Supporting Information

Broadband Optical Limiting of Novel Twisted Tetrathiafulvalene Incorporated Donor-Acceptor Material and Their Ormosil Gel Glasses

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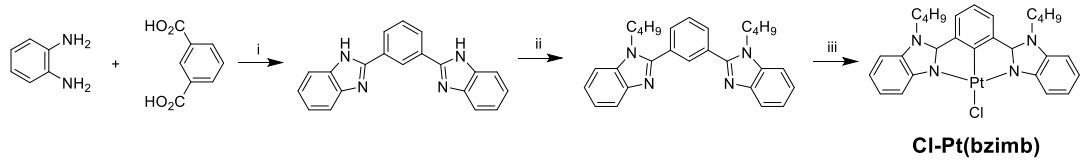
1. Characterization techniques.

All Chemicals were purchased from Alfa-Aesar, J&K, and Sigma-Aldrich, and used without further purification. All solvents were purified and dried following standard procedures unless otherwise stated. Flash chromatography was carried out with silica gel (200-300 mesh), and analytical TLC was performed with silica gel GF254 plates. ^{1}H NMR spectra were recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals.

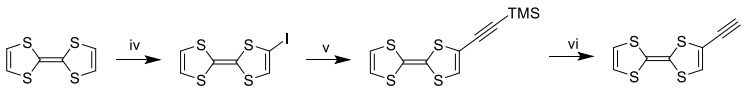
2. The synthetic procedures of compounds Cl-Pt(bzimb) and TTF-1

Compounds **TTF-1** and model compound **Cl-Pt(bzimb)** were synthesized according to previous reports.[S1] Because of the unstable properties to an acidic condition, the synthesis and characterization procedures of compound **TTF-1** and its precursor compounds should proceed under neutral or alkaline conditions.



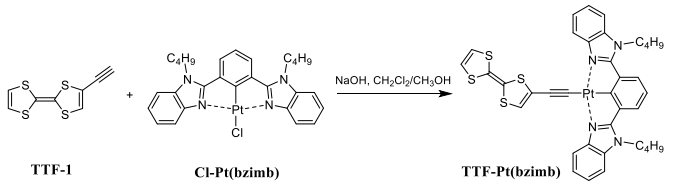
Cl-Pt(bzimb)

i: H_3PO_4, 230 °C, 5h; ii: DMF, NaH, 1-Bromobutane, 100 °C, N_2; iii: K_2PtCl_4, HOAc, H_2O, reflux, 24h.



TTF-1

iv: TMPMgCl·LiCl, THF, 25 °C; I_2; v: trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, CH_2Cl_2, rt; vi: K_2CO_3, H_2O/CH_3OH, rt.



TTF-1 **Cl-Pt(bzimb)** **TTF-Pt(bzimb)**

Scheme 1 The synthetic procedures of compounds **Cl-Pt(bzimb),** TTF-1 and **TTF-Pt(bzimb)**.

3. Thermogravimetric Analysis (TGA) of TTF-Pt(bzimb) and model compound Cl-Pt(bzimb)

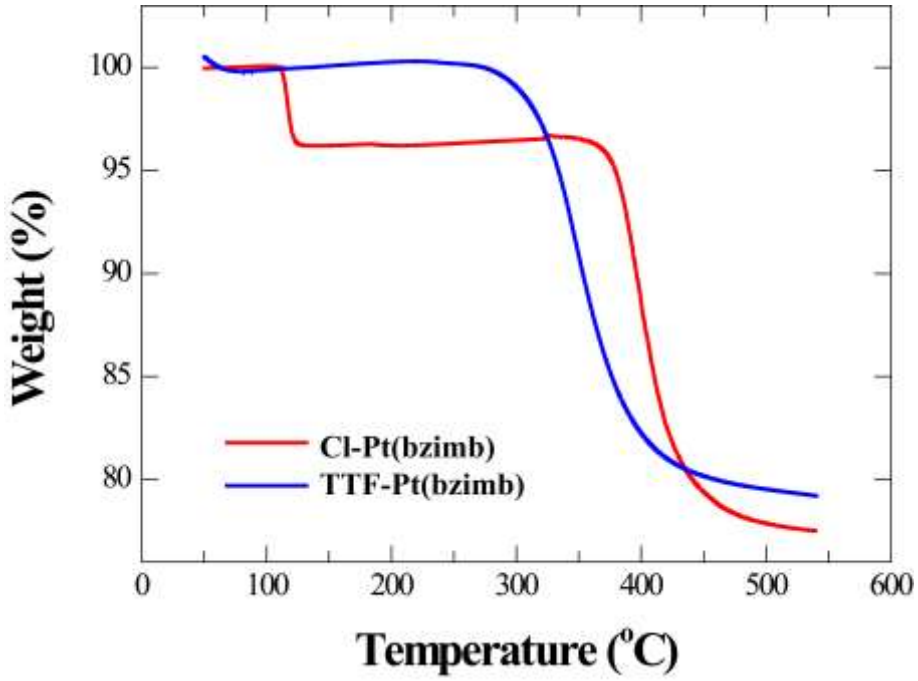


Fig. S1. TGA curves of **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)**: heating rate: 10 ^{o}C min^{-1}. From RT to 550 ^{o}C under a nitrogen atmosphere. The first mass loss of **Cl-Pt(bzimb)** at 112 ^{o}C is the loss of Cl atom, and this compound decomposed finally at 384 ^{o}C; The decomposition temperatures (5% mass loss) of **TTF-Pt(bzimb)** is of 335 ^{o}C.

4. DFT calculations

All the calculations were performed with the Gaussian 09 (Revision E.01) suite of program. [S2] Geometries optimization and frequency analysis were performed at the level of B3LYP/6-31g(d,p). Table S1 list the TD-DFT and DFT calculated HOMO/HOMO-1 and LUMO/LUMO+1, and Table S2 and S3 list the coordinates and energies at the optimized geometries of **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)**, and there were no any imaginary frequencies. Then the molecular orbitals were analyzed, the energy gaps (E_g) were obtained by $E_{LUMO} - E_{HOMO}$. Additionally, The range-separated hybrid functional CAM-B3LYP [S3] with SDD basis set[S4] for Pt atom and 6-31+G(d,p) basis set for other atoms was used for geometries optimization and Vibrational frequency analysis of **TTF-Pt(bzimb)**, and Integral Equation Formalism model (IEFPCM)[S5] was adopted to simulate the solvation effect with dichloromethane as solvent. The calculation results were listed in Fig. S4 and Table S5.

