as the working electrode and counter electrode, and saturated calomel electrode (SCE) as the reference electrode. Fluorescence emission spectra, fluorescence lifetimes (τ, non-deoxygenated solutions and solid samples) and quantum yields (Φ_F) were measured using an Edinburgh FS5 spectrophotometer. Fluorescence lifetimes (τ) of oxygen-free solution samples (bubbled with nitrogen for 15 min) were measured using a HORIBA FluoroMax-4 spectrophotometer. Powder X-ray diffraction (PXRD) data of solid states were measured with a Bruker AXS D8 Focus diffractometer using Cu-Kα1 x-ray source. Differential scanning calorimetry (DSC) was conducted on a PerkinElmer Diamond DSC with a heating rate of 10 °C·min^{-1} under nitrogen flow.

1.2 Synthesis



Scheme S1 Synthetic routes of ***cis*-MDF** and ***trans*-MDF**

Bis(2-bromo-9*H*-fluoren-9-yl)methane (**1**)

To a solution of 2-bromo-9*H*-fluorene (4.91 g, 20.0 mmol) in DMF (100 mL) at 0 °C, potassium *tert*-butoxide (0.34 g, 3.0 mmol) was added under argon atmosphere and stirred for 15 min. Then, paraformaldehyde (0.30 g, 10.0 mmol) was added and the reaction was stirred at 0 °C for 2 h. The mixture was poured into 200 mL of 5% HCl solution to quench the reaction, and a white precipitate was collected by filtration and washed with water. After drying, compound **1** was obtained as a white solid (3.08 g, 62% yield), which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77(d, J = 8.0 Hz, 2H), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.47-7.52 (m, 4H), 7.42 (t, J = 8.0 Hz, 2H), 7.31-7.36 (m, 2H), 4.29 (t, J = 8.0 Hz, 2H), 2.22-2.37 (m, 2H).

Bis(2-bromo-9-methyl-9*H*-fluoren-9-yl)methane (**2**)

To a solution of compound **1** (10.05 g, 20.0 mmol) in THF (150 mL) at 0 °C, potassium *tert*-butoxide (6.73 g, 60.0 mmol) was added and stirred for 1 h under argon atmosphere. Then, iodomethane (8.52 g, 60.0 mmol) was added and the reaction was stirred overnight. 200 mL of 5% HCl solution was poured into the reaction solution to quench the reaction. The resulting mixture was extracted with dichloromethane (3×200 mL), and the organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **2** as a white solid (8.33 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.19 (d, J = 8.0 Hz, 1H), 7.02-7.15 (m, 7H), 6.93-6.98 (m, 3H), 6.81-6.86 (m, 2H), 6.76 (s, 1H), 2.96-3.06 (m, 2H), 1.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.81, 150.88, 150.22, 149.58, 138.95, 138.85, 138.66, 138.44, 130.07, 129.46, 127.65, 127.36, 127.04, 126.89, 126.43, 126.34, 123.40, 122.99, 120.41, 120.36, 120.23, 119.99, 119.40, 119.23, 49.78, 49.74, 49.08, 48.86, 29.48, 29.43.

4-(9-((2-Bromo-9-methyl-9*H*-fluoren-9-yl)methyl)-9-methyl-9*H*-fluoren-2-yl)benzaldehyde (**3**)

To a solution of compound **2** (5.30 g, 10.0 mmol), (4-formylphenyl)boronic acid (1.50 g, 10.0 mmol) and $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol) in 1,2-dimethoxyethane (150 mL), Cs_2CO_3 (3.26 g, 10.0 mmol) dissolved in 10 mL H_2O was added. After being heated at reflux for 12 h under argon atmosphere, the mixture was cooled to room temperature. Then, the solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel to afford compound **3** as a white solid (2.23 g, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$, major isomer, δ): 10.08 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 1H), 6.74-7.20 (m, 13H), 3.09 (s, 2H), 1.38 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, two isomers, δ): 192.20, 192.12, 152.20, 151.10, 150.95, 150.60, 150.40, 149.80, 149.64, 147.59, 147.54, 140.68, 140.58, 139.03, 138.88, 138.82, 138.64,

137.39, 137.00, 134.95, 134.86, 130.32, 130.15, 129.68, 129.45, 127.87, 127.65, 127.39, 126.98, 126.85, 126.76, 126.53, 126.48, 126.42, 126.35, 126.29, 125.74, 123.46, 123.44, 123.20, 123.12, 122.92, 122.54, 120.32, 120.27, 120.12, 120.08, 119.70, 119.65, 119.57, 119.54, 119.26, 119.24, 49.90, 49.82, 49.74, 49.67, 49.21, 49.03, 29.72, 29.67, 29.63. (Ratio of the two isomers ≈ 3/1, as determined by the integration of protons at 7.94/7.99 and 7.62/7.76 ppm)

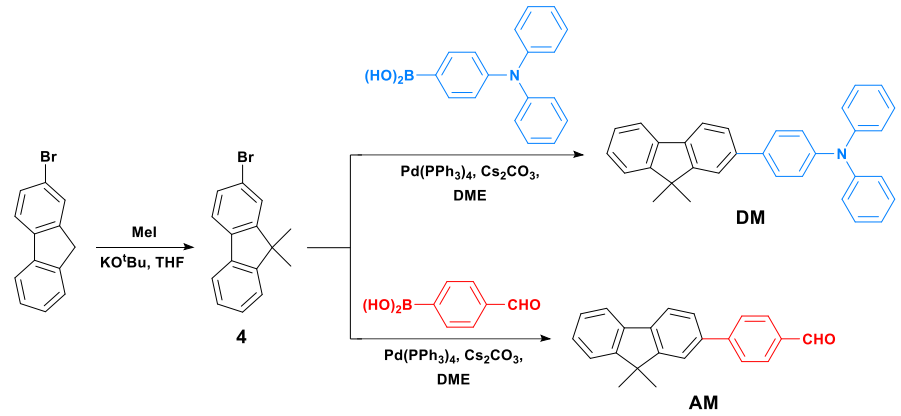
4-(9-((2-(4-(Diphenylamino)phenyl)-9-methyl-9*H*-fluoren-9-yl)methyl)-9-methyl-9*H*-fluoren-2-yl)benzaldehyde (***cis*-MDF** and ***trans*-MDF**)

To a solution of compound **3** (2.50 g, 4.5 mmol), (4-(diphenylamino)phenyl)boronic acid (1.50 g, 5.0 mmol) and $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol) in 1,2-dimethoxyethane (120 mL), Cs_2CO_3 (2.93 g, 9.0 mmol) dissolved in 4.5 mL H_2O was added. After being heated at reflux for 12 h under argon atmosphere, the mixture was cooled to room temperature. Then, the solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel to afford two light yellow solids.

***cis*-MDF** (0.30 g, 9% yield). IR (KBr, cm^{-1}) $\tilde{\nu}$: 3057, 3026, 2959, 2913, 2814, 2727, 1692, 1593, 1485, 1450, 1321, 1287, 1209, 1163, 818, 762, 733, 696. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.95 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.2 Hz, 4H), 6.96-7.22 (m, 22H), 6.73-6.78 (m, 2H), 3.17 (s, 2H), 1.37 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 191.89, 151.29, 151.18, 150.57, 149.76, 147.78, 147.56, 146.79, 140.76, 139.50, 139.12, 138.99, 138.41, 137.10, 135.21, 134.74, 130.09, 129.46, 127.68, 127.59, 126.56, 126.34, 126.06, 125.92, 125.85, 125.32, 124.57, 123.62, 123.53, 123.25, 123.12, 122.68, 121.08, 119.65, 119.52, 119.38, 119.12, 49.80, 49.64, 49.53, 29.87. HRMS (ESI) m/z: calcd for $C_{54}H_{41}NO$ $[M]^+$ 719.3183, found 719.3182.

***trans*-MDF** (0.85 g, 26% yield). IR (KBr, cm^{-1}) $\tilde{\nu}$: 3030, 2955, 2914, 2855, 2826, 2733, 1692, 1593, 1485, 1454, 1325, 1283, 1211, 1167, 820, 766, 745, 696. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.09 (s,

1H), 7.96 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.29-7.33 (m, 5H), 6.96-7.22 (m, 17H), 6.84-6.91 (m, 2H), 6.80 (t, J = 8.0 Hz, 1H), 6.73 (t, J = 8.0 Hz, 1H), 3.15 (s, 2H), 1.36 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 192.15, 150.91, 150.69, 150.62, 150.31, 147.92, 147.81, 146.82, 140.67, 139.53, 138.96, 138.86, 138.44, 137.09, 135.84, 134.86, 130.20, 129.42, 127.94, 127.68, 126.68, 126.54, 125.91, 125.77, 125.00, 124.39, 124.09, 123.36, 123.26, 123.00, 122.94, 122.31, 119.66, 119.48, 119.20, 49.91, 49.77, 49.24, 29.88, 29.80. HRMS (ESI) *m*/*z*: calcd for $C_{54}H_{41}NO$ $[M]^+$ 719.3183, found 719.3187.



Scheme S2 Synthetic routes of **DM** and **AM**

2-Bromo-9,9-dimethyl-9*H*-fluorene (**4**)

2-Bromo-9,9-dimethyl-9*H*-fluorene (**4**) was prepared using a literature procedure.[S2] White solids, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.69-7.71 (m, 1H), 7.58-7.60 (m, 2H), 7.42-7.48 (m, 2H), 7.34-7.36 (m, 2H), 1.49 (s, 6H).[S2]

4-(9,9-Dimethyl-9*H*-fluoren-2-yl)-*N*,*N*-diphenylaniline (**DM**)

To a solution of compound **4** (4.24 g, 15.5 mmol), (4-(diphenylamino)phenyl)boronic acid (5.38 g, 18.6 mmol) and $Pd(PPh_3)_4$ (0.90 g, 0.78 mmol) in 1,2-dimethoxyethane (260 mL), Cs_2CO_3 (10.11 g, 31.0 mmol) dissolved in 16 mL H_2O was added. After being heated at reflux for 12 h under argon atmosphere, the mixture was cooled to room temperature. Then, the solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel to afford **DM** (4.4825

g, 66% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.76 (d, J = 6.0 Hz, 1H), 7.74 (d, J = 6.0 Hz, 1H), 7.63 (s, 1H), 7.54-7.56 (m, 3H), 7.45 (d, J = 12.0 Hz, 1H), 7.31-7.36 (m, 5H), 7.14-7.18 (m, 7H), 7.04 (t, J = 6.0 Hz, 2H), 1.54 (s, 6H).[S3]

4-(9,9-Dimethyl-9*H*-fluoren-2-yl)benzaldehyde (**AM**)

