

Electronic Supplementary Information

Halogen-substituted triphenylamine derivatives with intense mechanoluminescence property

Jin Tu,^a Yunhao Fan,^a Jiaqiang Wang,^a Xiaoyu Li,^a Can Wang,^a Yanbin Gong,^a Mengmeng Han,^a Qianqian Li,^a and Zhen Li^{*a,b}

^a Sauvage Center for Molecular Sciences, Department of Chemistry, Wuhan University, Wuhan 430072, China.

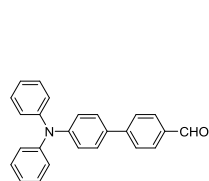
^b Institute of Molecular Aggregation Science, Tianjin University, Tianjin 300072, China

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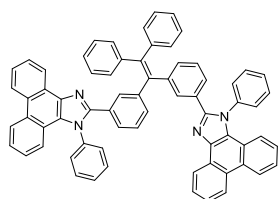
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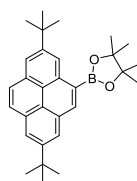
1. Chart S1. Some ML materials reported in previous studies.



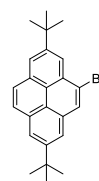
J. Mater. Chem. C., 2017, 5, 9879-9885



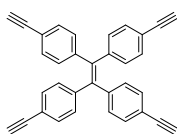
Chem. Commun., 2018, 54, 5598-5601



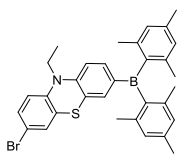
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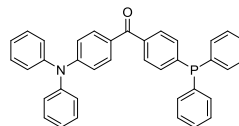
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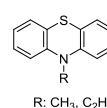
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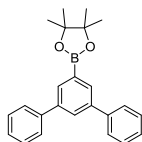


Chem. Sci. 2018, 9, 5787-5794

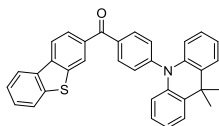


R: CH₃, C₂H₅

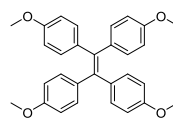
Angew. Chem. Int. Ed., 2017, 56, 15299-15303



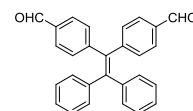
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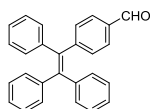
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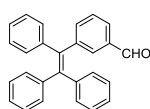
Mater. Horiz., 2016, 3, 220-225



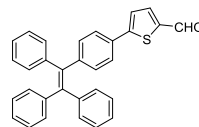
Chem. Sci., 2016, 7, 5307-5312



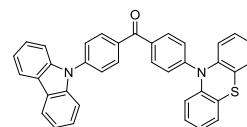
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Chem. Sci., 2016, 7, 5307-5312



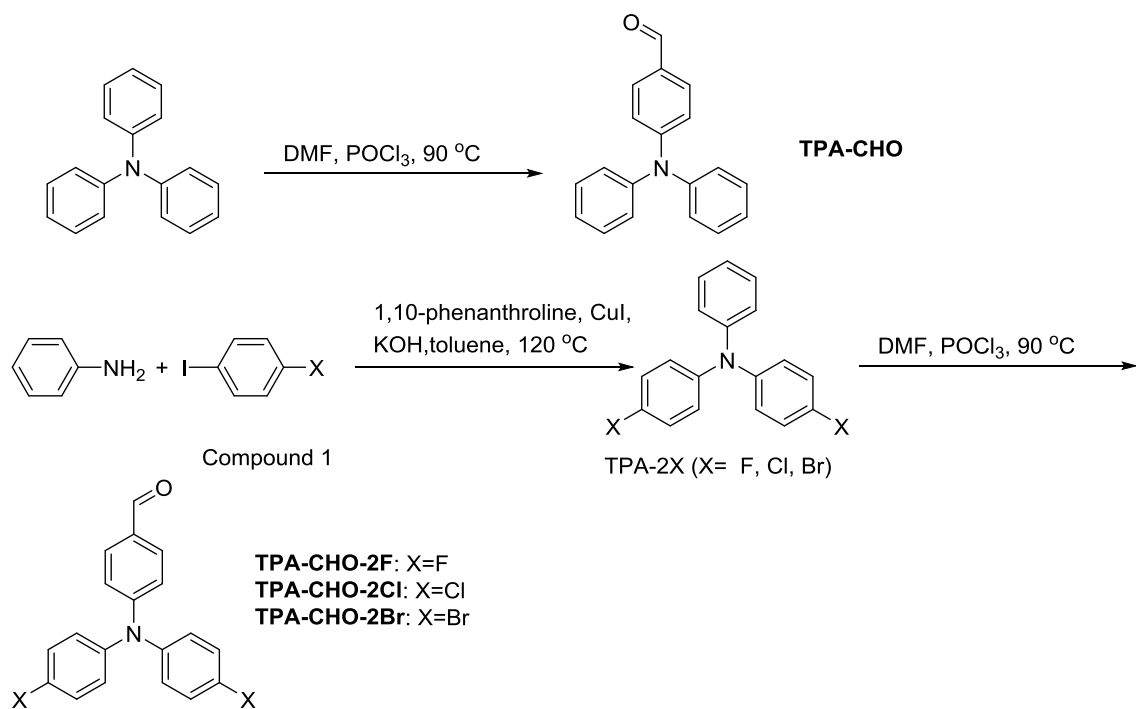
Chem. Sci., 2015, 6, 3236-3241



Angew. Chm. Int. Ed., 2015, 54, 874-878

2. Synthesis

2.1 Synthetic routes



Scheme S1. Synthetic routes of TPA-CHO and TPA-CHO-2X ($\text{X} = \text{F, Cl, Br}$).