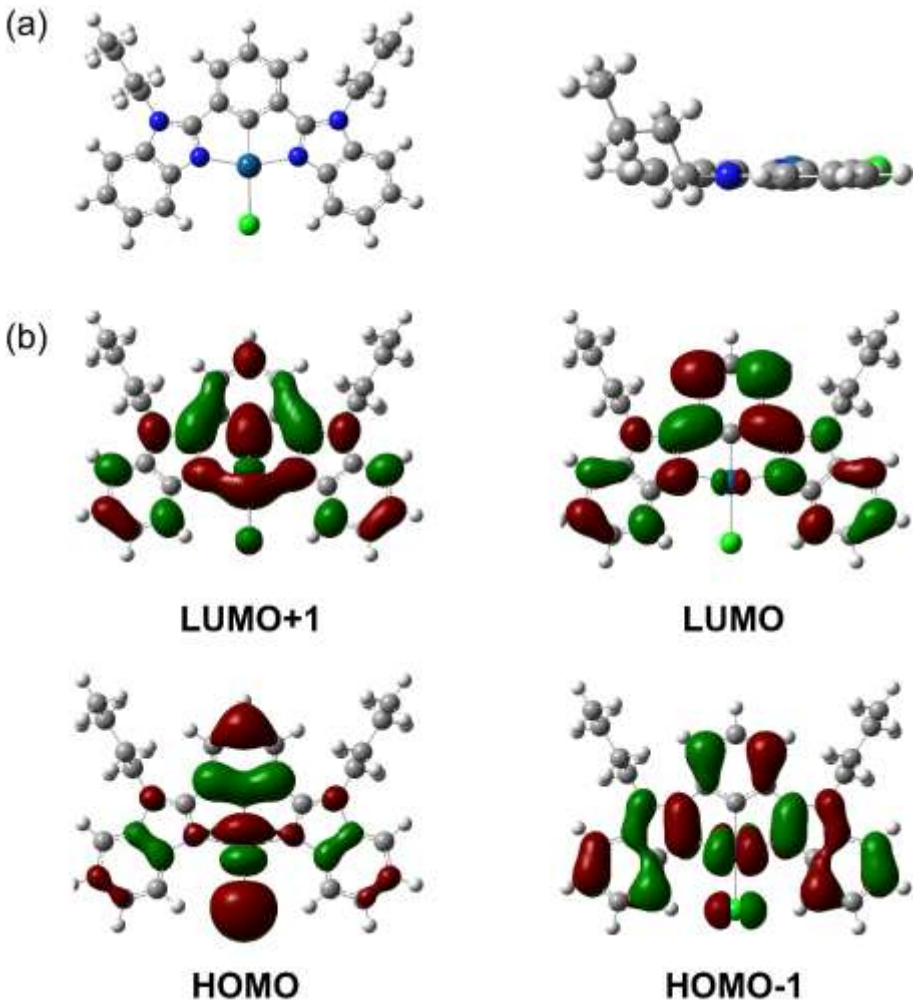


Fig. S2 The DFT calculated at the level of B3LYP/6-31g(d,p). (a) chemical structures (top and side view along Pt(bzimb) plane) and (b) the frontier molecular orbital distributions of model compound **Cl-Pt(bzimb)**.

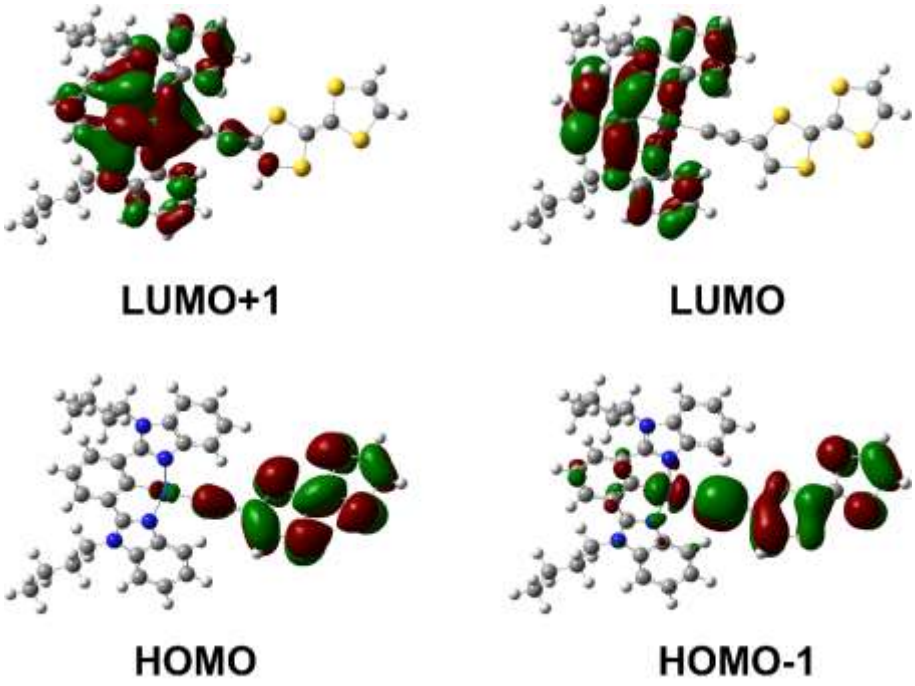


Fig. S3 The frontier molecular orbital distributions of compound **TTF-Pt(bzimb)** at the level of B3LYP/6-31g(d,p)**.**

Table S1. The calculated HOMO/HOMO-1 and LUMO/LUMO+1 energies of compound **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)** at the level of B3LYP/6-31g(d,p).

Compounds	E_{HOMO-1} [eV]	E_{HOMO} [eV]	E_{LUMO} [eV]	E_{LUMO+1} [eV]	E_g [eV]
TTF-Pt(bzimb)	-5.05	-3.96	-1.77	-1.31	2.19
Cl-Pt(bzimb)	-5.54	-5.30	-1.74	-1.22	3.56