To a solution of compound **4** (2.00 g, 7.3 mmol), (4-formylphenyl)boronic acid (1.35 g, 9.0 mmol) and $Pd(PPh_3)_4$ (0.43 g, 0.37 mmol) in 1,2-dimethoxyethane (260 mL), Cs_2CO_3 (4.89 g, 15.0 mmol) dissolved in 7.6 mL H_2O was added. After being heated at reflux for 12 h under argon atmosphere, the mixture was cooled to room temperature. Then, the solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel to afford **AM** (1.9761 g, 90% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 10.08 (s, 1H), 7.98 (d, J = 12.0 Hz, 2H), 7.82-7.84 (m, 3H), 7.77 (d, J = 6.0 Hz, 1H), 7.70 (s, 1H), 7.63 (d, J = 6.0 Hz, 1H), 7.47 (d, J = 6.0 Hz, 1H), 7.35-7.39 (m, 2H), 1.56 (s, 6H).[S4]

2. Figures and Tables

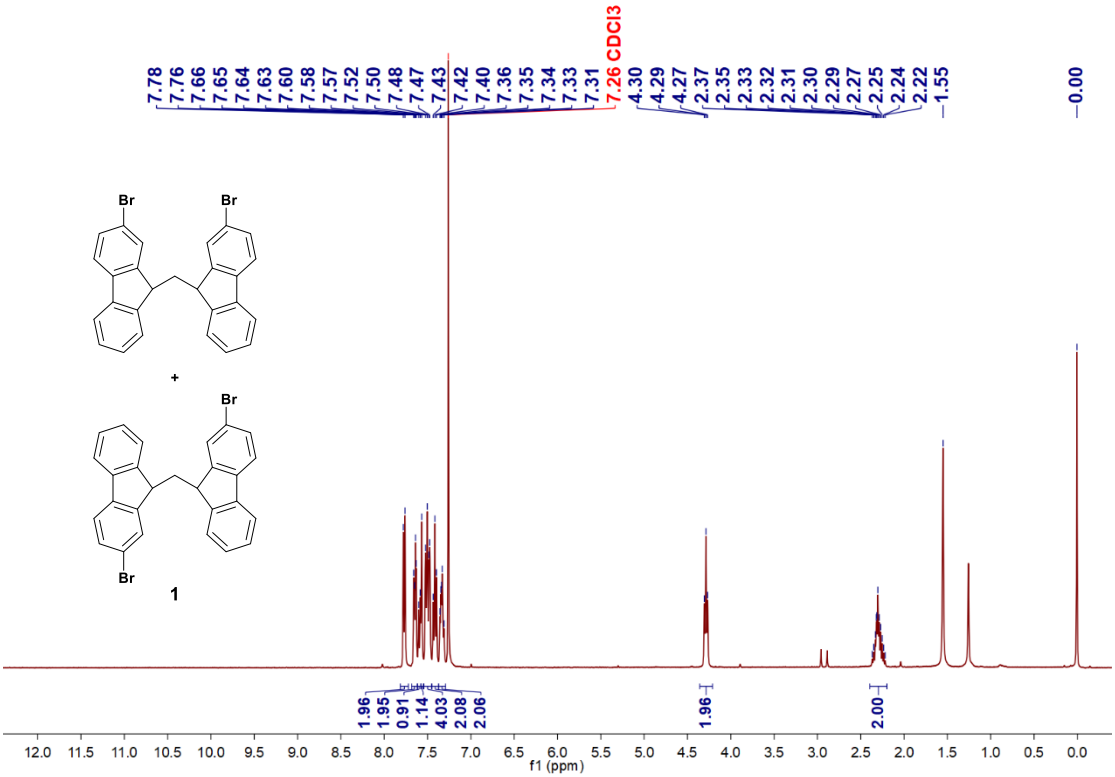


Fig. S1 ^{1}H NMR of **1** in $CDCl_3$

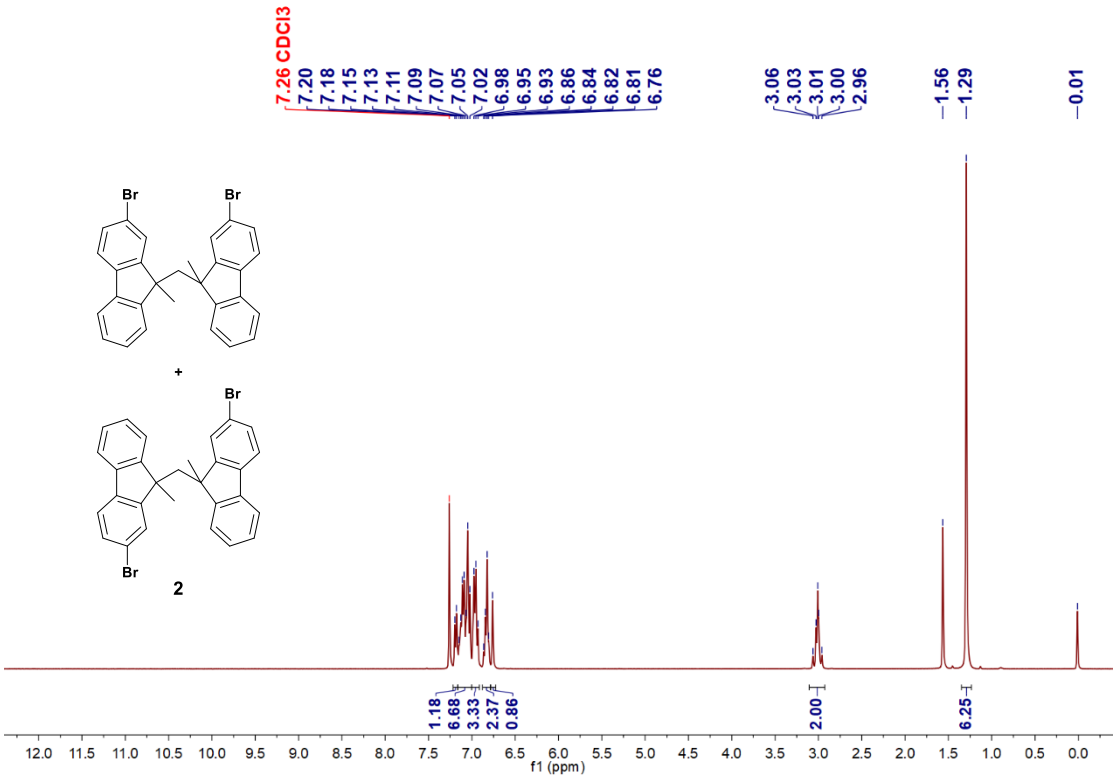


Fig. S2 ^{1}H NMR of **2** in $CDCl_3$

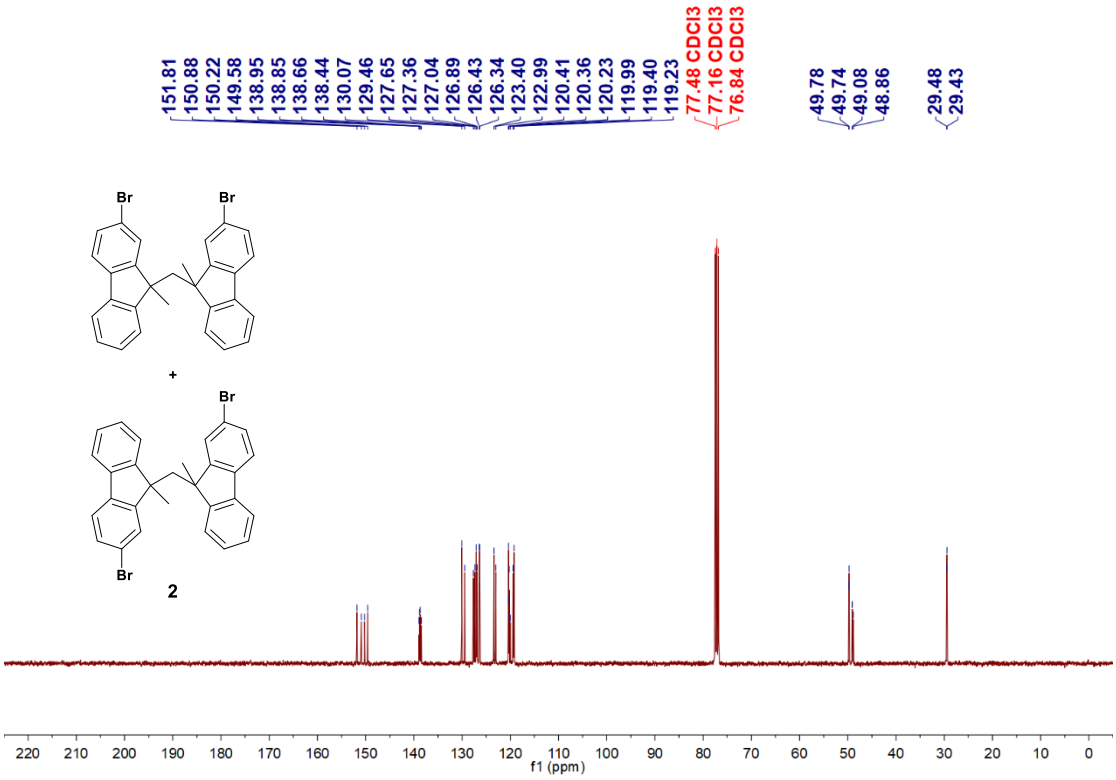


Fig. S3 ^{13}C NMR of **2** in $CDCl_3$

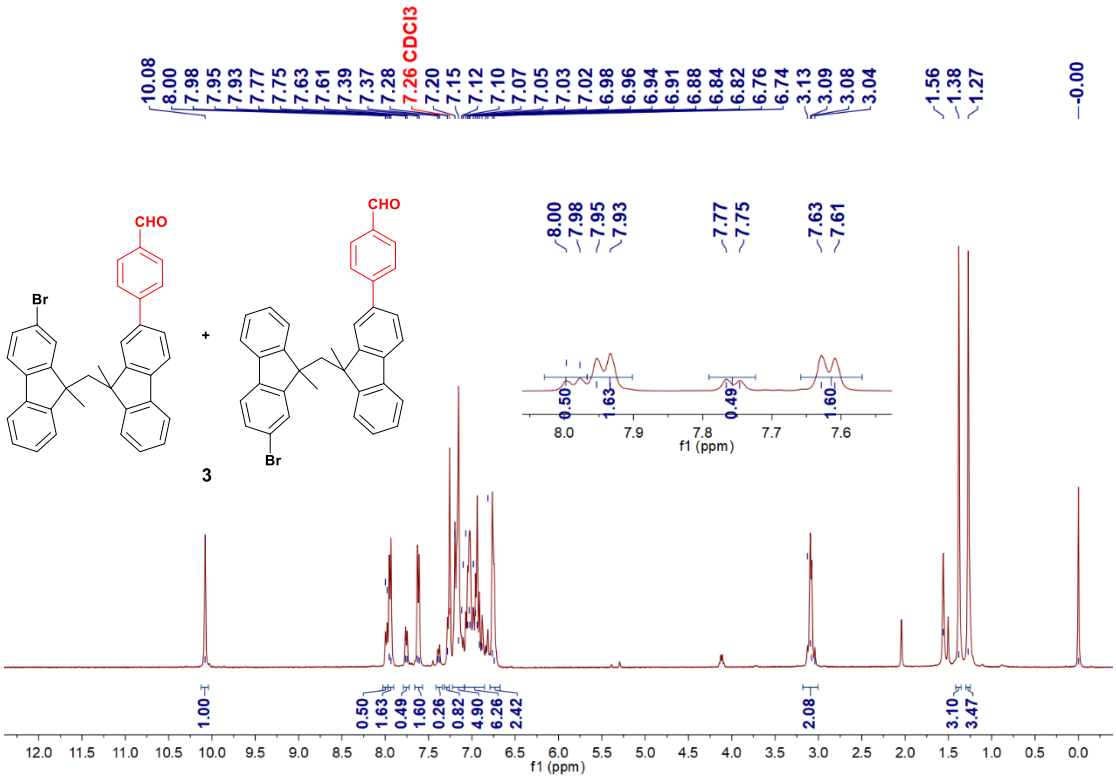


Fig. S4 ^{1}H NMR of **3** in $CDCl_3$

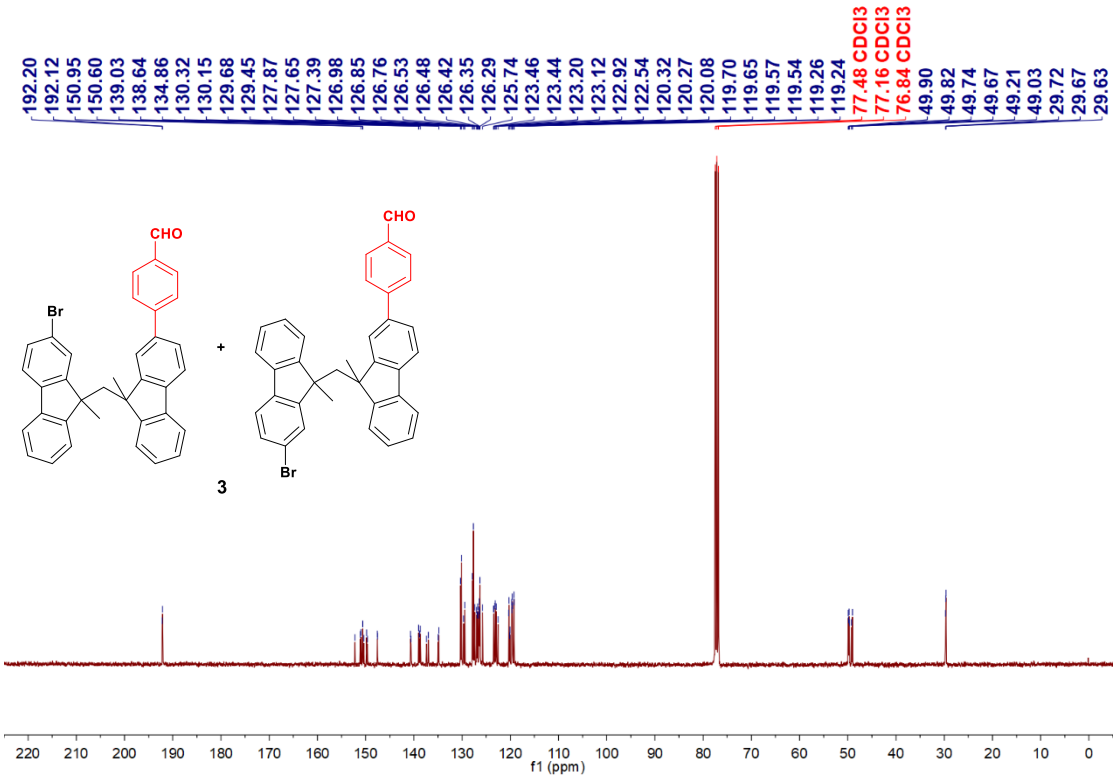


Fig. S5 ^{13}C NMR of **3** in $CDCl_3$

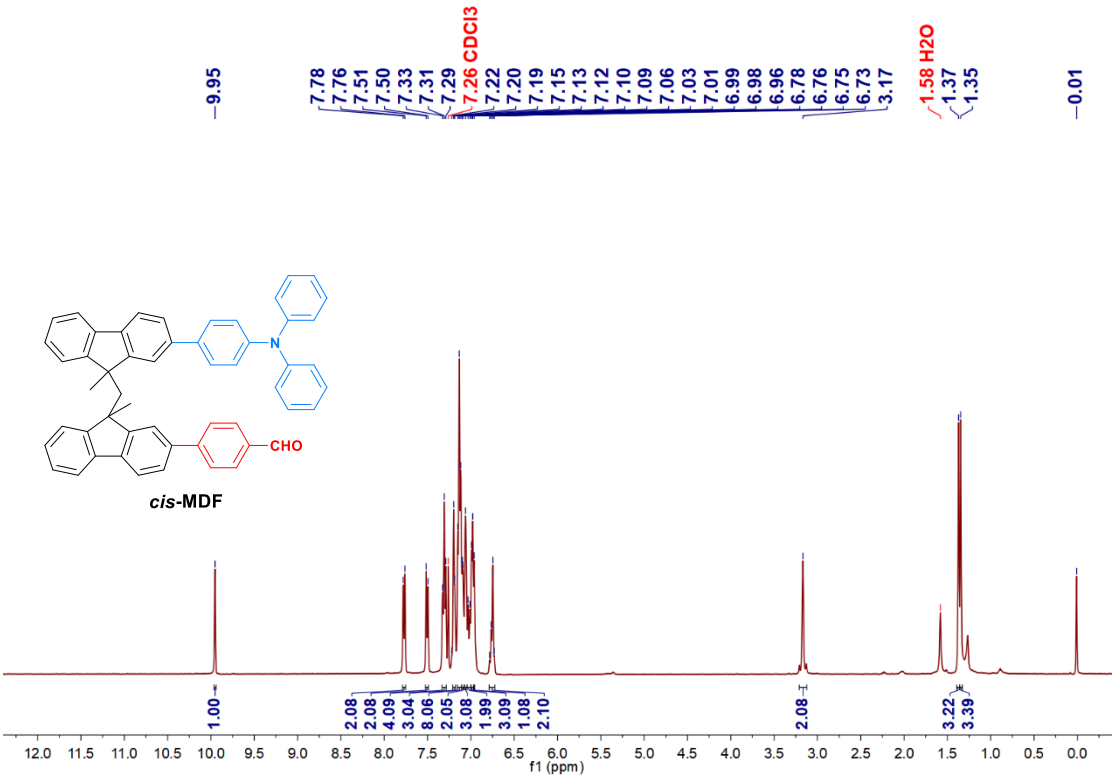


Fig. S6 ^{1}H NMR of ***cis*-MDF** in $CDCl_3$

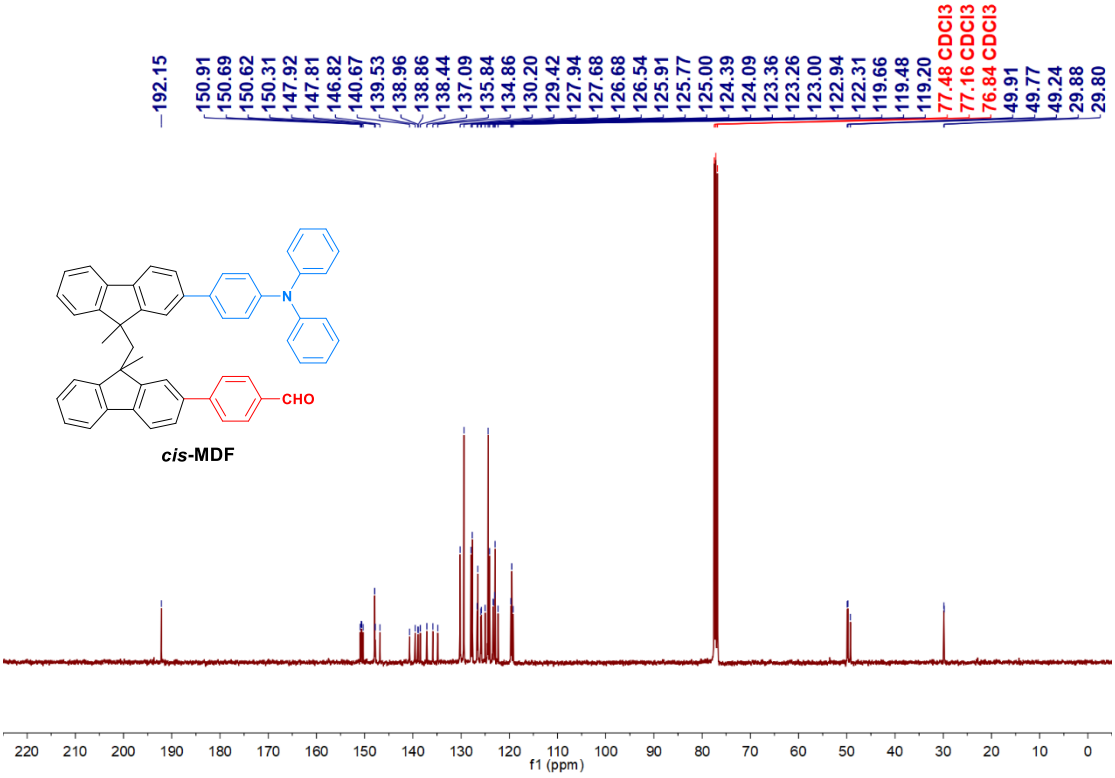


Fig. S7 ^{13}C NMR of ***cis*-MDF** in $CDCl_3$

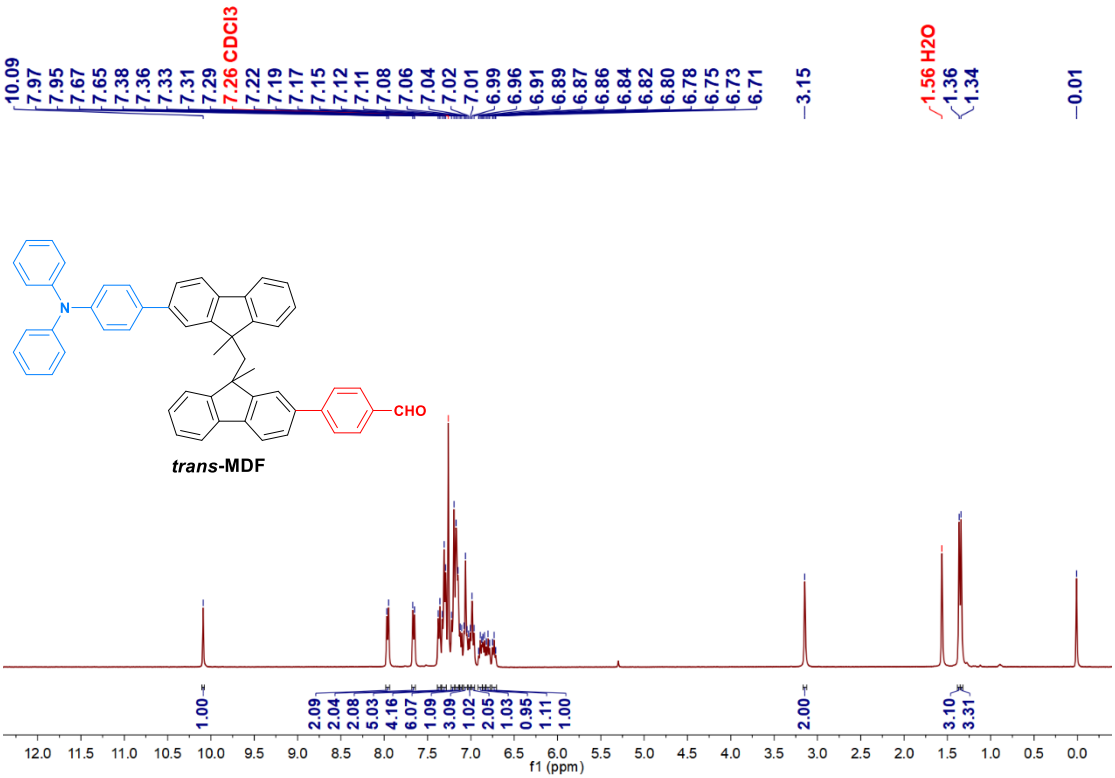


Fig. S8 ^{1}H NMR of ***trans*-MDF** in $CDCl_3$

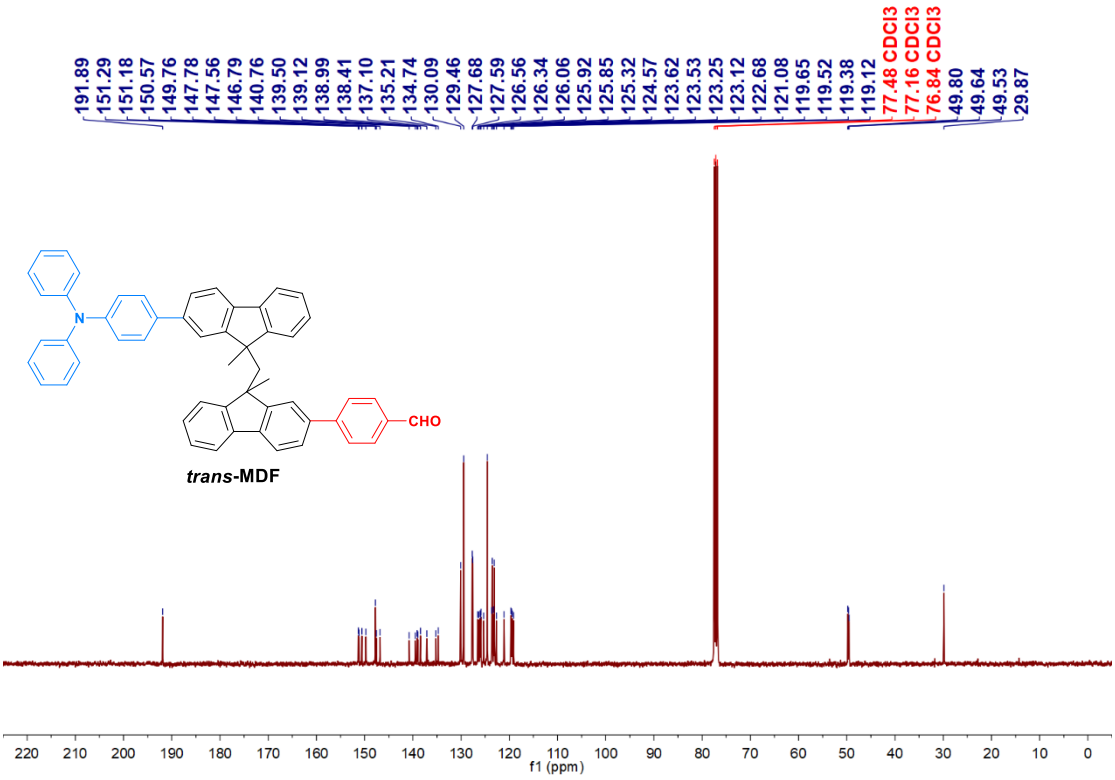


Fig. S9 ^{13}C NMR of ***trans*-MDF** in $CDCl_3$

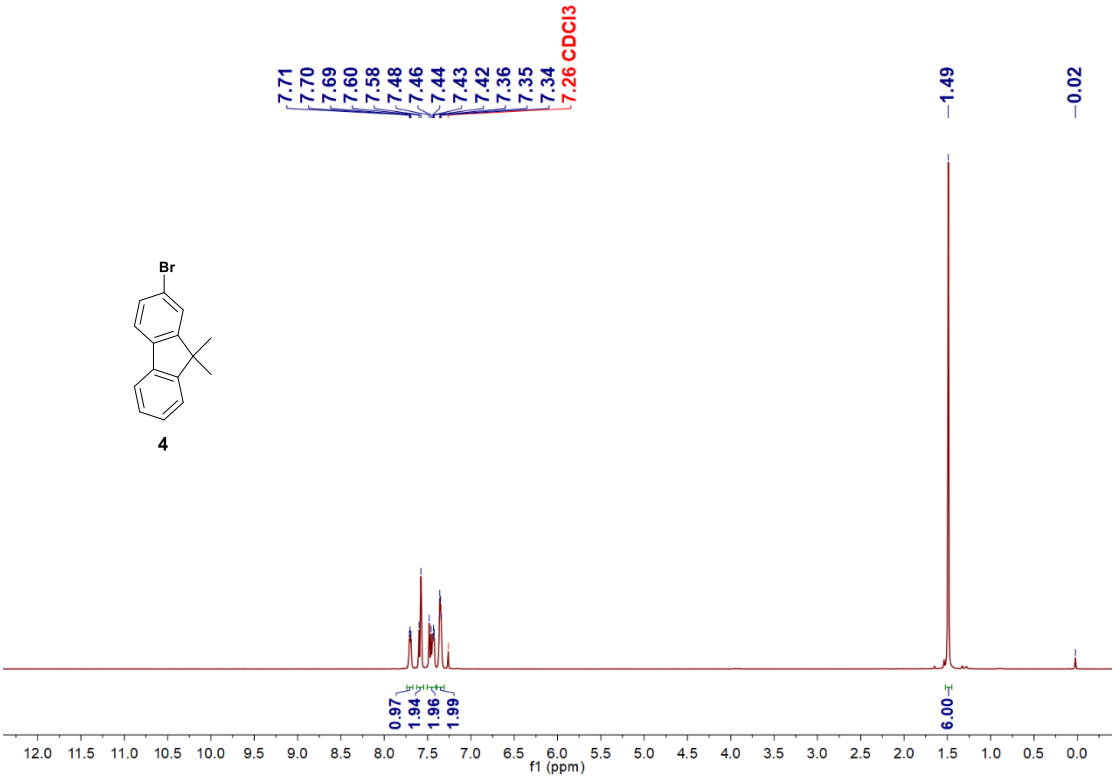


Fig. S10 ^{1}H NMR of **4** in $CDCl_3$

