Strategic Design of Thiophene-Fused Nickel Dithiolene Derivatives for Efficient NLO Response

Manoj Majumder and Anirban Misra*

Department of Chemistry, University of North Bengal, Darjeeling, 734013, West Bengal, India

***Phone: +919434228745; Email: anirbanmisra@yahoo.com**

Electronic Supplementary Information

X, Y, Z cartesian co-ordinate of the Optimized geometry of our studied systems.

1. Optimized minimum energy geometry of Th-NiTDT (1a)

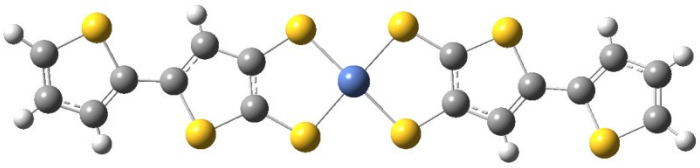

Figure S1. Thienyl expanded NiTDT (1a)

Atom	Bohr		
	X	Y	Z
Ni	0.00330600	0.07497000	-0.27086700
S	7.49106600	-1.48475600	0.37759800
S	4.47937600	1.67644700	0.01008800
S	1.40341600	1.73206000	-0.12581500
S	1.58628800	-1.39820600	-0.44762900
S	-1.61464900	1.53557900	-0.28137200

S	-1.34508500	-1.62557500	-0.07145200
S	-4.41859100	-1.66318800	0.11898000
S	-7.58727400	1.33222800	0.44101600
C	9.02163200	-0.72910700	0.53678300
C	6.72571600	0.04909000	0.13019600
C	5.26642200	0.11910900	-0.05122700
C	2.90996000	0.92773800	-0.16957800
C	3.03316500	-0.45636600	-0.29814200
C	4.39325700	-0.94168300	-0.23276300
H	4.64576200	-1.83395500	-0.30412700
C	-3.02340600	0.53052700	-0.11406400
C	-2.87127800	-0.84488800	-0.00130300
C	-5.27239200	-0.13559400	0.01639300
C	-6.73926700	-0.14543700	0.10274100
C	-9.10213200	0.50038600	0.42557400
C	-8.94231600	-0.81506700	0.17168000
H	-9.64971400	-1.41676700	0.11589400
C	-7.60004000	-1.18509700	-0.00330300
H	-7.33021900	-2.05818500	-0.17200200
C	-4.41396600	0.96048200	-0.10066100
H	-4.69299700	1.84687000	-0.16206700
C	7.64586700	1.04710400	0.17228800
H	7.42821000	1.94404000	0.05779700
C	8.97037300	0.59925000	0.40696400
H	9.70995700	1.15864300	0.46318800
H	-10.01972000	1.04731000	0.58228400
H	9.89381600	-1.34321400	0.71121800

2. Optimized minimum energy geometry of nTh-NiTDT (1b)

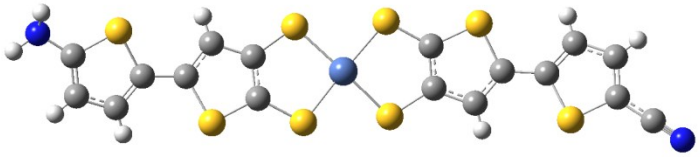

Figure S2. Neutral substituted thienyl expanded NiTDT (1b)

Atom	Bohr		
	X	Y	Z
Ni	-0.16608700	0.12181700	-0.32380300
S	7.37974300	-1.16013200	0.24676900
S	4.24525400	1.88878200	-0.02317400
S	1.16870600	1.82824000	-0.14272500
S	1.47191400	-1.28330700	-0.54574200
S	-1.84032800	1.51768900	-0.28795800
S	-1.44640400	-1.63426600	-0.16168300
S	-4.51502500	-1.79711700	0.04398100
S	-7.79514200	1.06281900	0.45909500
C	8.88073900	-0.35025800	0.41817400
C	6.55428300	0.34841000	0.04284200
C	5.09231400	0.36592900	-0.12894700
C	2.70539700	1.08469000	-0.21522600
C	2.88148500	-0.28991500	-0.37971000
C	4.25966600	-0.72331100	-0.33377200
H	4.54668700	-1.60272800	-0.42928400
C	-3.20767200	0.45505000	-0.13957200
C	-3.00149600	-0.91623400	-0.06304500
C	-5.42798200	-0.30218300	-0.01553400
C	-6.89325400	-0.37091200	0.07847700