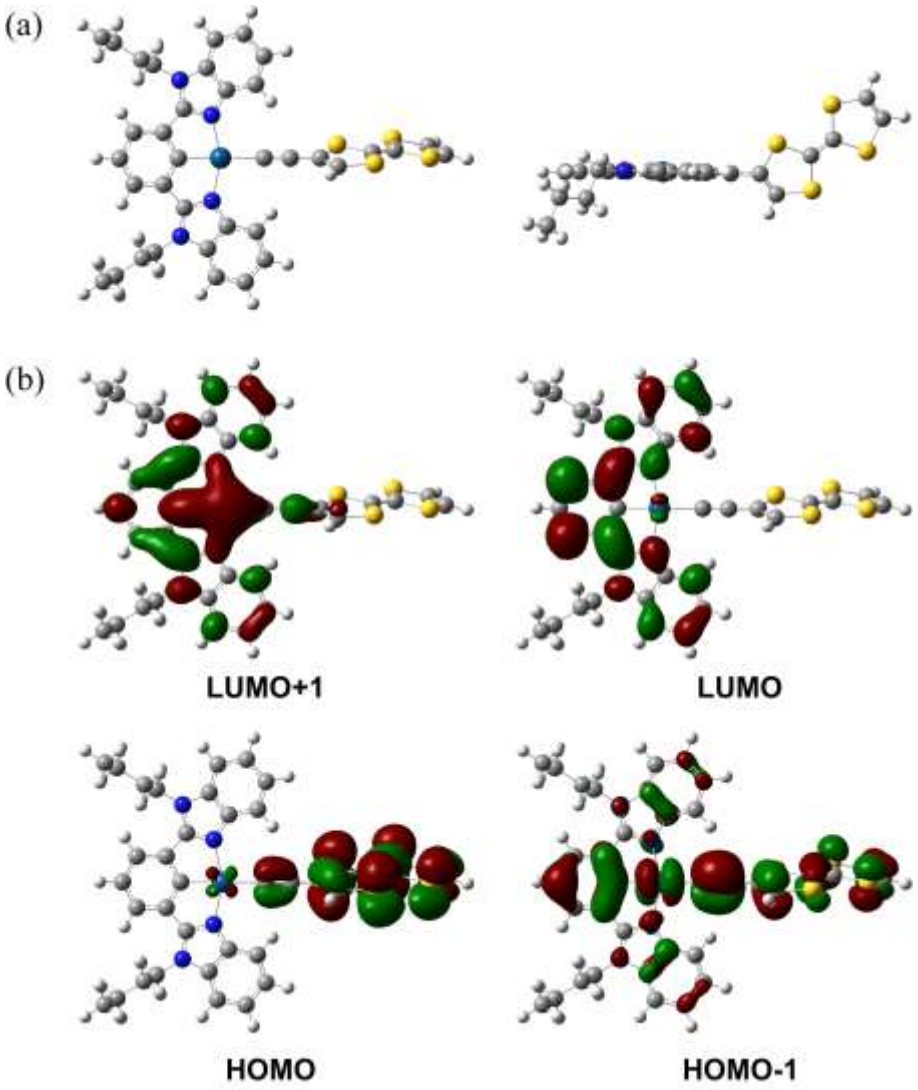


Fig. S4 The molecular structure (a) and frontier molecular orbital distributions (b) of compound **TTF-Pt(bzimb)** at the level of the range-separated hybrid functional CAM-B3LYP/6-31+g(d,p)**.**

Table S2. Coordinates and energy of compound **TTF-Pt(bzimb)** based TD-DFT calculations at the level of B3LYP/6-31g(d,p).

Labels	Atoms	X	Y	Z
1	C	-4.66848	2.06089	-0.61371
2	C	-3.30777	1.738091	-0.48557
3	C	-2.92373	0.382133	-0.44043
4	C	-3.87886	-0.65043	-0.5395
5	C	-5.23724	-0.31774	-0.66909
6	C	-5.61111	1.030278	-0.70419
7	C	-2.12324	2.588836	-0.35647
8	C	-3.20776	-1.94932	-0.46359
9	N	-1.96894	3.949064	-0.38335
10	C	-0.61421	4.221172	-0.19786
11	C	0.031161	2.971786	-0.07843
12	N	-0.92901	1.982243	-0.18257
13	N	-1.86896	-1.95602	-0.28413
14	C	-1.45897	-3.27563	-0.24541
15	C	-2.59873	-4.09257	-0.4054
16	N	-3.68417	-3.23019	-0.55217
17	C	0.092425	5.424768	-0.1324
18	C	1.469457	5.335557	0.05294
19	C	2.118852	4.089729	0.1711
20	C	1.41588	2.89218	0.108521
21	C	-0.1866	-3.83763	-0.08968
22	C	-0.10048	-5.22515	-0.09356
23	C	-1.24252	-6.03732	-0.24782
24	C	-2.51157	-5.48703	-0.40606
25	C	-3.00365	4.967172	-0.55038
26	C	-3.67504	5.373973	0.767825
27	C	-4.73826	6.4618	0.568184
28	C	-5.41324	6.879444	1.878486
29	C	-5.06846	-3.66342	-0.73039
30	C	-5.84611	-3.76702	0.588084
31	C	-7.28233	-4.26423	0.380594
32	C	-8.06813	-4.3732	1.69114
33	C	0.962026	-0.55601	0.122826
34	C	2.144917	-0.84124	0.32042
35	C	3.511173	-1.12954	0.511219
36	C	4.056086	-1.96914	1.419381
37	S	5.800627	-2.17954	1.46216
38	C	6.144074	-0.91405	0.252511
39	S	4.690565	-0.31438	-0.57908

40	C	7.392066	-0.47038	-0.01129
41	S	8.851804	-1.09105	0.816946
42	C	9.921256	0.153769	0.17193
43	C	9.425996	0.994336	-0.7431
44	S	7.743893	0.789783	-1.23081
45	H	-5.02034	3.086648	-0.62981
46	H	-6.01401	-1.07212	-0.72903
47	H	-6.66251	1.283881	-0.79762
48	H	-0.40072	6.387809	-0.2162
49	H	2.05521	6.24797	0.109991
50	H	3.194494	4.064879	0.314786
51	H	1.897563	1.925469	0.199373
52	H	0.679605	-3.19575	0.025427
53	H	0.870201	-5.69688	0.023983
54	H	-1.13155	-7.11735	-0.24264
55	H	-3.38619	-6.11926	-0.51996
56	H	-3.7377	4.596432	-1.27029
57	H	-2.52477	5.833387	-1.01683
58	H	-4.12878	4.488013	1.229386
59	H	-2.90376	5.725959	1.46396
60	H	-5.49938	6.103092	-0.13839
61	H	-4.27708	7.340249	0.096817
62	H	-6.16574	7.655396	1.707407
63	H	-5.91286	6.028944	2.355249
64	H	-4.68162	7.275277	2.591336
65	H	-5.55725	-2.97687	-1.42628
66	H	-5.03496	-4.63626	-1.22976
67	H	-5.85711	-2.78534	1.078018
68	H	-5.30809	-4.44463	1.262596
69	H	-7.80801	-3.58677	-0.30645
70	H	-7.26065	-5.24349	-0.11672
71	H	-9.08702	-4.73085	1.513533
72	H	-8.1379	-3.40203	2.193254
73	H	-7.58595	-5.07057	2.384897
74	H	3.472274	-2.54	2.130171
75	H	10.94291	0.163472	0.532081
76	H	9.99016	1.781469	-1.22863
77	Pt	-1.009803	-0.081182	-0.177445

Total energy: = -3322.2697 Hartrees

Table S3. Coordinates and energy of compound **TTF-Pt(bzimb)** based DFT calculations at the level of B3LYP/6-31g(d,p).