3.3 NMR spectra

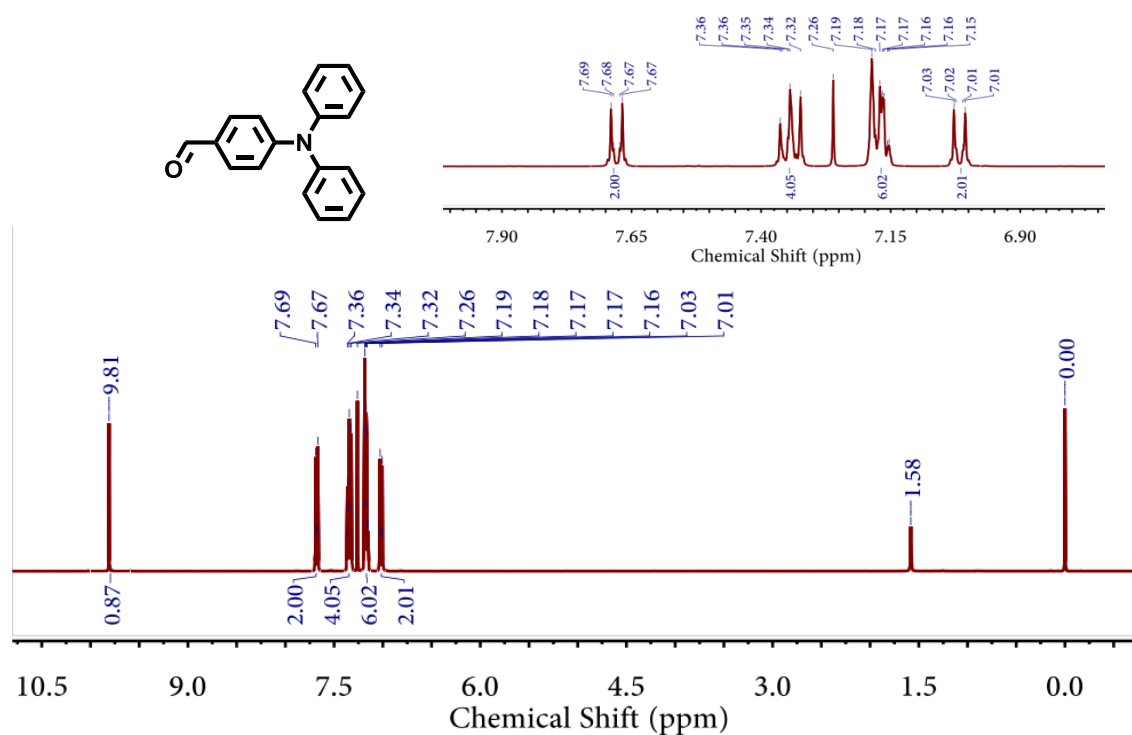


Fig. S1 ^1H NMR spectrum of TPA-CHO.

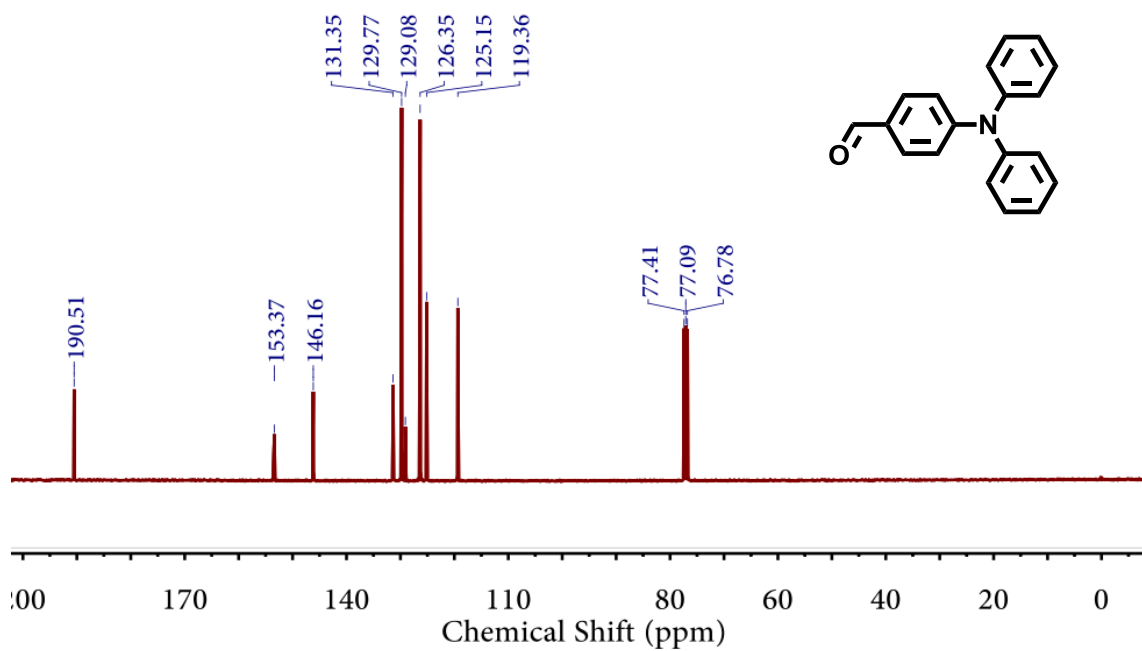


Fig. S2 ^{13}C NMR spectrum of TPA-CHO.

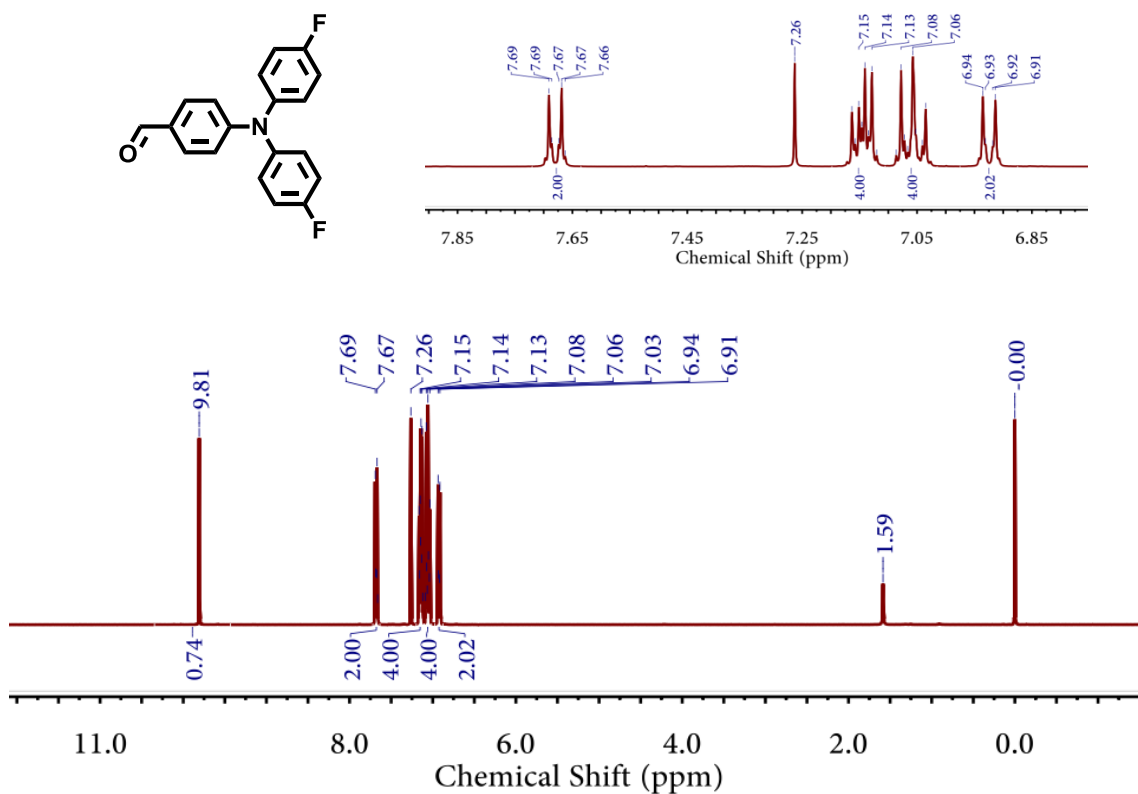


Fig. S3 ^1H NMR spectrum of TPA-CHO-2F.