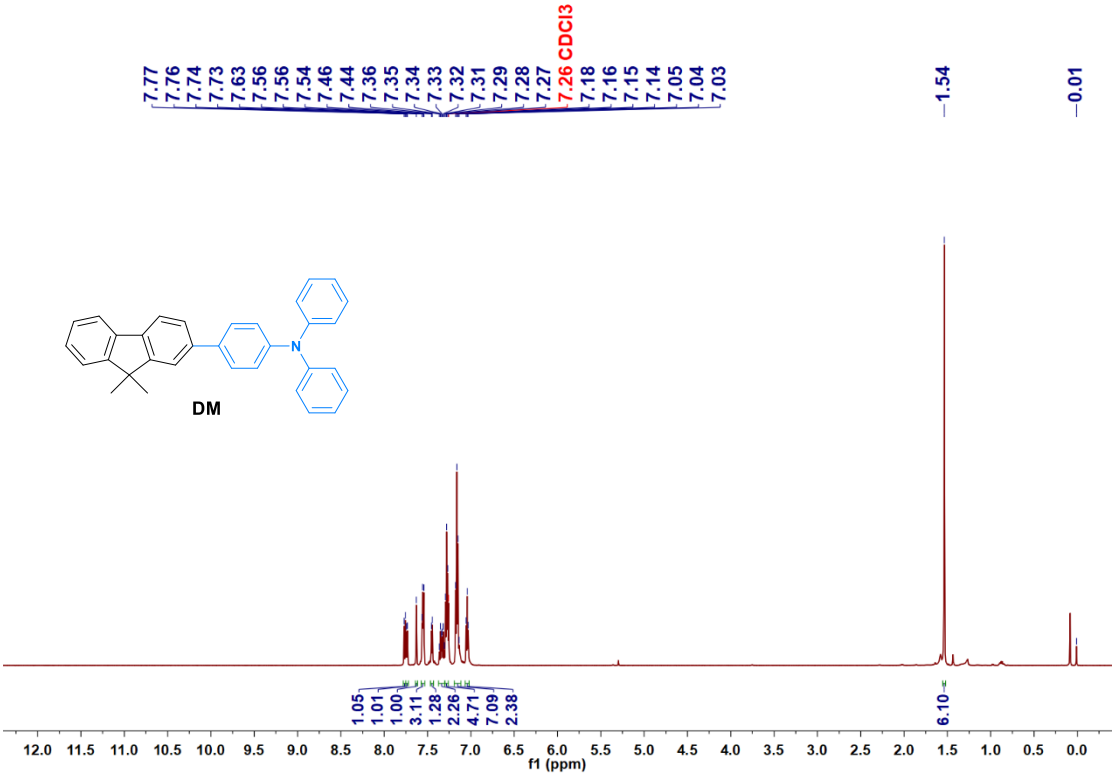


Fig. S11 ^{1}H NMR of **DM** in $CDCl_3$

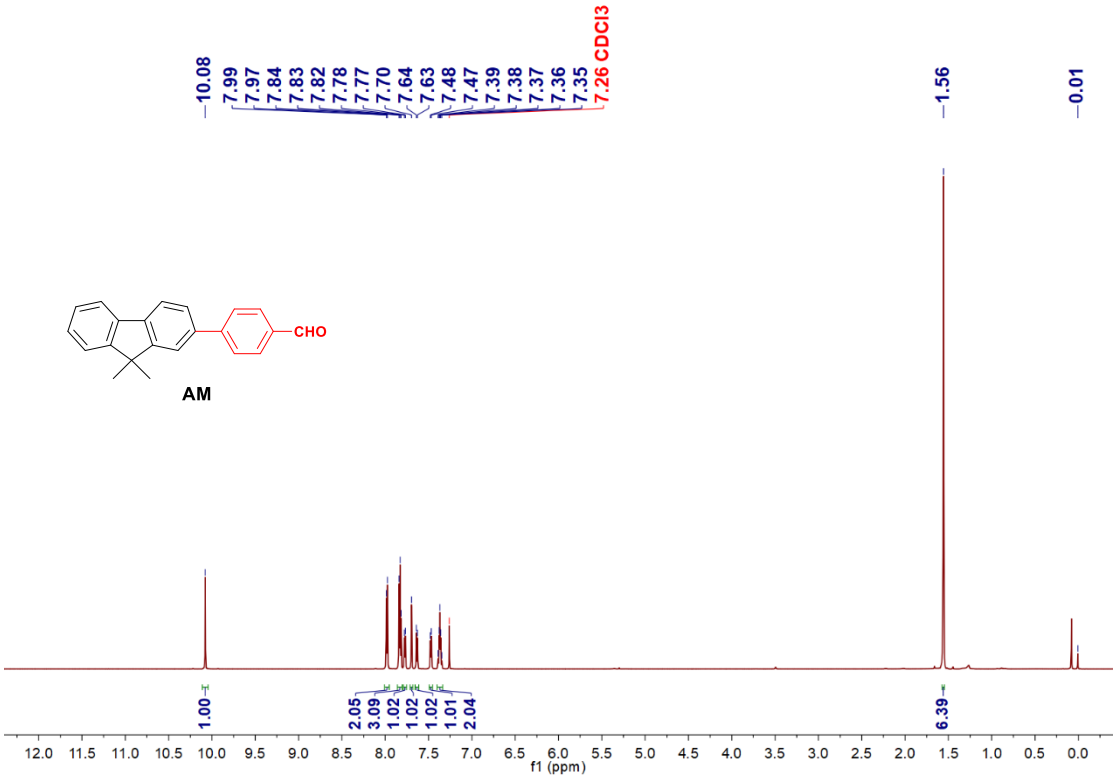


Fig. S12 ^{1}H NMR of **AM** in $CDCl_3$

Mass Spectrum List Report

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Comment			

Acquisition Parameter

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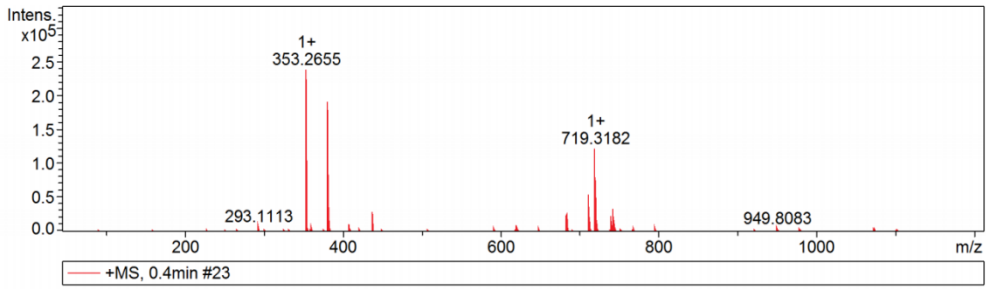

#	m/z	Res.	S/N	I	FWHM
1	293.1113	10359	179.4	8152	0.0283
2	353.2655	11382	5176.2	239565	0.0310
3	354.2697	12197	1014.9	47017	0.0290
4	355.2727	10610	115.5	5355	0.0335
5	360.3240	10639	148.6	6883	0.0339
6	381.2969	11651	4141.4	190565	0.0327
7	382.3009	11633	822.8	37855	0.0329
8	383.3044	10312	99.4	4576	0.0372
9	408.3086	12265	236.7	10826	0.0333
10	437.1934	11618	639.7	29227	0.0376
11	438.1979	11078	143.3	6542	0.0396
12	591.4986	10615	96.7	4571	0.0557
13	619.0364	12049	110.9	5288	0.0514
14	619.5294	11700	209.1	9965	0.0529
15	621.0336	10831	109.0	5192	0.0573
16	647.5594	12673	110.2	5282	0.0511
17	683.5438	12298	504.5	24439	0.0556
18	684.5490	13067	213.5	10344	0.0524
19	711.5746	13457	1139.9	55327	0.0529
20	712.5779	13846	435.6	21149	0.0515
21	719.3182	12523	2525.1	122618	0.0574
22	720.3213	13626	1568.2	76158	0.0529
23	721.3273	11821	328.8	15956	0.0610
24	739.6050	11645	432.2	20750	0.0635
25	740.6119	11813	169.0	8111	0.0627
26	742.3083	14417	712.6	34172	0.0515
27	743.3144	11598	356.3	17071	0.0641
28	767.4736	12087	124.2	5818	0.0635
29	795.5031	11313	117.4	5393	0.0703
30	949.8083	13206	108.5	4562	0.0719

Fig. S13 HRMS of ***cis*-MDF**

Mass Spectrum List Report

Analysis Info