Labels	Atoms	X	Y	Z
1	C	-4.76371	1.856656	-0.72697
2	C	-3.39384	1.613867	-0.53606
3	C	-2.9327	0.282708	-0.47118
4	C	-3.82157	-0.80376	-0.60566
5	C	-5.18983	-0.55075	-0.79591
6	C	-5.63972	0.772924	-0.85524
7	C	-2.26787	2.533708	-0.36337
8	C	-3.08044	-2.0616	-0.4954
9	N	-2.19489	3.901068	-0.38089
10	C	-0.86723	4.253139	-0.1421
11	C	-0.15242	3.044336	-0.00162
12	N	-1.0467	1.999138	-0.14496
13	N	-1.75055	-1.98971	-0.26967
14	C	-1.26722	-3.2835	-0.20357
15	C	-2.35209	-4.16572	-0.39596
16	N	-3.47942	-3.36852	-0.58928
17	C	-0.23809	5.496691	-0.04631
18	C	1.133785	5.490187	0.191244
19	C	1.852673	4.285378	0.329975
20	C	1.226635	3.047856	0.236824
21	C	0.028426	-3.77078	0.003138
22	C	0.194198	-5.15096	0.014053
23	C	-0.89294	-6.02833	-0.17489
24	C	-2.18479	-5.55263	-0.3829
25	C	-3.28126	4.858095	-0.57941
26	C	-4.02219	5.217238	0.714965
27	C	-5.11801	6.26533	0.484733
28	C	-5.8686	6.634018	1.767876
29	C	-4.83254	-3.88245	-0.79205
30	C	-5.63504	-4.0007	0.509657
31	C	-7.03855	-4.57653	0.283474
32	C	-7.84313	-4.70269	1.580721
33	C	0.982962	-0.43473	0.20349
34	C	2.174159	-0.66236	0.42416
35	C	3.549265	-0.8882	0.640634
36	C	4.11084	-1.65534	1.601615
37	S	5.859824	-1.79341	1.684709
38	C	6.180933	-0.67177	0.334302
39	S	4.706895	-0.0827	-0.47234

40	C	7.427392	-0.31251	-0.04016
41	S	8.907487	-0.91346	0.770018
42	C	10.01311	0.059342	-0.19572
43	C	9.497977	0.827047	-1.16243
44	S	7.753081	0.80771	-1.39792
45	H	-5.17218	2.860306	-0.76535
46	H	-5.91838	-1.3485	-0.8888
47	H	-6.69873	0.964113	-0.99832
48	H	-0.78511	6.428638	-0.1454
49	H	1.660634	6.436005	0.273139
50	H	2.921572	4.326089	0.514589
51	H	1.7612	2.110502	0.340344
52	H	0.851386	-3.07921	0.144484
53	H	1.185438	-5.56515	0.170501
54	H	-0.72074	-7.10017	-0.15732
55	H	-3.01656	-6.23512	-0.52409
56	H	-3.96575	4.450475	-1.32737
57	H	-2.83757	5.754329	-1.02362
58	H	-4.45819	4.307504	1.146747
59	H	-3.29472	5.589314	1.447315
60	H	-5.83216	5.890383	-0.2618
61	H	-4.67056	7.168647	0.048126
62	H	-6.64593	7.379031	1.572034
63	H	-6.35183	5.755765	2.210023
64	H	-5.18877	7.050972	2.518943
65	H	-5.34146	-3.23902	-1.51416
66	H	-4.73214	-4.8616	-1.26974
67	H	-5.70894	-3.01043	0.976564
68	H	-5.07854	-4.63379	1.211992
69	H	-7.58487	-3.93986	-0.42629
70	H	-6.95623	-5.56203	-0.19495
71	H	-8.83976	-5.11285	1.390868
72	H	-7.96946	-3.72782	2.06447
73	H	-7.34066	-5.36393	2.295198
74	H	3.538928	-2.20083	2.341363
75	H	11.0685	-0.0181	0.03604
76	H	10.07791	1.458765	-1.82441
77	Pt	-1.00543	-0.06815	-0.14311

Total energy: = -3322.2689 Hartrees

Table S4. Coordinates and energy of compound **Cl-Pt(bzimb)** based DFT calculations at the level of B3LYP/6-31g(d,p).

Labels	Atoms	X	Y	Z
1	C	-4.66848	2.06089	-0.61371
2	C	-3.30777	1.738091	-0.48557
3	C	-2.92373	0.382133	-0.44043
4	C	-3.87886	-0.65043	-0.5395
5	C	-5.23724	-0.31774	-0.66909
6	C	-5.61111	1.030278	-0.70419
7	C	-2.12324	2.588836	-0.35647
8	C	-3.20776	-1.94932	-0.46359
9	N	-1.96894	3.949064	-0.38335
10	C	-0.61421	4.221172	-0.19786
11	C	0.031161	2.971786	-0.07843
12	N	-0.92901	1.982243	-0.18257
13	N	-1.86896	-1.95602	-0.28413
14	C	-1.45897	-3.27563	-0.24541
15	C	-2.59873	-4.09257	-0.4054
16	N	-3.68417	-3.23019	-0.55217
17	C	0.092425	5.424768	-0.1324
18	C	1.469457	5.335557	0.05294
19	C	2.118852	4.089729	0.1711
20	C	1.41588	2.89218	0.108521
21	C	-0.1866	-3.83763	-0.08968
22	C	-0.10048	-5.22515	-0.09356
23	C	-1.24252	-6.03732	-0.24782
24	C	-2.51157	-5.48703	-0.40606
25	C	-3.00365	4.967172	-0.55038
26	C	-3.67504	5.373973	0.767825
27	C	-4.73826	6.4618	0.568184
28	C	-5.41324	6.879444	1.878486
29	C	-5.06846	-3.66342	-0.73039
30	C	-5.84611	-3.76702	0.588084
31	C	-7.28233	-4.26423	0.380594
32	C	-8.06813	-4.3732	1.69114
33	H	-5.02034	3.086648	-0.62981
34	H	-6.01401	-1.07212	-0.72903
35	H	-6.66251	1.283881	-0.79762
36	H	-0.40072	6.387809	-0.2162
37	H	2.05521	6.24797	0.109991
38	H	3.194494	4.064879	0.314786
39	H	1.897563	1.925469	0.199373