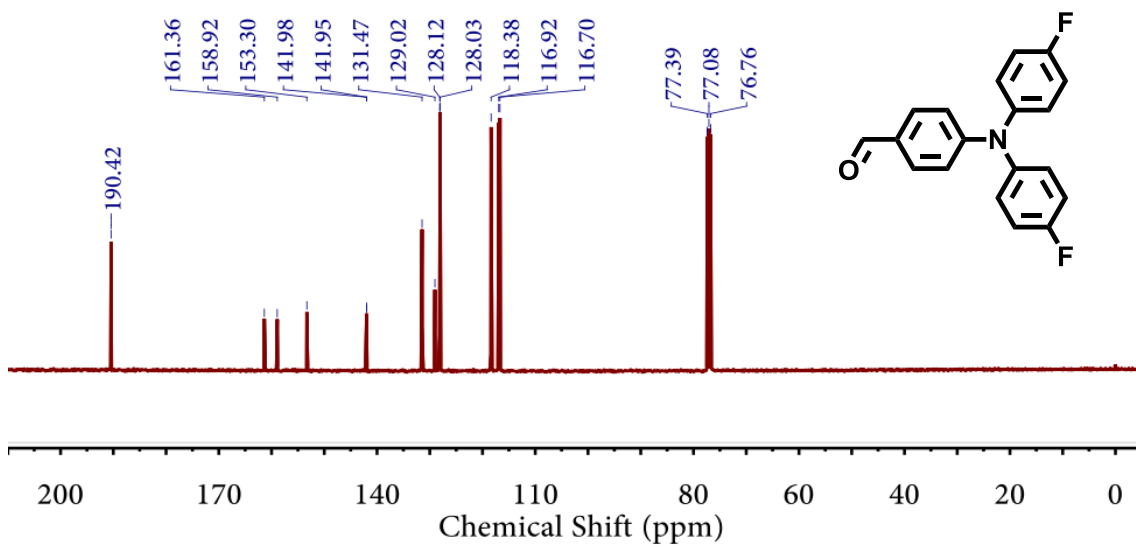


Fig. S4 ^{13}C NMR spectrum of TPA-CHO-2F.

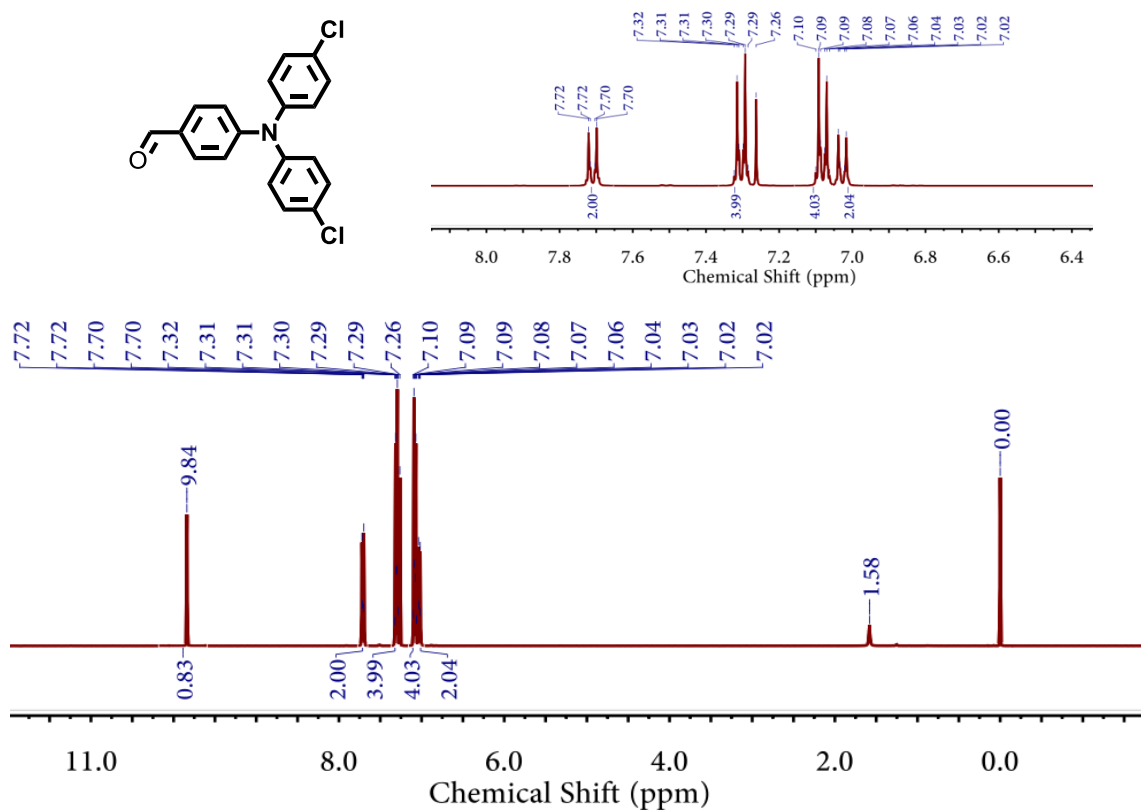


Fig. S5 ¹H NMR spectrum of TPA-CHO-2Cl.