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Comment			

Acquisition Parameter

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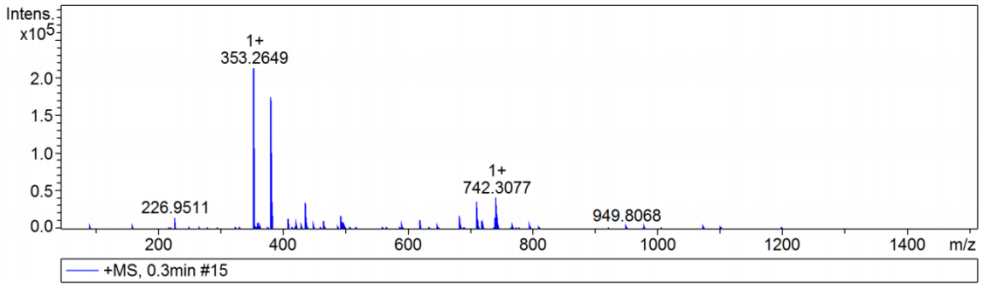

#	m/z	Res.	S/N	I	FWHM
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3	354.2692	11824	1056.2	42177	0.0300
4	360.3230	11875	227.0	9103	0.0303
5	381.2962	11710	4278.6	174165	0.0326
6	382.3007	11859	885.8	36071	0.0322
7	408.3081	11864	333.9	13849	0.0344
8	421.2529	12287	160.2	6690	0.0343
9	437.1925	12353	840.7	35715	0.0354
10	438.1972	12505	215.1	9146	0.0350
11	466.1904	12557	261.6	11395	0.0371
12	493.1475	12045	410.1	18175	0.0409
13	493.6492	12173	296.2	13131	0.0406
14	494.1488	12683	352.3	15623	0.0390
15	494.6497	12769	211.7	9397	0.0387
16	495.1490	11462	137.9	6125	0.0432
17	497.1448	13377	199.6	8871	0.0372
18	497.6450	11762	141.3	6282	0.0423
19	498.1450	12769	143.5	6373	0.0390
20	619.5283	11649	240.9	11358	0.0532
21	683.5431	12168	391.2	18608	0.0562
22	684.5497	10379	131.7	6267	0.0660
23	711.5734	12655	765.5	36569	0.0562
24	712.5787	12395	296.9	14186	0.0575
25	719.3187	13163	237.6	11365	0.0546
26	720.3240	12294	161.8	7742	0.0586
27	739.6058	12073	330.7	15826	0.0613
28	740.6099	12127	140.1	6702	0.0611
29	742.3077	13695	870.6	41615	0.0542
30	743.3115	13444	446.7	21344	0.0553

Fig. S14 HRMS of ***trans*-MDF**

Table S1 Crystal data and structure refinements for ***cis*-MDF**

Empirical formula	$C_{54}H_{41}NO$
Formula weight	719.88
Temperature	113.15 K
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 16.6138(4) Å α = 90 deg. B = 20.4490(3) Å β = 105.048(2) deg. C = 11.6823(3) Å γ = 90 deg.