40	H	0.679605	-3.19575	0.025427
41	H	0.870201	-5.69688	0.023983
42	H	-1.13155	-7.11735	-0.24264
43	H	-3.38619	-6.11926	-0.51996
44	H	-3.7377	4.596432	-1.27029
45	H	-2.52477	5.833387	-1.01683
46	H	-4.12878	4.488013	1.229386
47	H	-2.90376	5.725959	1.46396
48	H	-5.49938	6.103092	-0.13839
49	H	-4.27708	7.340249	0.096817
50	H	-6.16574	7.655396	1.707407
51	H	-5.91286	6.028944	2.355249
52	H	-4.68162	7.275277	2.591336
53	H	-5.55725	-2.97687	-1.42628
54	H	-5.03496	-4.63626	-1.22976
55	H	-5.85711	-2.78534	1.078018
56	H	-5.30809	-4.44463	1.262596
57	H	-7.80801	-3.58677	-0.30645
58	H	-7.26065	-5.24349	-0.11672
59	H	-9.08702	-4.73085	1.513533
60	H	-8.1379	-3.40203	2.193254
61	H	-7.58595	-5.07057	2.384897
62	Pt	-1.0098	-0.08118	-0.17745
63	Cl	1.182933	-0.60921	0.156466

Total energy: = -1883.2225 Hartrees

Table S5. Coordinates and energy of compound **TTF-Pt(bzimb)** based DFT calculations at the level of the range-separated hybrid functional CAM-B3LYP/6-31+g(d,p).

Labels	Atoms	X	Y	Z
1	C	1.87302	0.1781	-0.63579
2	C	3.26184	0.21239	-0.79309
3	C	3.90592	1.44734	-0.8844
4	C	3.20022	2.64999	-0.82171
5	C	1.81105	2.61771	-0.66617
6	C	1.15859	1.38154	-0.5657
7	H	3.86253	-0.68765	-0.83552
8	H	4.98392	1.4732	-1.00033
9	H	3.75542	3.57776	-0.8841
10	C	0.8306	3.70505	-0.56213
11	C	-1.18236	4.53441	-0.29513
12	C	-0.29429	5.60742	-0.45993
13	C	-2.54817	4.7569	-0.10487
14	C	-0.72704	6.9334	-0.43832
15	C	-2.98104	6.07312	-0.08335
16	H	-3.22624	3.92069	0.01778
17	C	-2.08425	7.14635	-0.24736
18	H	-0.04207	7.76487	-0.56004
19	H	-4.03536	6.28411	0.06261
20	H	-2.46254	8.16293	-0.22292
21	C	0.94954	-0.9546	-0.50041
22	C	-1.01741	-1.87866	-0.20454
23	C	-0.07449	-2.90877	-0.33551
24	C	-2.36938	-2.16571	-0.00287
25	C	-0.43735	-4.25407	-0.26888
26	C	-2.7331	-3.50124	0.06235
27	H	-3.08986	-1.36264	0.09654
28	C	-1.78159	-4.53107	-0.06853
29	H	0.29056	-5.05205	-0.36317
30	H	-3.77475	-3.76186	0.21858
31	H	-2.10633	-5.56461	-0.00957
32	C	2.18702	5.82718	-0.851
33	C	2.93769	6.13276	0.44278
34	H	1.88907	6.75381	-1.34671
35	H	2.81536	5.28867	-1.56214
36	C	4.18128	6.98456	0.19264
37	H	2.26271	6.65329	1.13203
38	H	3.2217	5.19376	0.93234

39	C	4.94492	7.29772	1.47727
40	H	4.84405	6.46506	-0.51079
41	H	3.8863	7.92102	-0.29672
42	H	5.82854	7.90908	1.27338
43	H	4.315	7.84553	2.18579
44	H	5.27975	6.37928	1.9705
45	C	2.41758	-3.00929	-0.7131
46	C	3.18246	-3.21265	0.59258
47	H	3.01525	-2.46904	-1.44894
48	H	2.17214	-3.97237	-1.16612
49	C	4.48561	-3.98139	0.37913
50	H	3.39601	-2.23807	1.04706
51	H	2.5426	-3.75376	1.29925
52	C	5.25446	-4.20198	1.67983
53	H	4.26359	-4.95028	-0.08488
54	H	5.11862	-3.43666	-0.33263
55	H	6.182	-4.75367	1.50257
56	H	5.51669	-3.24803	2.14907
57	H	4.65709	-4.7732	2.39795
58	N	1.15648	-2.29462	-0.53059
59	N	-0.35127	-0.6745	-0.31326
60	N	-0.45395	3.36386	-0.36449
61	N	0.96728	5.05241	-0.63594
62	Pt	-0.80297	1.33489	-0.28483
63	C	-2.83929	1.29182	0.01565
64	C	-4.05044	1.27673	0.20701
65	C	-5.4542	1.24626	0.39716
66	C	-6.133	1.64782	1.4849
67	S	-6.44365	0.57567	-0.92796
68	H	-5.66187	2.05457	2.37046
69	C	-8.00587	0.92405	-0.1694
70	S	-7.8767	1.47887	1.51063
71	C	-9.18244	0.77455	-0.80198
72	S	-9.31449	0.20853	-2.4809
73	C	-11.68141	0.91865	-1.5077
74	C	-11.04025	0.51187	-2.60257
75	H	-12.74401	1.11989	-1.45415
76	H	-11.50962	0.33689	-3.56256
77	S	-10.74758	1.11797	-0.03341