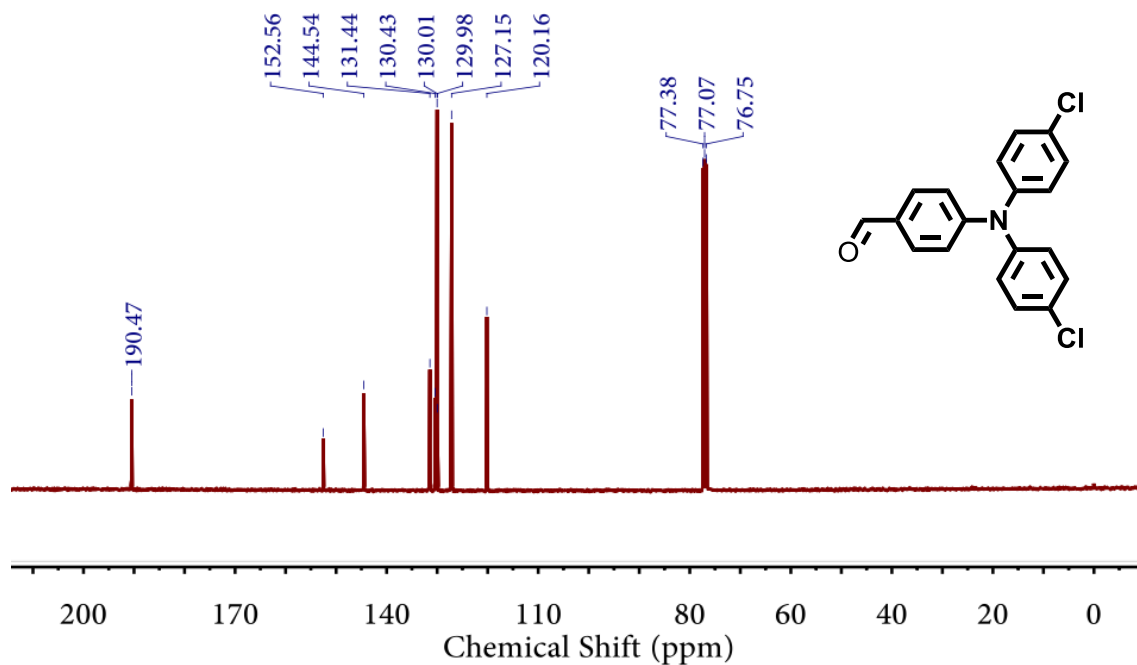


Fig. S6 ¹³C NMR spectrum of TPA-CHO-2Cl.

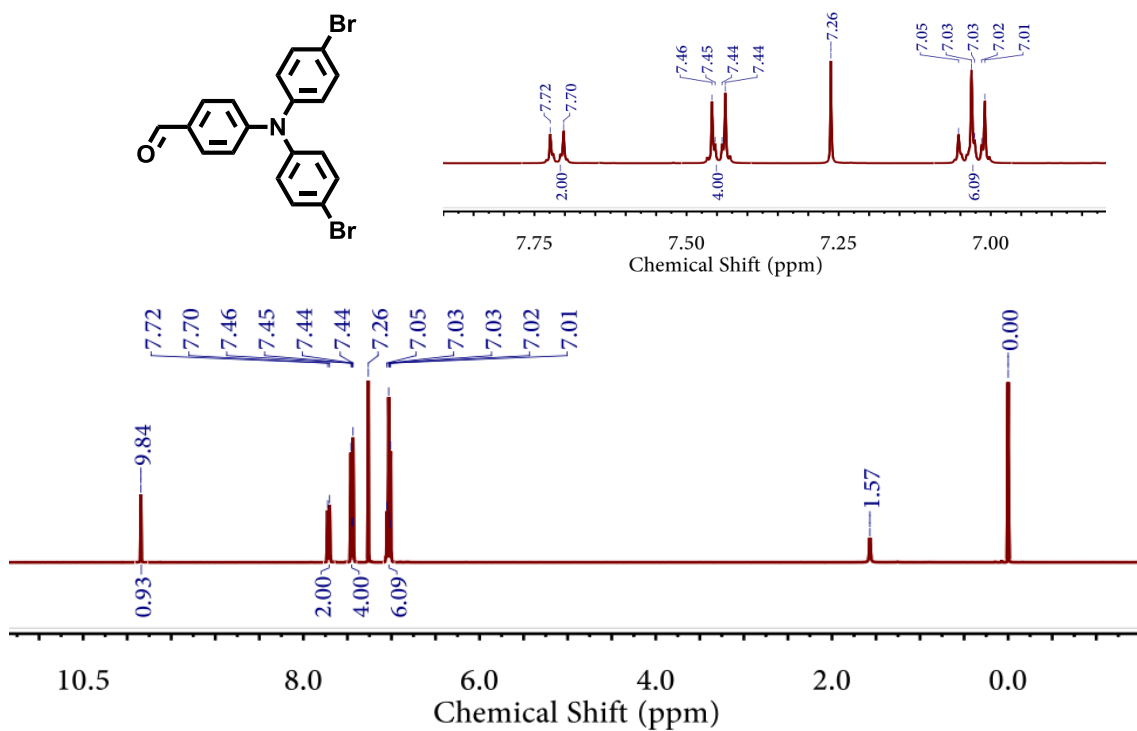


Fig. S7 ^1H NMR spectrum of TPA-CHO-2Br.

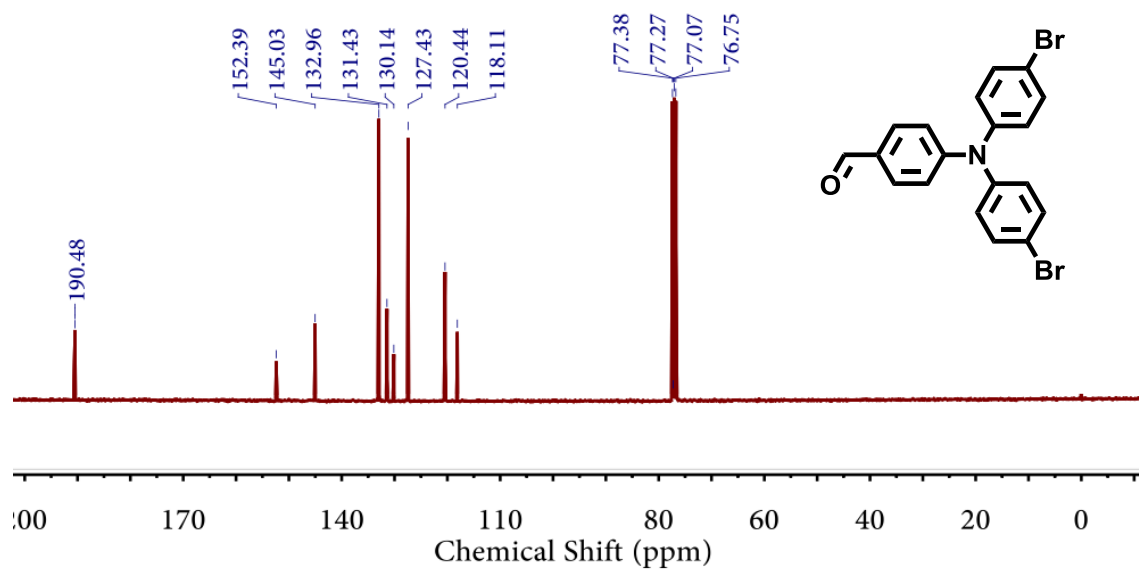


Fig. S8 ^{13}C NMR spectrum of TPA-CHO-2Br.