Volume	3832.79(15) $Å^3$
Z	4
Calculated density	1.248 g/cm^3
μ	0.073 mm^{-1}
F(000)	1520.0
Crystal size	0.26 x 0.22 x 0.20 mm^3
Radiation	MoKα (λ = 0.71073)
2θ range for data collection	3.226 to 56.564 deg.
Index ranges	$-22 \leq h \leq 22$, $-27 \leq k \leq 27$, $-12 \leq l \leq 15$
Reflections collected	37187
Independent reflections	9479 [R_{int} = 0.0507, R_{sigma} = 0.0443]
Data / restraints / parameters	9479 / 0 / 507
Goodness-of-fit on F^2	1.046
Final R indices [l > = 2σ (l)]	R_1 = 0.0506, wR_2 = 0.1097
Final R indices [all data]	R_1 = 0.0683, wR_2 = 0.1214
Largest diff. peak and hole	0.26 and -0.22 $eÅ^{-3}$

Table S2 Crystal data and structure refinements for ***trans*-MDF**

Empirical formula	$C_{54}H_{41}NO$
Formula weight	719.88
Temperature	113.15 K
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.91390(10) Å α = 92.6830(10) deg. B = 17.2889(2) Å β = 90.8740(10) deg. C = 22.2185(2) Å γ = 90.5800(10) deg.
Volume	3803.42(7) $Å^3$
Z	4
Calculated density	1.257 g/cm^3
μ	0.564 mm^{-1}
F(000)	1520.0
Crystal size	0.28 x 0.25 x 0.19 mm^3
Radiation	CuKα (λ = 1.54184)
2θ range for data collection	7.968 to 177.508 deg.
Index ranges	$-12 \le h \le 12$, $-16 \le k \le 22$, $-26 \le l \le 28$
Reflections collected	54694
Independent reflections	15831 [R_{int} = 0.0612, R_{sigma} = 0.0461]
Data / restraints / parameters	15831 / 0 / 1014
Goodness-of-fit on F^2	1.044
Final R indices [$I >= 2\sigma(I)$]	R_1 = 0.0444, wR_2 = 0.1044
Final R indices [all data]	R_1 = 0.0589, wR_2 = 0.1110
Largest diff. peak and hole	0.30 and -0.22 $eÅ^{-3}$