Total energy: = -3321.3154 Hartrees

5. The partial UV-vis spectra of compound TTF-Pt(bzimb) and Cl-Pt(bzimb)

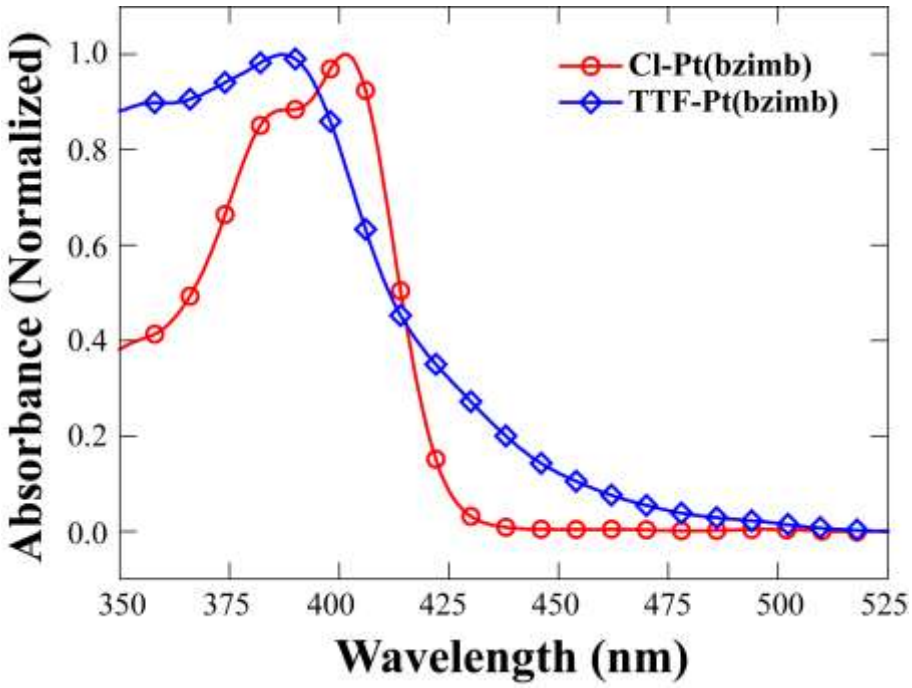


Fig. S5 The partial normalized UV-vis spectra of compound **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)** at the wavelength of 350-525 nm.

6. Cyclic voltammograme of TTF-Pt(bzimb) and Cl-Pt(bzimb).

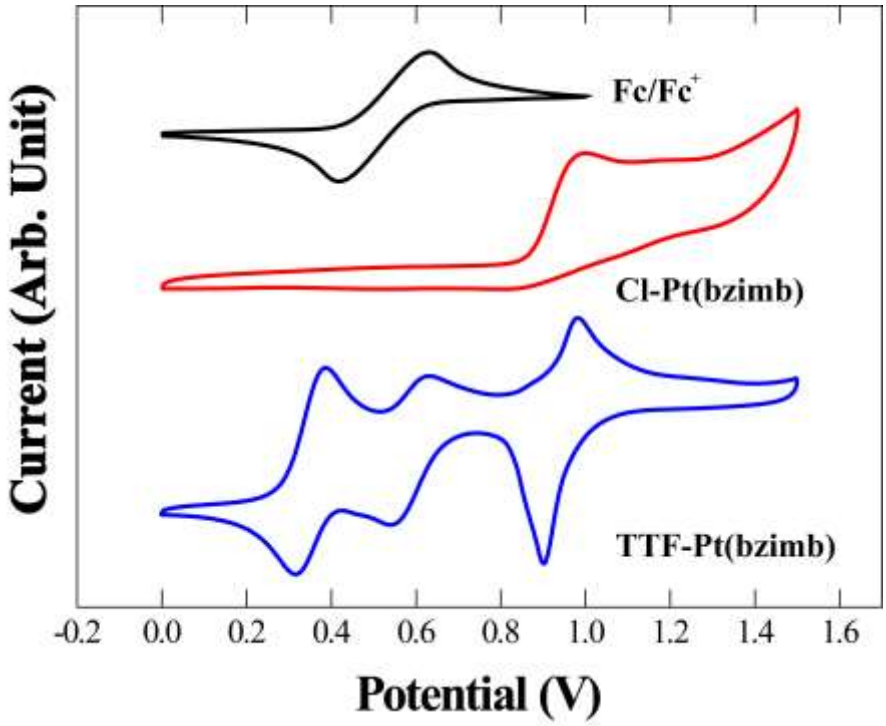


Fig. S6 Cyclic voltammograme of **TTF-Pt(bzimb)** and **Cl-Pt(bzimb)**. (condition: *c* = 5 × 10^{-4} M in CH_2Cl_2 solution, (*n*-Bu)$_4NPF_6$ was used as supporting electrolyte; Pt/C as working electrode, Pt as counter electrode, and Ag/Ag^+ as reference electrode; scan speed 50 mV s^{-1}; V *vs* Fc/Fc^+; temperature 25 ^oC).

7. Z-scan measurements

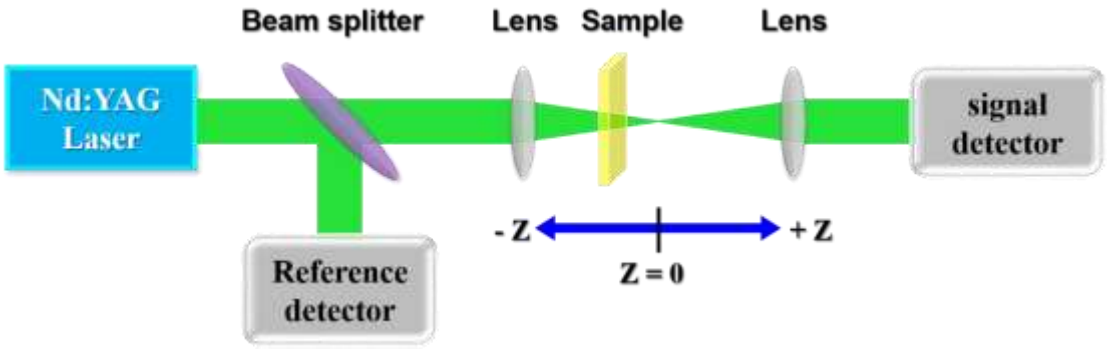


Fig. S7 The typical double-beams experimental arrangement of Z-scan measurement

The detail description of Z-scan measurement: The Z-scan method was introduced in 1989 by Sheik-Bahae *et al.*[S6] using to determine the magnitude of the excited-state absorption cross-section, nonlinear absorption coefficient and the sign and magnitude of the nonlinear refractive index. In this work, the optical performances are collected using Z-scan technology with FWHM of 8 ns laser pulses with a repetition frequency of 10 Hz from an Nd:YAG laser (Spectra-Physics Quanta-Ray INDI Pulsed Nd:YAG Laser, optical parametric oscillator) under wavelength of 532 and 1064 nm. The spatial and temporal profiles of the laser pulses presented an approximately Gaussian distribution. As shown in Fig. S7, the laser beam has been divided into two beams: one laser beam is collected directly by reference detector to monitor energy fluctuations. Meanwhile, another beam is focused with the lens on samples to detect the transmittance as the sample is scanned through the Z-direction to tune the intensities on it. Herein, our measurements were processed under the open-aperture configuration. The Z-scan curves, which are the normalized transmittance as a function of the sample position (Z), were measured with an open aperture.