C	-9.27652400	0.17324400	0.42979400
C	-9.06755500	-1.12764300	0.14051600
H	-9.75172100	-1.75490700	0.07313000
C	-7.71295500	-1.44025600	-0.05040400
H	-7.41026800	-2.29759700	-0.24352700
C	-4.61387300	0.82957200	-0.10856900
H	-4.92712700	1.70527600	-0.14484600
C	7.43485100	1.37978800	0.10619400
H	7.18221900	2.27082000	0.01638300
C	8.77705100	0.97846300	0.32324000
H	9.49475500	1.56489500	0.38982700
N	-10.49898200	0.85050100	0.59082800
H	-10.51665200	1.49321900	1.37321400
H	-11.28645200	0.21761600	0.64671600
C	10.07353000	-1.08462900	0.61837700
N	11.05205000	-1.68330800	0.78500800

3. Optimized minimum energy geometry of zTh-NiTDT (1c)

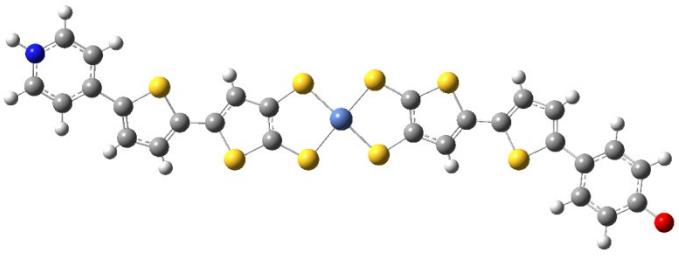

Figure S3. Ionic substituted thienyl expanded NiTDT (1c)

Atom	Bohr		
	X	Y	Z
Ni	0.00330600	0.07497000	-0.27086700
S	7.49106600	-1.48475600	0.37759800

S	4.47937600	1.67644700	0.01008800
S	1.40341600	1.73206000	-0.12581500
S	1.58628800	-1.39820600	-0.44762900
S	-1.61464900	1.53557900	-0.28137200
S	-1.34508500	-1.62557500	-0.07145200
S	-4.41859100	-1.66318800	0.11898000
S	-7.58727400	1.33222800	0.44101600
C	9.02163200	-0.72910700	0.53678300
C	6.72571600	0.04909000	0.13019600
C	5.26642200	0.11910900	-0.05122700
C	2.90996000	0.92773800	-0.16957800
C	3.03316500	-0.45636600	-0.29814200
C	4.39325700	-0.94168300	-0.23276300
H	4.64576200	-1.83395500	-0.30412700
C	-3.02340600	0.53052700	-0.11406400
C	-2.87127800	-0.84488800	-0.00130300
C	-5.27239200	-0.13559400	0.01639300
C	-6.73926700	-0.14543700	0.10274100
C	-9.10213200	0.50038600	0.42557400
C	-8.94231600	-0.81506700	0.17168000
H	-9.64971400	-1.41676700	0.11589400
C	-7.60004000	-1.18509700	-0.00330300
H	-7.33021900	-2.05818500	-0.17200200
C	-4.41396600	0.96048200	-0.10066100
H	-4.69299700	1.84687000	-0.16206700
C	7.64586700	1.04710400	0.17228800
H	7.42821000	1.94404000	0.05779700
C	8.97037300	0.59925000	0.40696400
H	9.70995700	1.15864300	0.46318800
C	10.26431140	-1.60408077	0.78531632
C	10.13185931	-2.98855737	0.89555425

C	11.52225936	-1.01252460	0.90010474
C	11.25706491	-3.78115864	1.12120289
H	9.13987580	-3.45455160	0.80577735
C	12.64804085	-1.80531720	1.12483973
H	11.62685686	0.07862756	0.81306824
C	12.51563353	-3.18942410	1.23553490
H	11.15265901	-4.87236661	1.20873055
H	13.63980543	-1.33866132	1.21489259
C	-10.41096447	1.28050942	0.64910257
C	-10.37107082	2.65208412	0.90141738
C	-11.63629058	0.61595325	0.59921125
C	-11.55624510	3.35873850	1.10445248
H	-9.40484190	3.17557325	0.94144968
C	-12.82197628	1.32285899	0.80130918
H	-11.66792631	-0.46502587	0.40018276
H	-11.52484264	4.43971414	1.30395703
H	-13.78796975	0.79869624	0.76150635
H	-13.71648123	3.25141127	1.21409761
N	-12.78214157	2.69401840	1.05403848
O	13.66913133	-4.00235199	1.4668163