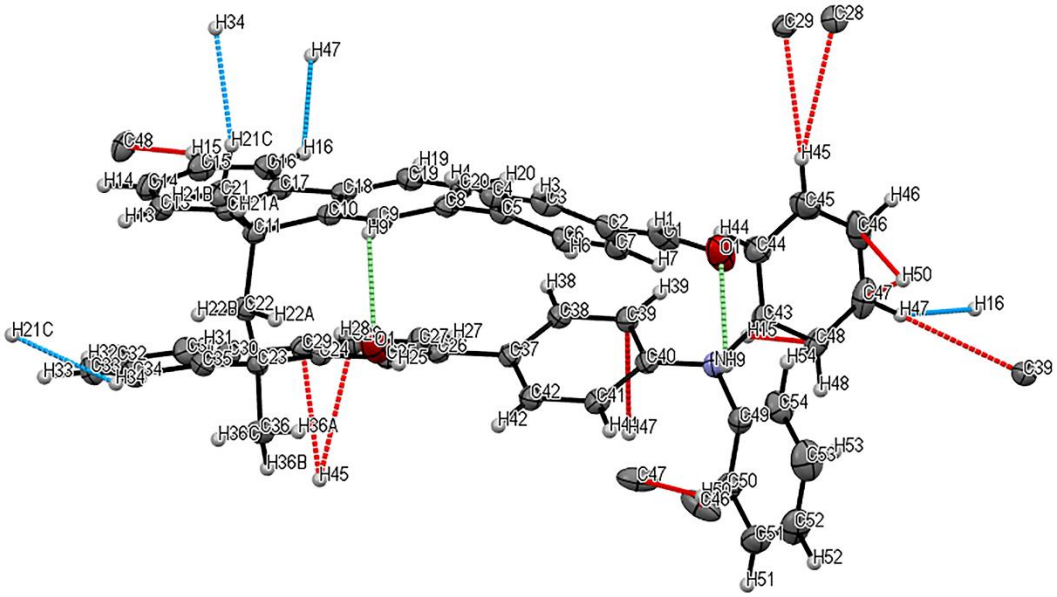

Fig. S15 The short contacts between molecules for ***cis*-MDF**

Table S3 The short contacts between molecules for ***cis*-MDF**

Contact (number)		Distance (Å)
O···H (2)	O1···H9	2.611
H···π (12)	H15···C48	2.810
	H45···C28	2.899
	H45···C29	2.666
	H47···C39	2.819
	H50···C46	2.853
	H50···C47	2.898
H···H (4)	H16···H47	2.370
	H21c···H34	2.353

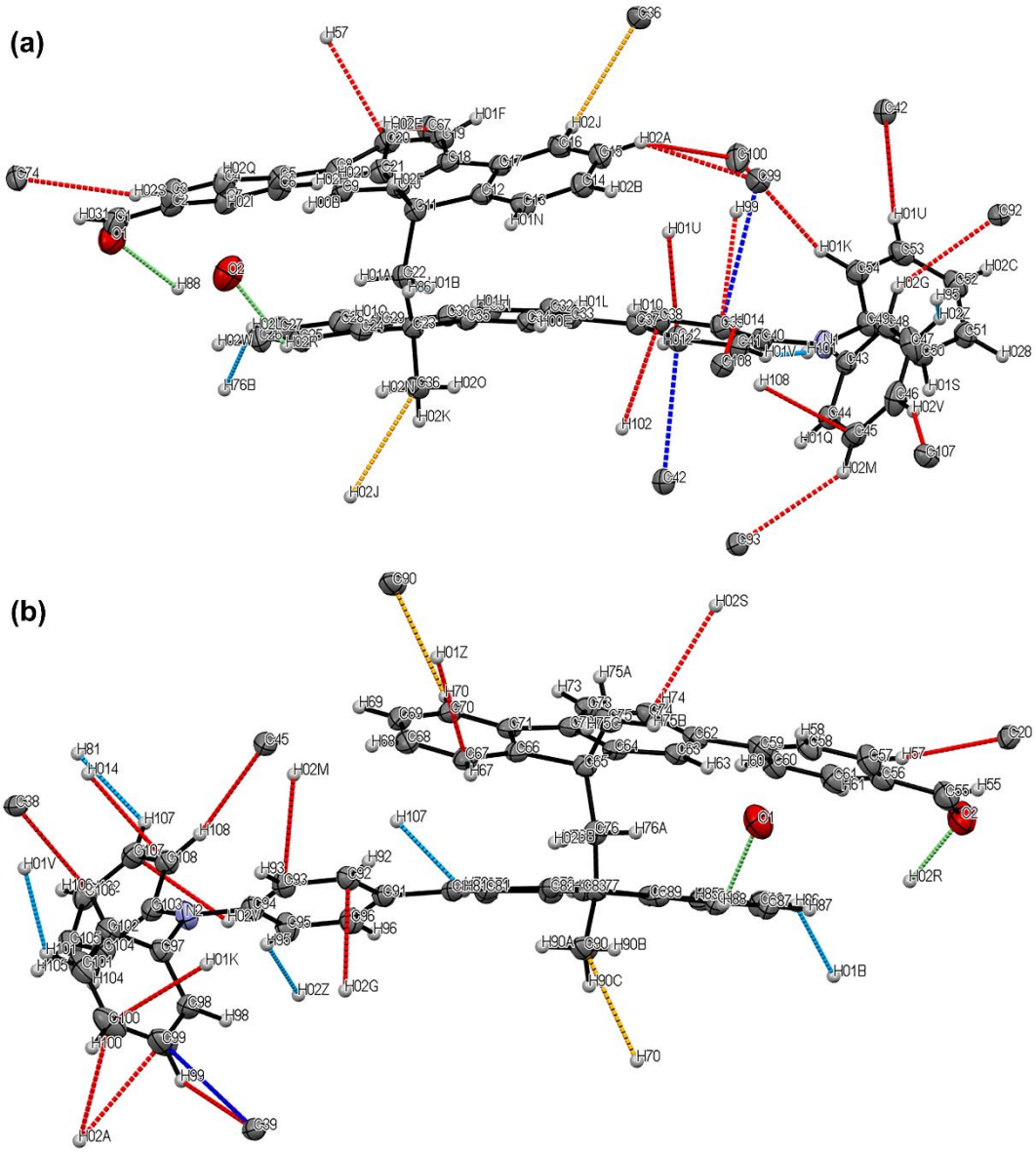

Fig. S16 The short contacts between molecules for (a) isomer-1 and (b) isomer-2 of ***trans*-MDF**

Table S4 The short contacts between molecules for isomer-1 of ***trans*-MDF**

Contact (number)		Distance (Å)
O···H (2)	O2···H02r / O1···H88	2.604 / 2.591
H···π (15)	H01k···C100	2.871
	H01z···C67	2.857
	H01u···C42 (2)	2.890
	H02a···C99	2.796
	H02a···C100	2.818
	H02g···C92	2.783
	H02m···C93	2.824
	H02s···C74	2.735
	H02v···C107	2.778
	H014···C108	2.853
	H57···C20	2.691
	H99···C39	2.577
	H102···C38	2.699
	H108···C45	2.650
π···π (2)	C39···C99	3.372
	C42···C42	3.204
H···C (2)	H02j···C36 (2)	2.889
H···H (4)	H01b···H86	2.238
	H01v···H101	2.253
	H02l···H76b	2.240
	H02z···H95	2.268

Table S5 The short contacts between molecules for isomer-2 of ***trans*-MDF**

Contact (number)		Distance (Å)
O···H (2)	O2···H02r / O1···H88	2.604 / 2.591
H···π (13)	H01k···C100	2.871
	H01z···C67	2.857
	H02a···C99	2.796
	H02a···C100	2.818
	H02g···C92	2.783
	H02m···C93	2.824
	H02s···C74	2.735
	H02v···C107	2.778
	H014···C108	2.853
	H57···C20	2.691
	H99···C39	2.577
	H102···C38	2.699
	H108···C45	2.650
π···π (1)	C39···C99	3.372
H···C (2)	H70···C90 (2)	2.882
H···H (6)	H01b···H86	2.238
	H01v···H101	2.253
	H02l···H76b	2.240
	H02z···H95	2.268
	H81···H107 (2)	2.323

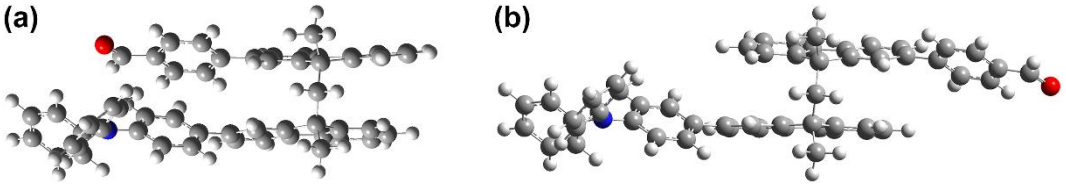

Fig. S17 The optimized molecular geometries of (a) ***cis*-MDF** and (b) ***trans*-MDF**