8. Reference

[S1] (a) J. Nafe, F. Auras, K. Karaghiosoff, T. Bein, P. Knochel, *Org. Lett.* , **2015**, *17*, 5356; (b) C. Goze, S. Liu, C. Leiggener, L. Sanguinet, E. Levillain, A. Hauser, S. Decurtins, *Tetrahedron*, **2008**, *64*, 1345; (c) F. K. Kong, M. C. Tang, Y. C. Wong, M. Y. Chan, V. W. Yam, *J. Am. Chem. Soc.*, **2016**, *138*, 6281.

[S2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

[S3] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, A Long-Range Corrected Time-Dependent Density Functional Theory. *J. Chem. Phys.*, 2004, **120**, 8425.

[S4](a) D. Andrae, U. Haussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta. 1990, 77, 123. (b) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866.

[S5] J. Tomasi, B. Mennucci and R. Cammi, Quantum Mechanical Continuum Solvation Models. *Chem. Rev.*, 2005, **105**, 2999.

[S6] (a) M. Sheik-Bahae, A. A. Said and E. W. Van Stryland, *Opt. Lett.*, **1989**, *14*, 955; (b) M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, **1990**, *26*, 760.

9. ^{1}H and ^{13}C NMR spectra of compound TTF-Pt(bzimb)

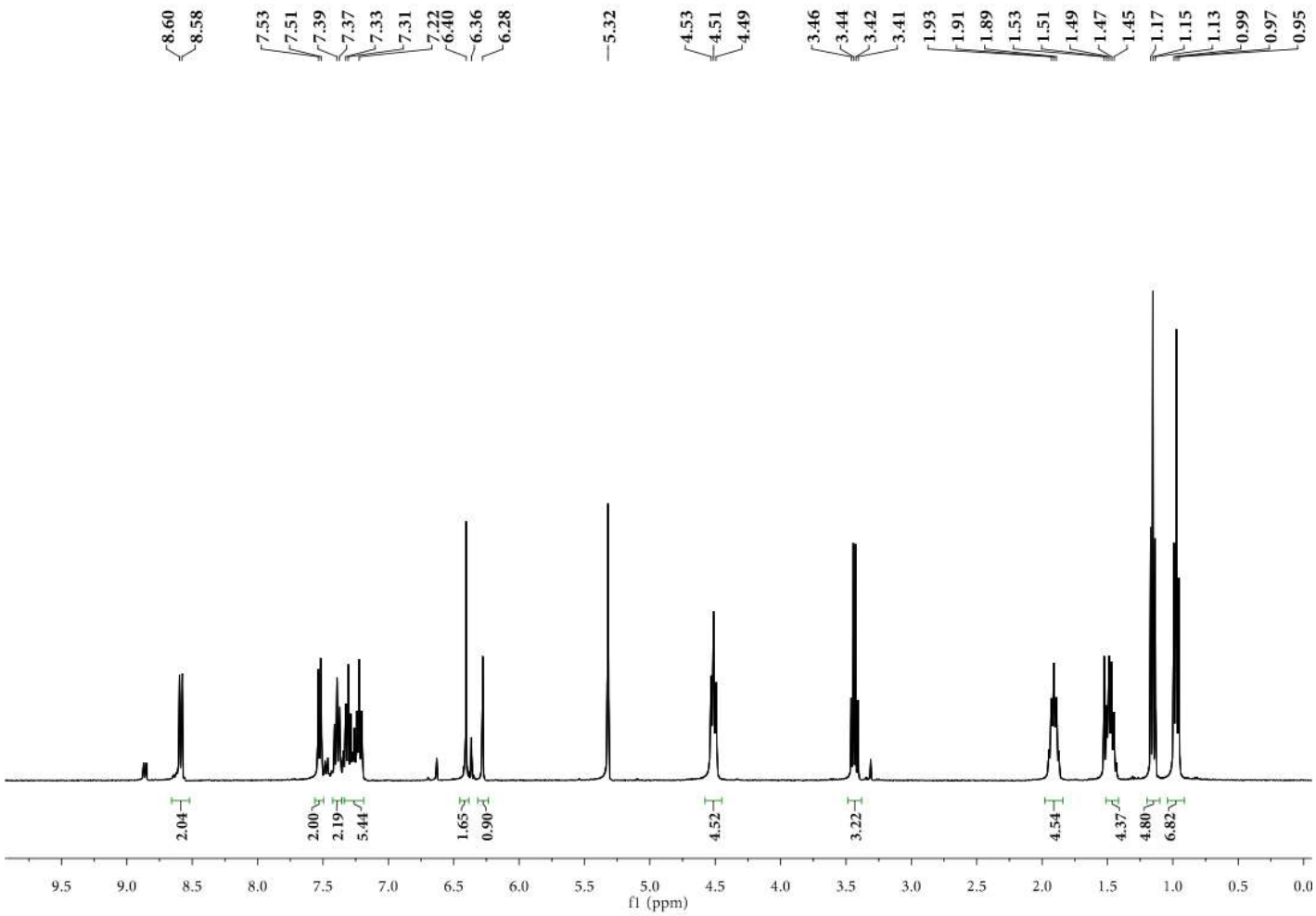


Figure S8. ^{1}H NMR spectrum of compound **TTF-Pt(bzimb)** (400 MHz, CD_2Cl_2).