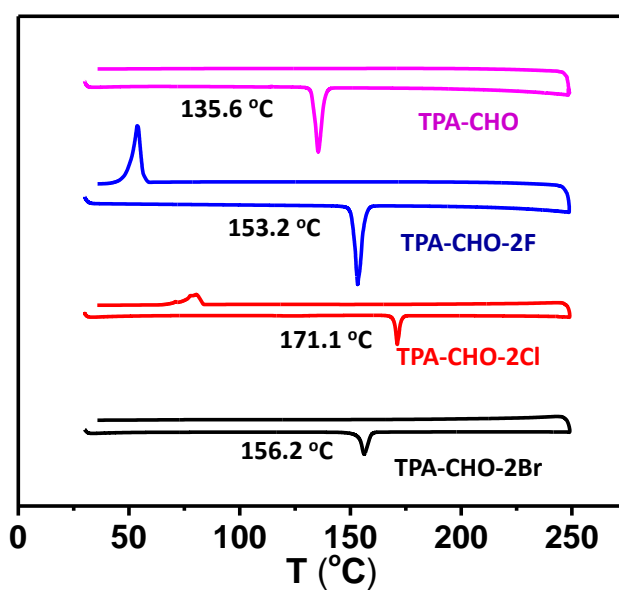
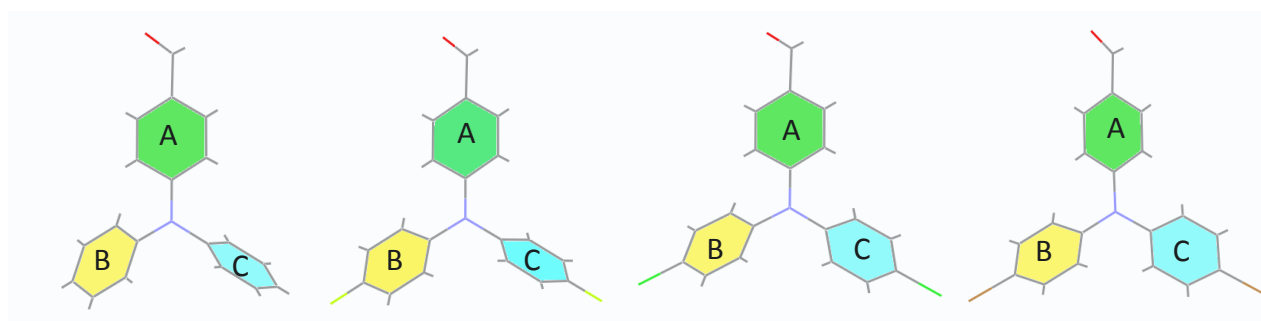


Fig. S9 DSC curves of TPA-CHO and TPA-CHO-2X (X= F, Cl, Br).



Compound	ϑ°				
	A-B	B-C	A-C	Average ^[a]	A1
TPA-CHO	66.67	80.69	71.29	72.9	3.10
TPA-CHO-2F	67.79	87.84	67.96	74.53	5.60
TPA-CHO-2Cl	68.81	68.80	53.57	63.7	3.05
TPA-CHO-2Br	67.99	66.79	53.26	62.68	3.70

Fig. S10 The images of TPA derivatives in crystal (up) and the value of torsion of phenyl ring in crystal (bottom). [a]. Average means the average value of A-B, B-C and A-C.

Table S1 Summary of crystal data and intensity collection parameters of **TPA-CHO** and **TPA-CHO-2X** (X= F, Cl, Br).

Compound	TPA-CHO	TPA-CHO-2F	TPA-CHO-2Cl	TPA-CHO-2Br
Empirical formula	C ₁₉ H ₁₅ NO	C ₁₉ H ₁₃ F ₂ NO	C ₁₉ H ₁₃ Cl ₂ NO	C ₁₉ H ₁₃ Br ₂ NO
Formula weight	273.32	309.30	342.20	431.12
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Temp. / K	296(2) K	297(2) K	296(2) K	296(2) K
Space group	P2(1)/c	Pbca	Pc	Pc
a/Å	12.0916(17)	13.173(4)	9.117(4)	9.244(4)
b/Å	11.4255(16)	13.212(4)	8.400(3)	8.389(4)
c/Å	10.9413(16)	17.216(5)	11.068(4)	11.306(5)
α/°	90	90	90	90
β/°	101.999(3)	90	107.736(7)	107.570(8)
γ/°	90	90	90	90
volume/Å ³	1478.5(4)	2996.2(16)	807.2(6)	835.9(6)
Z	4	8	2	2
Dcalcd./ gcm ⁻³	1.228	1.371	1.408	1.713
F(000)	576	1280	352	424
Index ranges	-15<=h<=11, -14<=k<=14, -13<=l<=13	-15<=h<=15, -15<=k<=12, -20<=l<=20	-11<=h<=11, -9<=k<=10, -12<=l<=13	-10<=h<=10, -9<=k<=9, -13<=l<=10
Reflections collected	9559	19399	5621	5366
Independent reflections	3056 [R(int) = 0.0288]	2564 [R(int) = 0.0930]	2737 [R(int) = 0.0345]	2547 [R(int) = 0.0795]
Completeness to theta = 24.776°	99.8%	99.7%	99.8%	99.8%
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	3056/0/191	2564/0/219	2737/2/208	2547/12/182
Goodness-of-fit on F ²	1.188	1.014	1.188	0.959
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0928	R1=0.0453, wR2=0.0993	R1 = 0.0429, wR2 = 0.1121	R1 = 0.0582, wR2 = 0.1391
R indices (all data)	R1 = 0.0594, wR2 = 0.1052	R1 = 0.0948, wR2 = 0.1206	R1 = 0.0544, wR2 = 0.1219	R1 = 0.1002, wR2 = 0.1605
Largest diff. peak and hole/ e.Å ⁻³	0.148 and -0.158	0.151 and -0.137	0.176 and -0.182	0.488 and -0.477