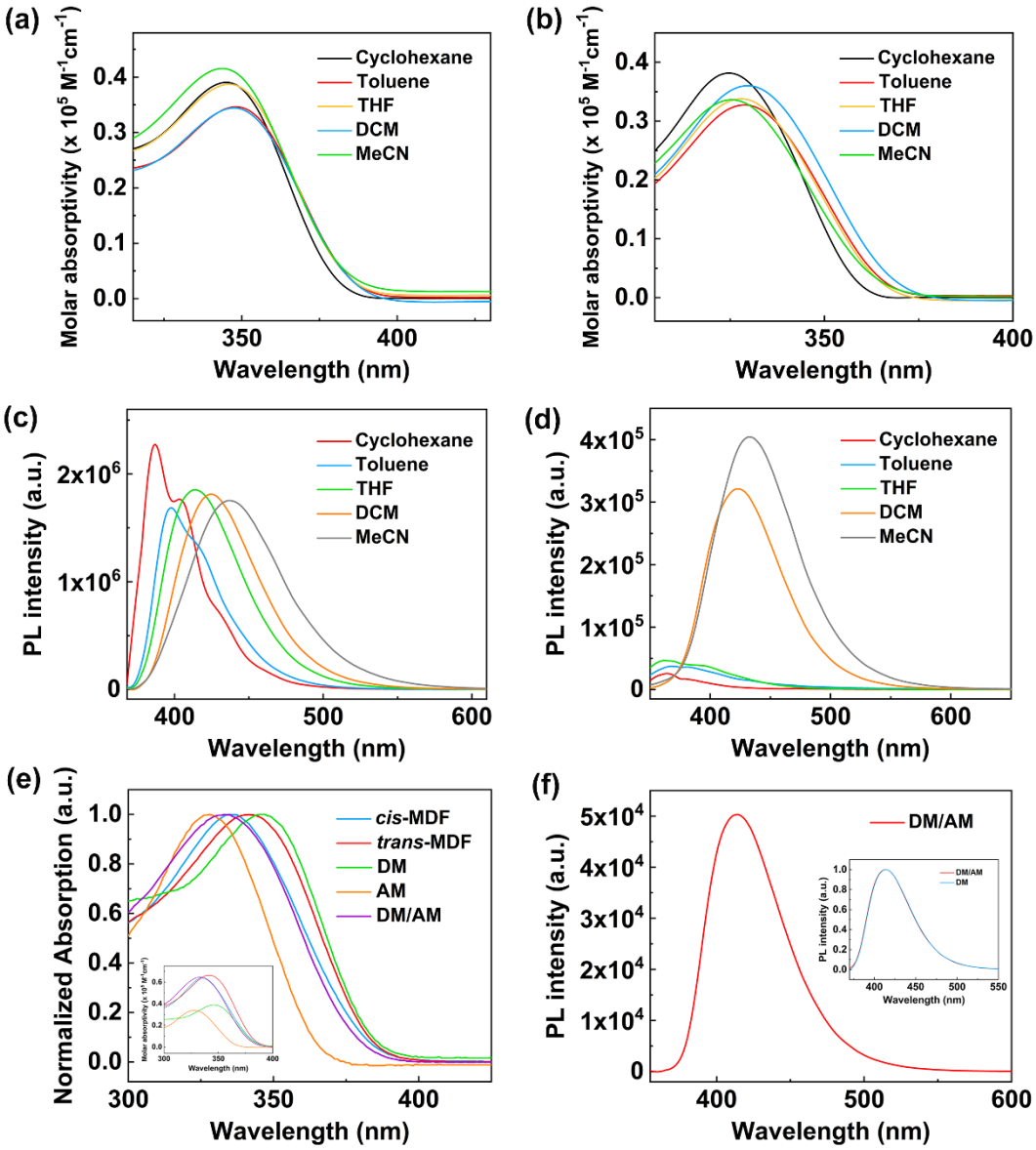

Fig. S18 UV absorption and fluorescence spectra of (a, c) **DM** (λ_{exc}: 346 nm) and (b, d) **AM** (λ_{exc}: 328 nm) in different solvents. (e) Normalized UV absorption spectra of ***cis*-MDF**, ***trans*-MDF**, **DM**, **AM** and **DM**/**AM** in THF (inset: un-normalized ones). (f) Fluorescence spectra of **DM**/**AM** in THF (λ_{exc}: 333 nm, inset: normalized fluorescence spectra of **DM**/**AM** and **DM**). (10 μM)

Table S6 Photophysical data of ***cis*-MDF**, ***trans*-MDF**, **DM** and **AM** in different solvents

	Solvent	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\lambda^a$ (nm)	τ_1 (ns)	τ_2 (ns)	A_1/A_2	χ^2	Φ_F (%)
***cis*-MDF**	Cyclohexane	334	387	173	0.46	2.64	98.00/2.00	1.13	**4.8**
			405		0.47	4.05	98.02/1.98	1.26	
			507		10.19	-	100/0	1.17	
	Toluene	338	398	195	0.33	3.80	94.90/5.10	1.26	3.3
			533		11.99	-	100/0	1.24	
	THF	335	406	220	-	-	-	-	2.1
			555		12.78	-	100/0	1.14	
	DCM	337	596	259	6.93	-	100/0	1.08	0.3
	MeCN	333	614	281	-	-	-	-	-
***trans*-MDF**	Cyclohexane	339	391	~ 81	0.10	1.72	97.80/2.20	1.24	1.4
			403		0.09	1.70	97.22/2.78	1.20	
			~ 420		0.12	2.54	95.10/4.90	1.24	
	Toluene	343	447	104	1.20	2.54	30.15/69.85	1.23	**18.1**
	THF	340	540	200	3.99	13.50	65.13/34.87	1.17	6.2
	DCM	343	619	276	1.41	7.91	74.91/25.09	1.09	0.8
	MeCN	339	-	-	-	-	-	-	-
DM	Cyclohexane	344	386	60	0.92	-	100/0	1.15	55.5
			404		0.92	-	100/0	1.21	
	Toluene	349	397	65	1.00	-	100/0	1.04	79.7
			414		1.00	-	100/0	1.02	
	THF	346	414	68	1.40	-	100/0	1.17	72.3
	DCM	347	425	78	1.67	-	100/0	1.29	81.1
	MeCN	344	438	94	2.07	-	100/0	1.27	79.4
AM	Cyclohexane	325	-	-	-	-	-	-	-
	Toluene	329	-	-	-	-	-	-	-
	THF	328	-	-	-	-	-	-	-
	DCM	328	424	96	0.10	1.70	92.66/7.34	1.30	1.3
	MeCN	325	434	109	0.10	2.19	89.55/10.45	1.24	1.9

[a] Stokes shift calculated based on ICT emission.

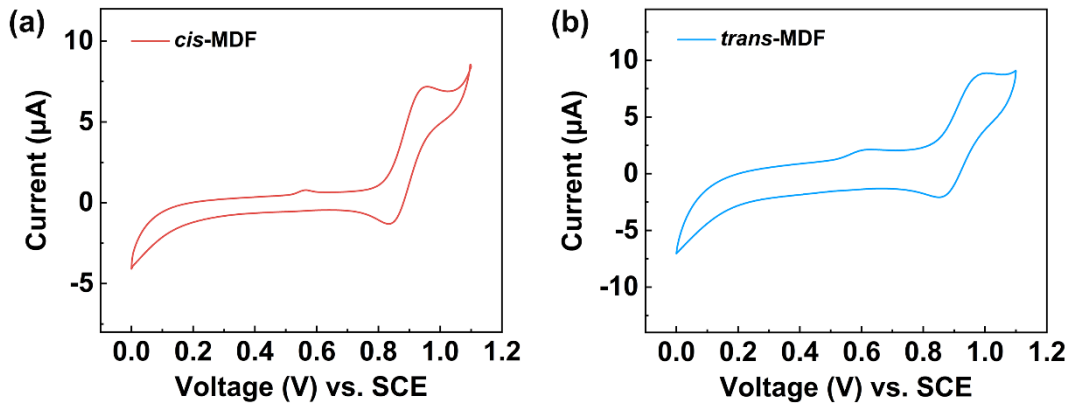

Fig. S19 Cyclic voltammetry curves of (a) ***cis*-MDF** and (b) ***trans*-MDF**

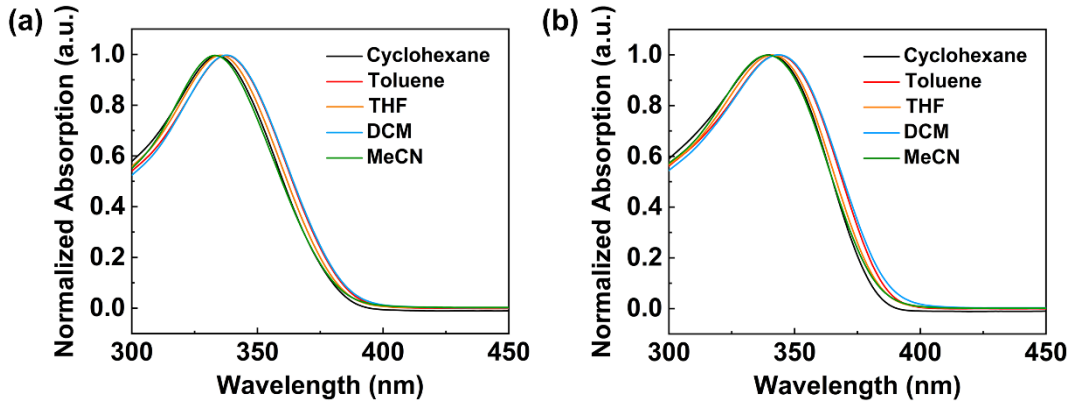

Fig. S20 UV absorption spectra of (a) ***cis*-MDF** and (b) ***trans*-MDF** in different solvents (10 μM)

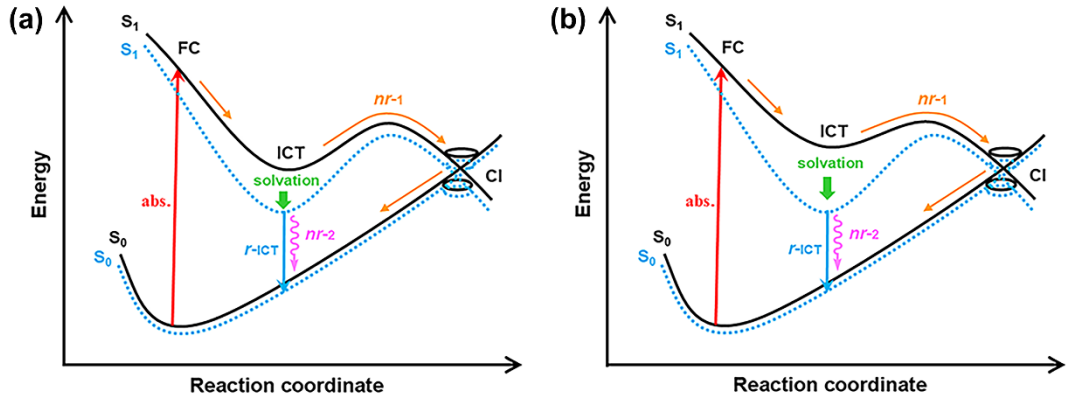

Fig. S21 Schematic representation of the proposed mechanism for the polarity-dependent (a) downhill and (b) up-down type emission of ***cis*-MDF** and ***trans*-MDF**, respectively (LE states are not shown for clarity)