4. Optimized minimum energy geometry of Ph-NiTDT (2a)

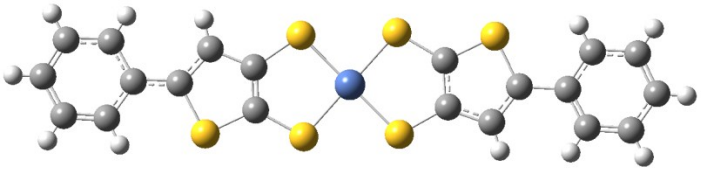

Figure S4. Phenyl expanded NiTDT (2a)

Atom	Bohr		
	X	Y	Z
Ni	1.02100000	5.44800000	4.03400000
S	0.15200000	6.38900000	5.77900000

S	2.77400000	6.68100000	4.39800000
S	-3.38200000	4.11500000	5.15800000
S	-0.71700000	4.24100000	3.65400000
S	1.90900000	4.48700000	2.29600000
S	5.43100000	6.76700000	2.90100000
C	6.92400000	5.78100000	0.74100000
C	7.93500000	6.65300000	1.12600000
H	7.80400000	7.21300000	1.85800000
C	9.15000000	6.70200000	0.42400000
H	9.83100000	7.27600000	0.69300000
C	9.31000000	5.87800000	-0.66800000
H	10.08500000	5.92100000	-1.18100000
C	8.29800000	4.98000000	-0.99200000
H	8.42400000	4.39100000	-1.70000000
C	7.12800000	4.94600000	-0.29500000
H	6.46500000	4.34100000	-0.53800000
C	-4.84200000	5.05900000	7.30700000
C	-5.85000000	4.11800000	7.01700000
H	-5.73800000	3.55000000	6.28900000
C	-6.96400000	4.00900000	7.75200000
H	-7.60400000	3.37600000	7.52300000
C	-7.17800000	4.82300000	8.84700000
H	-7.96100000	4.74100000	9.34300000
C	-6.25100000	5.73400000	9.19300000
H	-6.39100000	6.27300000	9.93700000
C	-5.08300000	5.87800000	8.44900000
H	-4.45400000	6.51400000	8.69900000
C	3.83200000	6.16200000	3.12700000
C	3.49500000	5.16500000	2.14200000
C	4.54300000	4.93000000	1.18400000
H	4.50700000	4.32700000	0.47700000

C	5.61800000	5.76000000	1.49600000
C	-2.45300000	5.93300000	6.82200000
H	-2.35300000	6.54200000	7.51800000
C	-3.61600000	5.15400000	6.56700000
C	-1.42900000	5.61600000	5.80900000
C	-1.78400000	4.71300000	4.91000000

5. Optimized minimum energy geometry of nPh-NiTDT (2b)

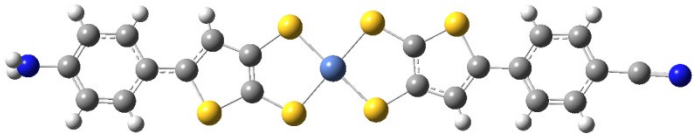

Figure S5. Neutral substituted Phenyl expanded NiTDT (1b)

Atom	Bohr		
	X	Y	Z
Ni	-0.48339625	5.90987938	-1.47930245
S	-2.06614785	6.90572311	-0.38895405
S	0.90484888	7.07261223	-0.27654654
S	-4.91218570	4.77443947	-2.71351243
S	-1.84959365	4.77231780	-2.68816610
S	1.11148722	4.89333925	-2.55433821
S	3.95535528	7.03093985	-0.24956336
C	6.28340403	5.95946604	-1.38929048
C	7.00352628	6.79274221	-0.54205689
H	6.54872982	7.36584601	0.03352735
C	8.40756721	6.78315635	-0.54473672
H	8.88725964	7.33119259	0.03418422
C	9.05583030	5.94107615	-1.42091930
C	8.30336321	5.08254587	-2.21605642
H	8.74066092	4.48094535	-2.77364814