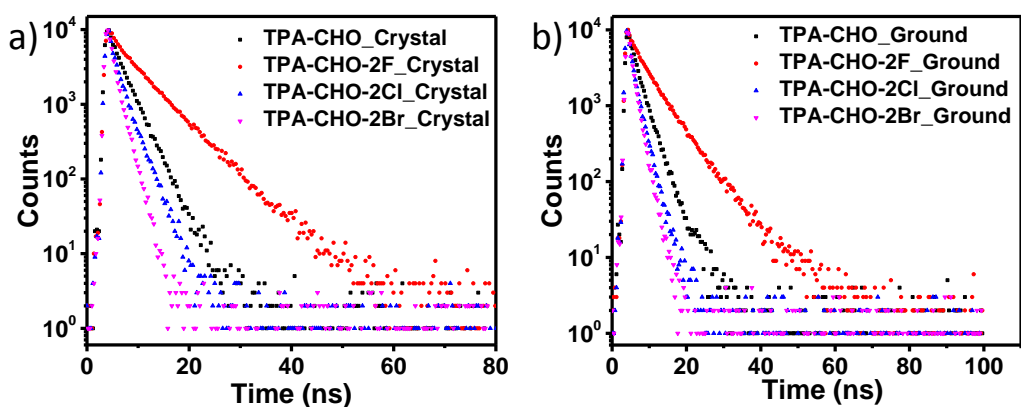


Fig. S11 Emission decay of TPA-CHO and TPA-CHO-2X (X= F, Cl, Br) a) before and b) after grinding.

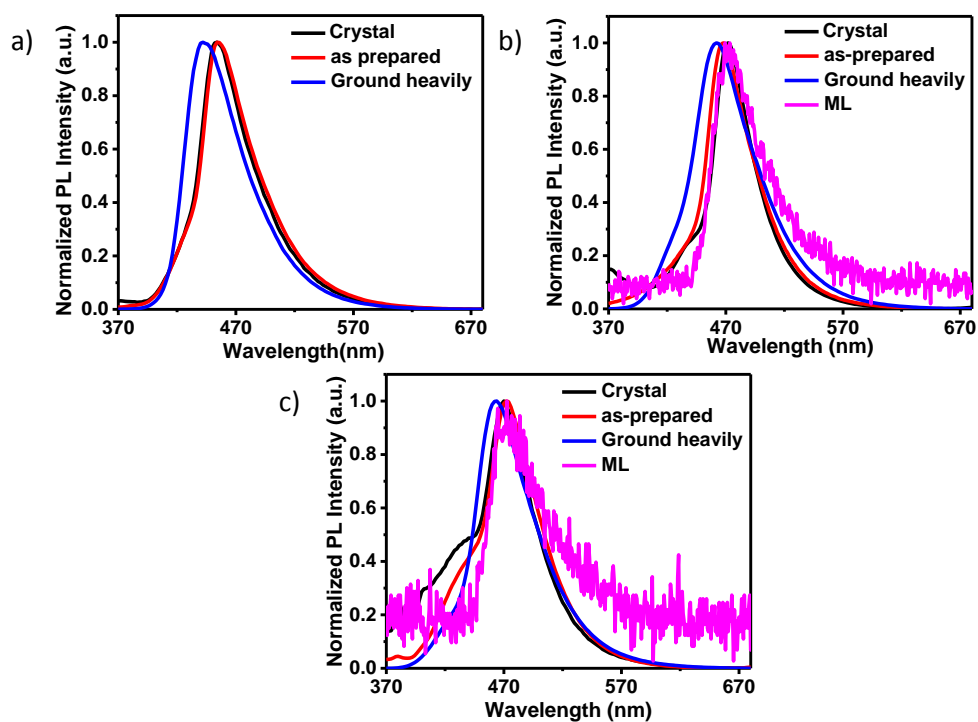


Fig. S12 PL spectra of TPA-CHO a), TPA-CHO-2Cl b) and TPA-CHO-2Br c) in crystal, after grinding, as-prepared state and ML spectra of TPA-CHO-2Cl and TPA-CHO-2Br.

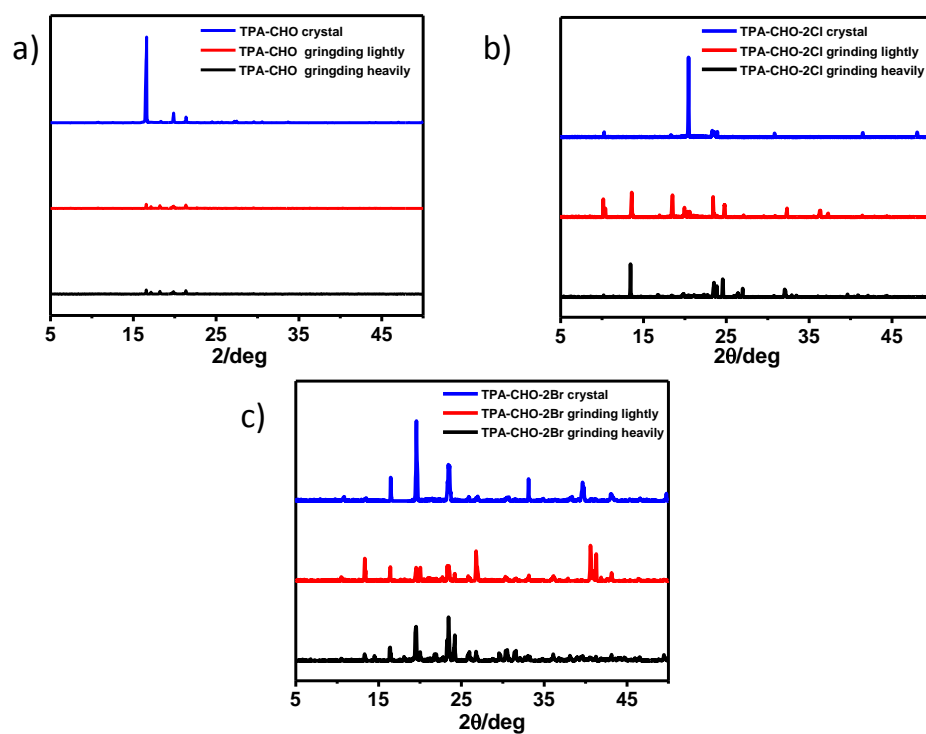


Fig. S13 XRD patterns of TPA-CHO and TPA-CHO-2X (X= Cl, Br).

Table S2 Single crystal information and ML activities of TPA-CHO and TPA-CHO-2X (X= F, Cl, Br).