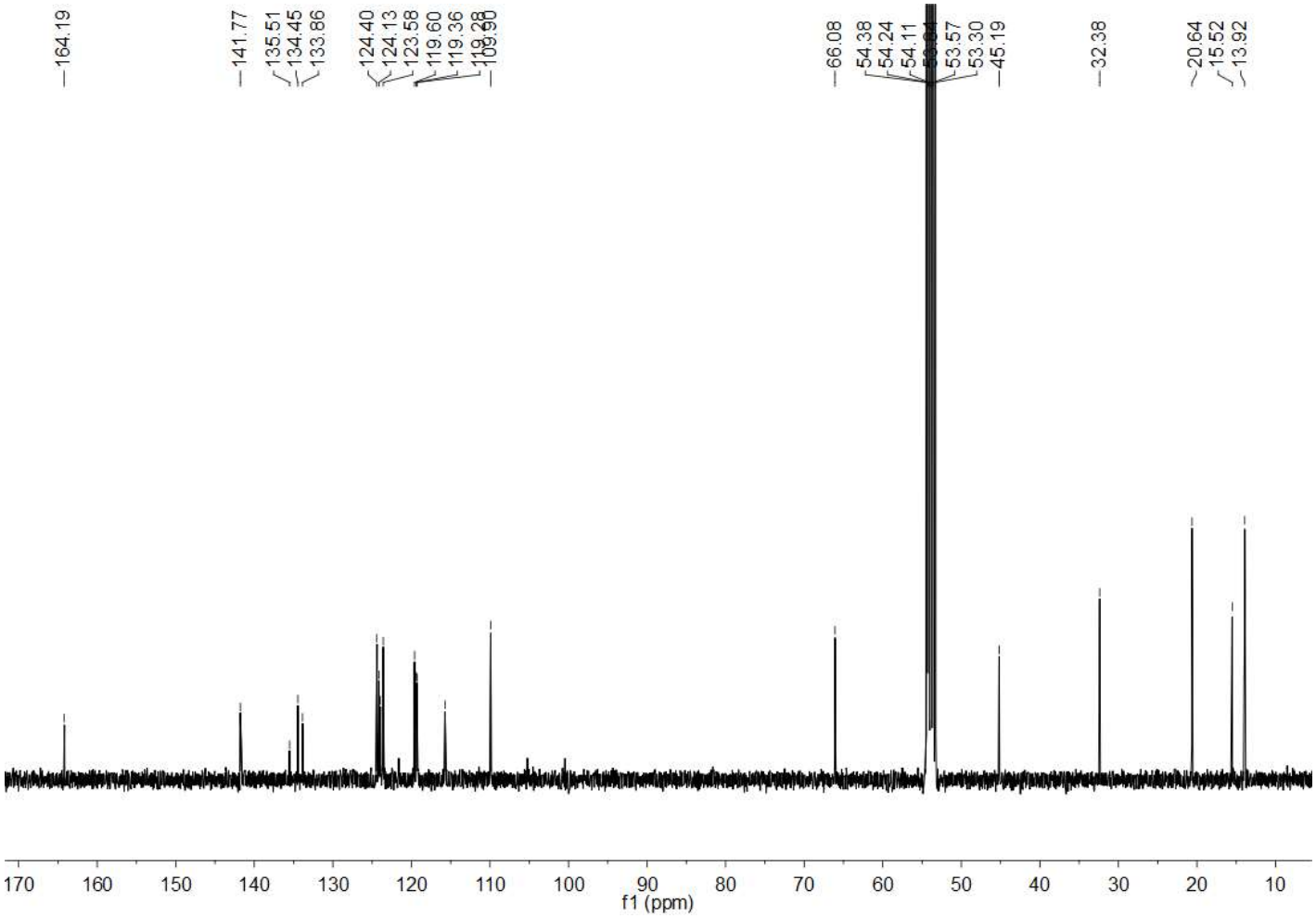


Fig. S9 ^{13}C NMR spectrum of compound **TTF-Pt(bzimb)** (100 MHz, CD_2Cl_2)

10. FTIR spectrum of compound TTF-Pt(bzimb)

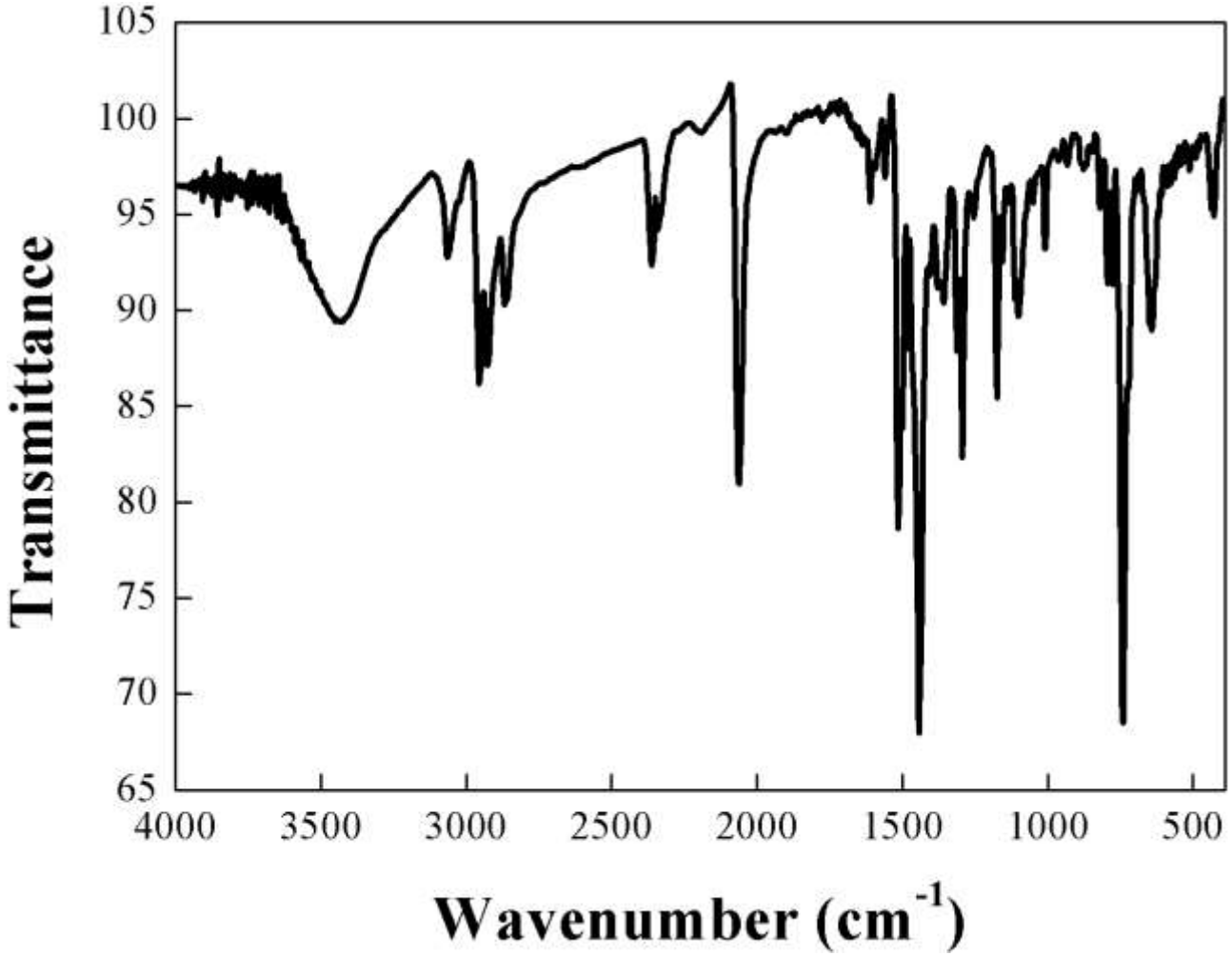


Fig. S10 FTIR spectrum of compound **TTF-Pt(bzimb)**