C	6.94141082	5.10518363	-2.19512274
H	6.46305824	4.52571478	-2.74287967
C	-7.20792795	5.80245244	-1.56734757
C	-7.97566647	4.90117429	-2.33149433
H	-7.53965145	4.32091563	-2.91316673
C	-9.31118573	4.84696809	-2.25054986
H	-9.77776405	4.23872136	-2.77502158
C	-10.00812637	5.68134510	-1.39878361
C	-9.33969040	6.55665647	-0.62678014
H	-9.80913671	7.10928930	-0.04551073
C	-7.95146053	6.64347565	-0.68823139
H	-7.50474661	7.25541278	-0.15100089
C	2.43272151	6.49576832	-0.85708277
C	2.59003546	5.50278775	-1.89006143
C	3.96514873	5.21358464	-2.20105666
H	4.26106770	4.60477046	-2.83865470
C	4.77531605	6.00141494	-1.38569090
C	-4.86085770	6.57051032	-0.78775129
H	-5.09561979	7.18252484	-0.12773463
C	-5.77350696	5.83794094	-1.59697836
C	-3.48254784	6.19977256	-1.15930132
C	-3.37974854	5.30241409	-2.12564239
N	-11.47523762	5.61233392	-1.33721873
C	10.59280332	5.94913299	-1.51709113
H	-12.02814262	6.14243984	-1.98009024
H	-11.92035174	5.03528235	-0.65246701
N	12.05991393	5.95682361	-1.60889152

6. Optimized minimum energy geometry of zPh-NiTDT (2c)

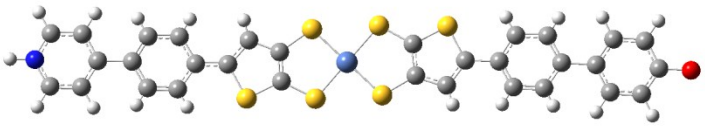

Figure S6. Ionic substituted Phenyl expanded NiTDT (2c)

Atom	Bohr		
	X	Y	Z
Ni	-0.27429200	0.03643100	-0.07163100
S	-1.83914500	1.53204400	-0.07823900
S	1.13434700	1.69214400	-0.08375200
S	-4.72247300	-1.58696900	-0.14181100
S	-1.66042800	-1.60686300	-0.08179200
S	1.30231200	-1.46222900	-0.03928100
S	4.18359200	1.64664100	0.00615500
C	6.49227000	0.05435100	0.04445800
C	7.22705600	1.23346800	0.02203800
H	6.78250300	2.05069700	-0.01101100
C	8.63069500	1.20801400	0.04610900
H	9.12002400	1.99931400	0.04624000
C	9.26392100	-0.01481300	0.07364000
C	8.49632100	-1.17263200	0.14960900
H	8.92285700	-1.99590700	0.21553600
C	7.13499400	-1.12543600	0.12900000
H	6.64642600	-1.91537100	0.17312400
C	-6.99963700	-0.01997900	-0.14349700
C	-7.78328800	-1.18407100	-0.01533600
H	-7.35764100	-2.01040500	0.01854700

C	-9.11959600	-1.14565500	0.06153300
H	-9.59691900	-1.93830800	0.14274000
C	-9.80162300	0.05464500	0.02233900
C	-9.11772900	1.20798900	-0.08280600
H	-9.57730200	2.01560400	-0.09720100
C	-7.72813600	1.20542600	-0.16953700
H	-7.27061200	2.01016900	-0.24501400
C	2.65173400	0.85578100	-0.03690900
C	2.79141600	-0.57868700	-0.01246200
C	4.16117900	-1.01994900	0.00562200
H	4.44625600	-1.90497300	0.02039000
C	4.98518500	0.10379000	-0.00406000
C	-4.63932500	1.04554800	-0.14242600
H	-4.86320400	1.94841800	-0.14343000
C	-5.56480000	-0.03480000	-0.17036400
C	-3.26781900	0.50437200	-0.10592500
C	-3.18093700	-0.81550900	-0.10674400
C	10.73507000	-0.10123600	0.07061700
C	11.41088300	-1.28911700	-0.33782700
C	11.54778400	1.00114600	0.47021500
C	12.78620100	-1.37784800	-0.34911000
H	10.82670600	-2.13671100	-0.68260800
C	12.92384900	0.92876900	0.47203800
H	11.06981100	1.91307200	0.81495100
C	13.62057000	-0.26964300	0.05946400
H	13.28969700	-2.28151700	-0.67682400
H	13.53176700	1.76795800	0.79417400

C	-11.26319800	0.06391200	0.10547600
C	-12.04900000	1.24303600	-0.16049000
C	-12.03297500	-1.10178700	0.45991800
C	-13.41130400	1.24893600	-0.08246600
H	-11.56457900	2.16483000	-0.45880000
C	-13.39509500	-1.08310300	0.54221900
H	-11.53445800	-2.03309400	0.69848500
H	-14.01359500	2.12279800	-0.29252300
H	-13.98403200	-1.94688300	0.82059900
H	-15.11029200	0.09832400	0.33159500
N	-14.10616800	0.08941400	0.27216900
O	14.90758300	-0.34497200	0.05562600