Compound	Crystal system	Space group	Symmetry	ML Active
TPA-CHO	Monoclinic	P2(1)/c	Centrosymmetric	Inactive
TPA-CHO-2F	Orthorhombic	Pbca	Centrosymmetric	Active
TPA-CHO-2Cl	Monoclinic	Pc	Noncentrosymmetric	Active
TPA-CHO-2Br	Monoclinic	Pc	Noncentrosymmetric	Active

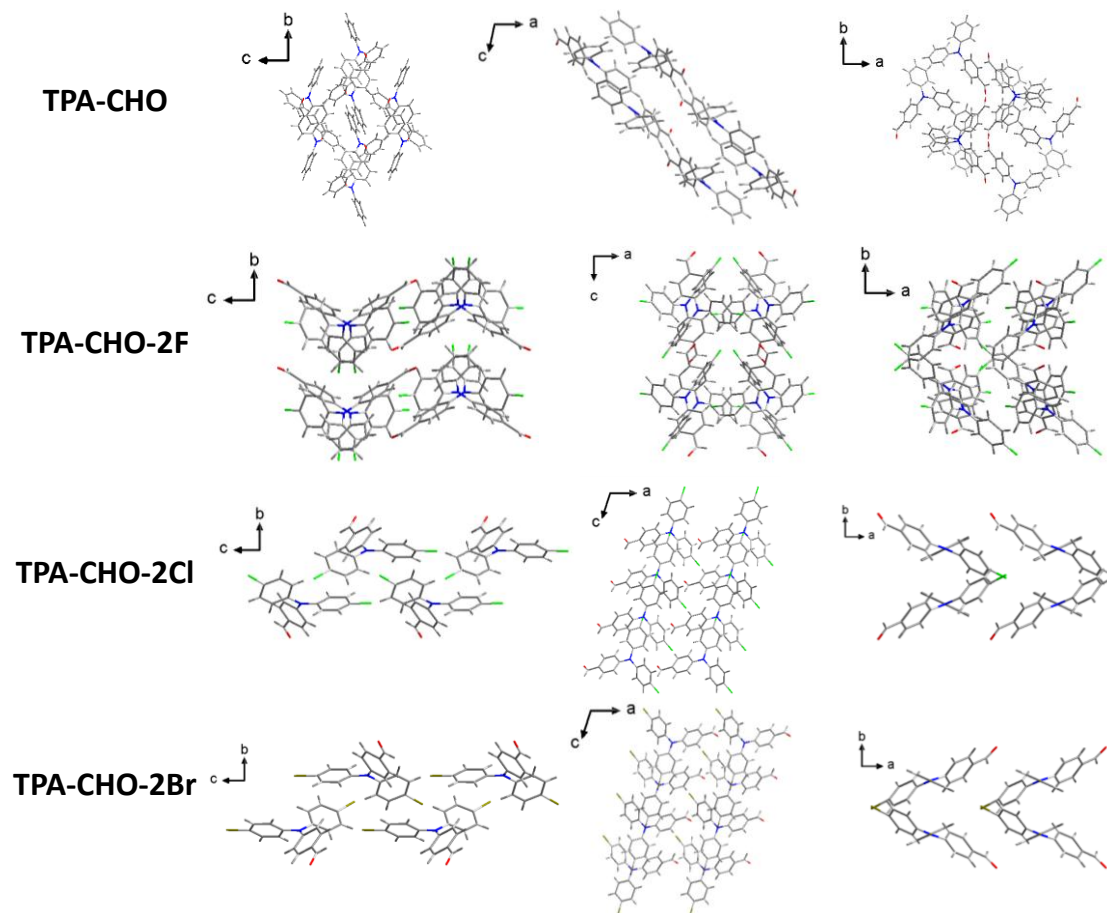


Fig. S14 The stacking models of those TPA derivatives in crystal in different viewing directions.

Table S3 The number of C-H \cdots π , C-H \cdots O and C-H \cdots X (X= F, Cl and Br) interactions in the crystals of TPA-CHO, TAP-CHO-2F, TAP-CHO-2Cl and TAP-CHO-2Br.

Crystal	Intramolecular C-H \cdots O	No.	Intramolecular C-H \cdots π	No.	Intramolecular C-H \cdots X	No.
TPA-CHO _a	2.753-3.075	6	3.247-3.553	4	-	-
TPA-CHO _b	2.753-3.075	6	3.247-3.553	4	-	-
TPA-CHO-2F _a	2.462-3.886	5	3.466-3.978	11	2.479-3.804	16
TPA-CHO-2F _b	2.462-3.886	5	3.466-3.978	11	2.479-3.804	16
TPA-CHO-2Cl _a	2.895-2.895	2	3.049-3.8012	4	2.998-3.357	11
TPA-CHO-2Cl _b	2.895-2.895	2	3.049-3.8012	4	2.998-3.357	11
TPA-CHO-2Br _a	2.846-2.846	2	3.176-3.916	4	3.093-3.427	11
TPA-CHO-2Br _b	2.846-2.846	2	3.176-3.916	4	3.093-3.427	11

Table S4 Summarization of the C-H...O and C-H... π interactions in crystal cell of **TPA-CHO_a** crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.753
	2	2.732
	3	2.894
	4	2.894
	5	3.075
	6	3.075
C-H... π	1	3.247
	2	3.247
	3	3.553
	4	3.553

Table S5 Summarization of the C-H...O and C-H... π interactions in crystal cell of **TPA-CHO_b** crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.753
	2	2.732
	3	3.075
	4	3.075
	5	2.894
	6	2.894
C-H... π	1	3.553
	2	3.553
	3	3.247
	4	3.247

Table S6 Summarization of the C-H...O, C-H... π and C-H...F interactions in crystal cell of TPA-CHO-2F_a crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.462
	2	2.602
	3	2.602
	4	3.886
	5	3.886
C-H... π	1	3.466
	2	3.466
	3	3.698
	4	3.702
	5	3.702
	6	3.704
	7	3.704
	8	3.938
	9	3.943
	10	3.976
	11	3.978
C-H...F	1	2.479
	2	2.479
	3	2.663
	4	2.902
	5	2.902
	6	2.903
	7	2.903
	8	3.270
	9	3.434
	10	3.434
	11	3.500
	12	3.500
	13	3.670
	14	3.670
	15	3.804
	16	3.804

Table S7 Summarization of the C-H...O, C-H... π and C-H...F interactions in crystal cell of TPA-CHO-2F_b crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.462
	2	2.602
	3	2.602
	4	3.886
	5	3.886
C-H... π	1	3.466
	2	3.466
	3	3.698
	4	3.702
	5	3.702
	6	3.704
	7	3.704
	8	3.938
	9	3.943
	10	3.976
	11	3.978
C-H...F	1	2.479
	2	2.479
	3	2.663
	4	2.902
	5	2.902
	6	2.903
	7	2.903
	8	3.270
	9	3.434
	10	3.434
	11	3.500
	12	3.500
	13	3.670
	14	3.670
	15	3.804
	16	3.804