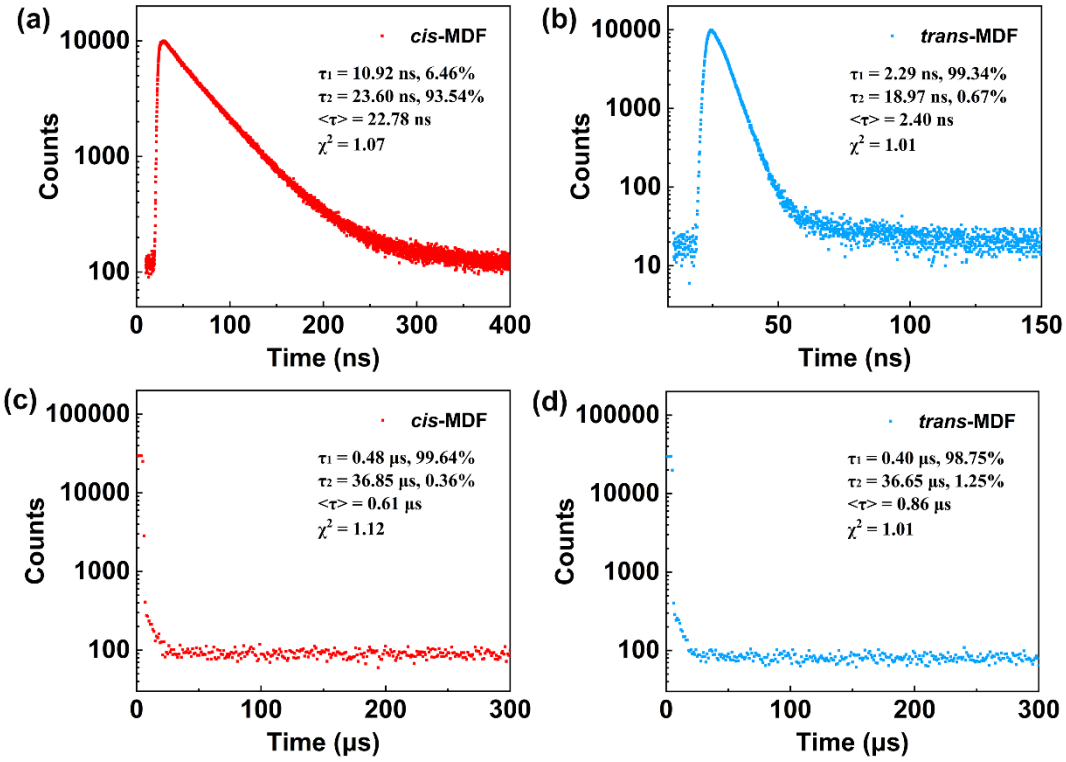

Fig. S22 Time-resolved fluorescence decay curves of (a, c) ***cis*-MDF** and (b, d) ***trans*-MDF** in deoxygenated toluene

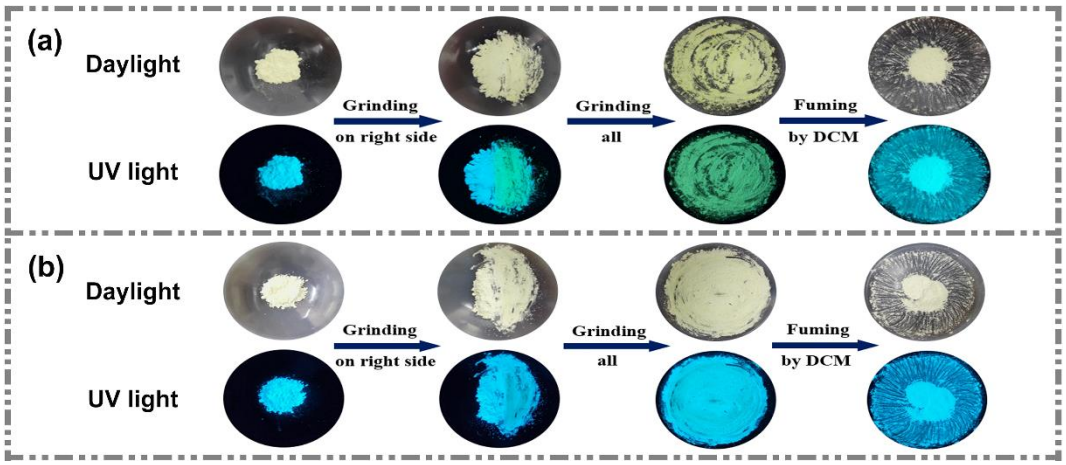

Fig. S23 Photographs of (a) ***cis*-MDF** and (b) ***trans*-MDF** in different solid states taken under daylight and 365 nm UV illumination, respectively

Table S7 Photophysical data of ***cis*-MDF** and ***trans*-MDF** in different solid states

	$\lambda_{pristine}$ / nm (Φ_F)	λ_{gound} / nm (Φ_F)	λ_{fumed} / nm (Φ_F)	$\Delta\lambda^a$ / nm
***cis*-MDF**	478 (0.130)	513 (0.105)	480 (0.117)	35
***trans*-MDF**	472 (0.282)	481 (0.136)	472 (0.218)	9

[a] Grinding-induced spectral shift, $\Delta\lambda = \lambda_{gound} - \lambda_{pristine}$.

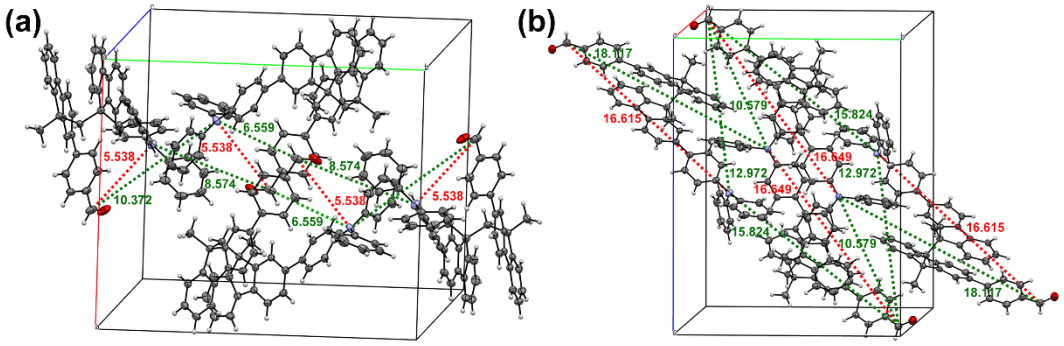

Fig. S24 The stacking molecules of (a) ***cis*-MDF** and (b) ***trans*-MDF** in one-unit cell. Dashed red and green lines illustrate the intramolecular and intermolecular N···C=O distances (Å), respectively

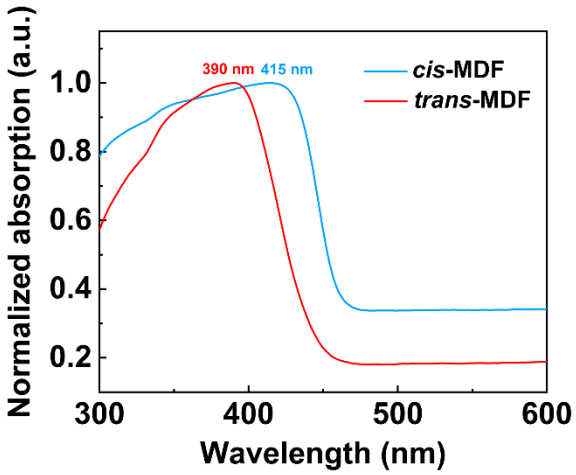

Fig. S25 Normalized absorption spectra of pristine ***cis*-MDF** and ***trans*-MDF**

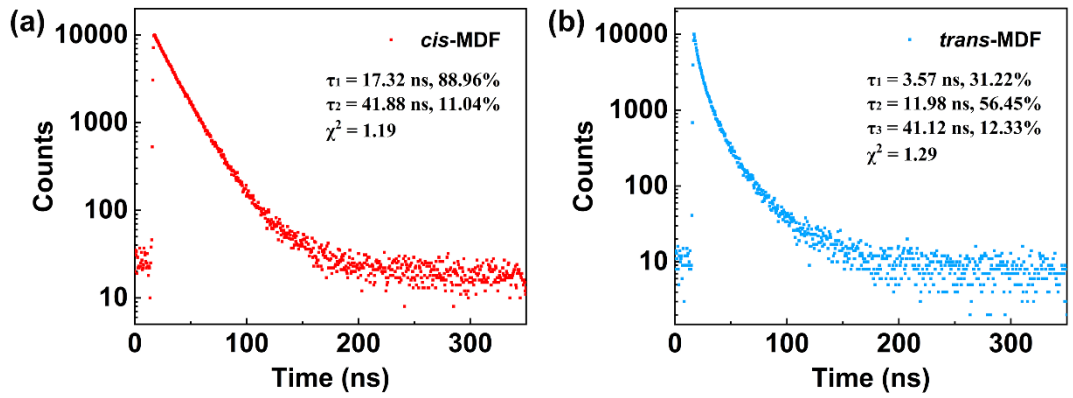

Fig. S26 Time-resolved fluorescence decay curves of pristine (a) ***cis*-MDF** and (b) ***trans*-MDF**

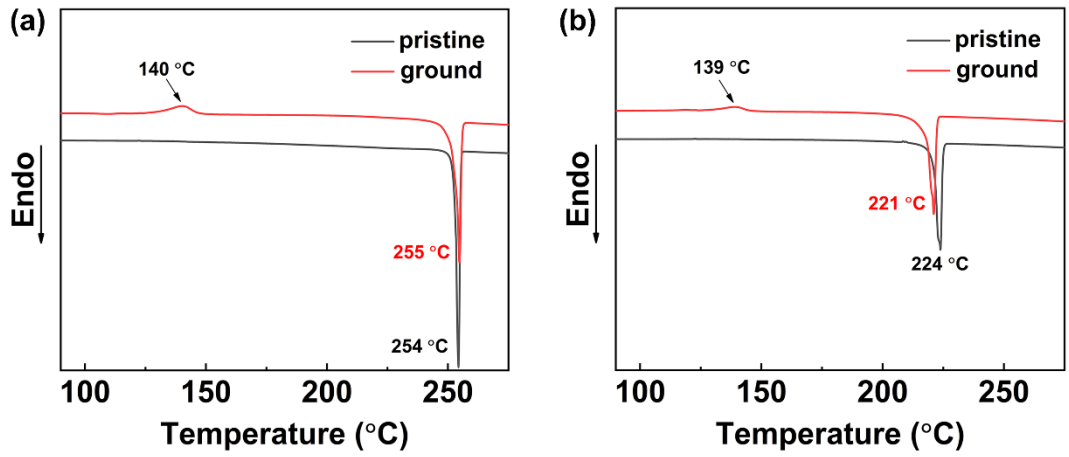

Fig. S27 DSC curves of (a) ***cis*-MDF** and (b) ***trans*-MDF** in different solid states

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