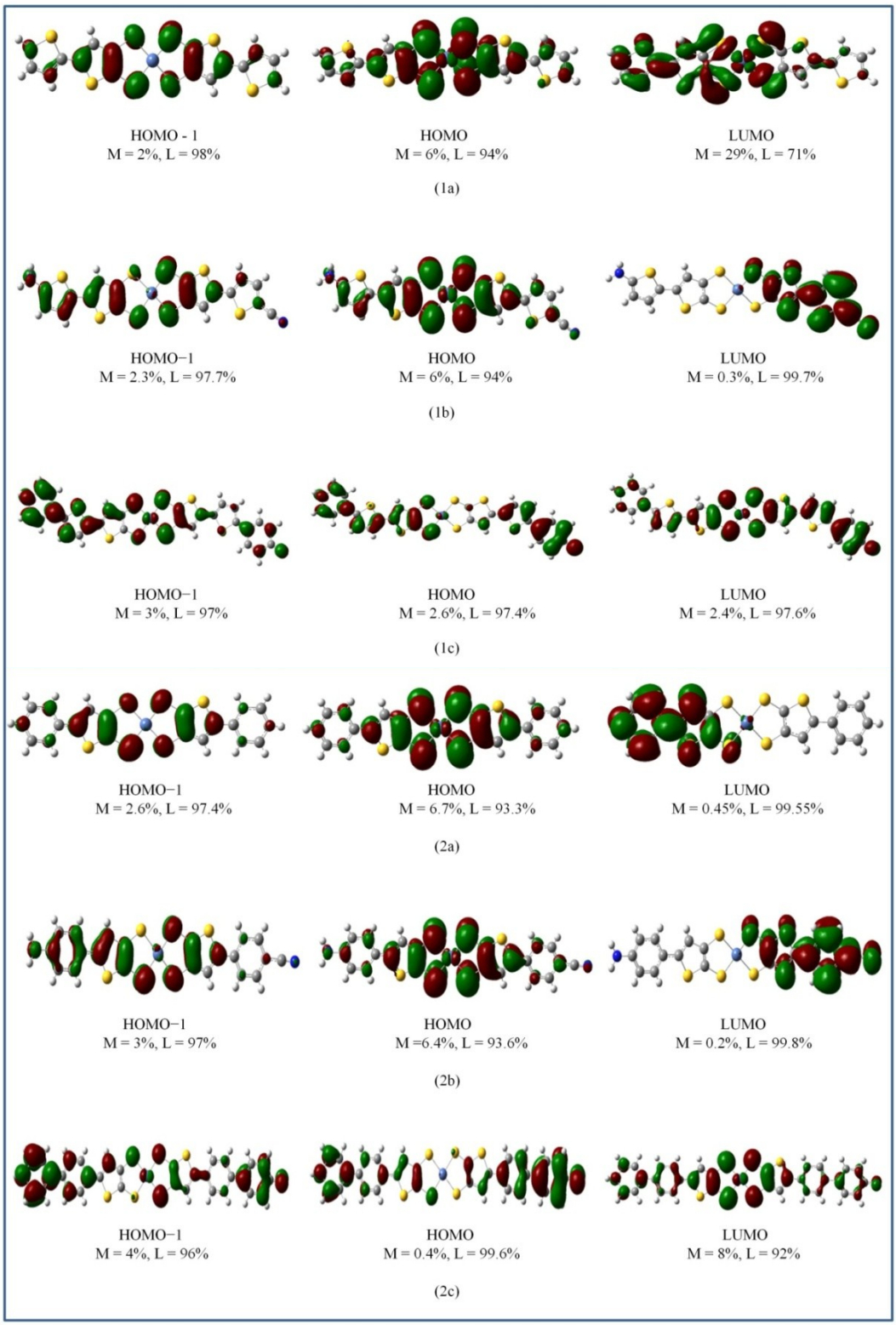

Figure S7. Electron density contours of the MOs of the systems under study.

Table S1: TDDFT calculated transitions for Thienyl (1a) and Phenyl (2a) expanded analogues of NiTDT core and its derivative (1b, 1c & 2b, 2c) at B3LYP and CAM-B3LYP/6-311g(d,p) level of theory.

Model Compound	B3LYP/6-311G(d,p)		CAM-B3LYP/6-311G(d,p)	
	Wavelength	Osc	Wavelength	Osc
1a	978	0.2706	1173	0.2274
1b	1008	0.2750	1229	0.1749
1c	1818	0.5838	1371	0.6975
2a	933	0.2947	1103	0.2589
2b	925	0.4192	1057	0.2089
2c	1224	0.5810	1414	0.3635