Table S8 Summarization of the C-H...O, C-H... π and C-H...Cl interactions in crystal cell of TPA-CHO-2Cl_a crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.895
	2	2.895
C-H... π	1	3.812
	2	3.812
	3	3.049
	4	3.049
C-H...Cl	1	3.168
	2	3.168
	3	3.357
	4	2.998
	5	3.186
	6	3.186
	7	3.313
	8	3.343
	9	3.313
	10	3.343
	11	3.357

Table S9 Summarization of the C-H...O, C-H... π and C-H...Cl interactions in crystal cell of TPA-CHO-2Cl_b crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.895
	2	2.895
C-H... π	1	3.812
	2	3.812
	3	3.049
	4	3.049
C-H...Cl	1	3.168
	2	3.168
	3	3.357
	4	2.998
	5	3.186
	6	3.186
	7	3.313
	8	3.343
	9	3.313
	10	3.343
	11	3.357

Table S10 Summarization of the C-H...O, C-H... π and C-H...Br interactions in crystal cell of TPA-CHO-2Br_a crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.846
	2	2.846
C-H... π	1	3.176
	2	3.176
	3	3.916
	4	3.916
C-H...Br	1	3.395
	2	3.270
	3	3.292
	4	3.145
	5	3.395
	6	3.270
	7	3.292
	8	3.145
	9	3.427
	10	3.093
	11	3.427

Table S11 Summarization of the C-H...O, C-H... π and C-H...Br interactions in crystal cell of TPA-CHO-2Br_b crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.846
	2	2.846
C-H... π	1	3.176
	2	3.176
	3	3.916
	4	3.916
C-H...Br	1	3.395
	2	3.270
	3	3.292
	4	3.145
	5	3.395
	6	3.270
	7	3.292
	8	3.145
	9	3.427
	10	3.093
	11	3.427

Table S12 Summarization of the C-H...O and C-H... π interactions between **TPA-CHO_a** and **TPA-CHO_b** crystal.

Type of Interaction	No.	d/Å
C-H...O	1	2.515
	2	2.515
	3	2.515
	4	2.515
C-H... π	1	3.288
	2	3.288
	3	3.505
	4	3.505
	5	3.877
	6	3.877
	7	3.877
	8	3.877
	9	3.071
	10	3.071
	11	3.071
	12	3.808
	13	3.071
	14	3.808

Table S13 Summarization of the C-F...F-C, C-H...O and C-H...F interactions between **TPA-CHO-2F_a** and **TPA-CHO-2F_b** crystal.

Type of Interaction	No.	d/Å
C-F...F-C	1	3.863
C-H...O	1	3.263
	2	3.263
	3	3.173
	4	3.173
	5	2.915
	6	2.915
	7	2.915
	8	2.915
	9	3.966
	10	3.966
	11	3.966
	12	3.966
	1	2.447

C-H...F	2	2.447
	3	3.528
	4	3.528
	5	3.675
	6	3.675
	7	3.675
	8	3.675
	9	3.320
	10	3.320
	11	3.320
	12	3.320
	13	3.398
	14	3.398

Table S14 Summarization of the C-H...Cl and C-H... π interactions between **TPA-CHO-2Cl_a** and **TPA-CHO-2Cl_b** crystal.

Type of Interaction	No.	d/Å
C-H...Cl	1	3.335
	2	3.951
	3	3.335
	4	3.951
	5	3.335
	6	3.951
	7	3.546
	8	2.984
	9	2.984
	10	3.546
	11	3.546
	12	3.546
	13	2.984
	14	2.984
	15	3.546
	16	2.984
	17	2.984
	18	3.975
	19	3.060
	20	3.975
	21	3.060
	22	3.975
	23	3.975
	24	3.975
	25	3.060

	26	3.975
	27	3.886
	28	3.886
	29	3.886
	30	3.951
	31	3.951
	32	3.335
	33	3.335
	34	3.335
C-H... π	1	3.779
	2	3.779
	3	3.781
	4	3.779
	5	3.779
	6	3.779
	7	3.583
	8	3.597
	9	3.583
	10	3.597
	11	3.597
	12	3.597

Table S15 Summarization of the C-H...Br and C-H... π interactions between **TPA-CHO-2Br_a** and **TPA-CHO-2Br_b** crystal.

Type of Interaction	No.	d/Å
C-H...Cl	1	2.979
	2	3.954
	3	2.979
	4	3.954
	5	2.979
	6	3.954
	7	2.979
	8	3.954
	9	2.979
	10	3.954
	11	2.979
	12	3.954
	13	3.642
	14	3.372
	15	3.131
	16	3.904
	17	3.642
	18	3.372

	19	3.642
	20	3.372
	21	3.131
	22	3.904
	23	3.642
	24	3.372
	25	3.642
	26	3.372
	27	3.131
	28	3.904
	29	3.642
	30	3.372
C-H... π	1	3.637
	2	3.637
	3	3.637
	4	3.637
	5	3.637
	6	3.637
	7	3.897
	8	3.897
	9	3.897
	10	3.897
	11	3.897
	12	3.897

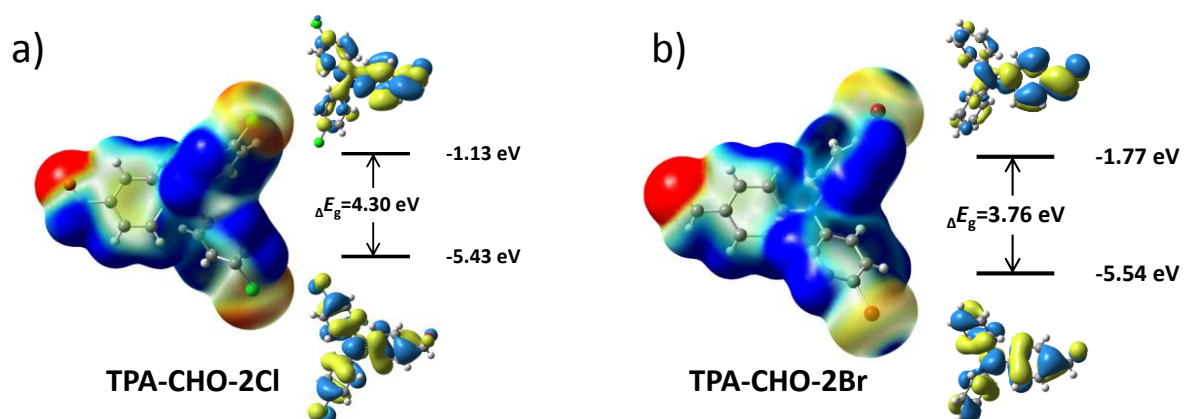


Fig. S15 a) Electrostatic potential diagram and HOMO and LUMO of **TPA-CHO-2Cl** a) and **TPA-CHO-2Br** b).