

SUPPORTING INFORMATION

Mixed-ligand Pt(II) dithione-dithiolato complexes: influence of the dicyanobenzodithiolato ligand on the second-order-NLO Properties

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List of bond distances [Å] and angles [deg] for [Pt(Bz₂pipdt)(dcbdt)] (Table S1) and DFT optimized geometries for [Pt(Bz₂pipdt)(dcbdt)] and [Pt(Bz₂pipdt)(dmit)] (Tables S2 and S3); drawing, relative energy and percent compositions of the most significant orbitals obtained by DFT calculations in vacuum and in DMF for [Pt(Bz₂pipdt)(dcbdt)] and [Pt(Bz₂pipdt)(dmit)] (Tables S4 and S5); Simulated visible spectra for [Pt(Bz₂pipdt)(dcbdt)] and [Pt(Bz₂pipdt)(dmit)] (Figures S1 and S2).

Table S1. Bond lengths [Å] and angles [deg] for [Pt(Bz₂pipdt)(dcbdt)].

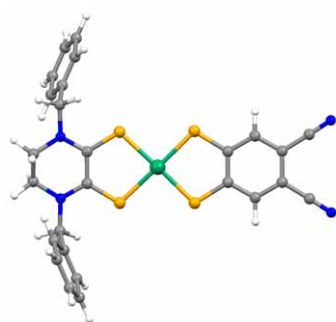
Pt-S(2)	2.2734(10)
Pt-S(2)#1	2.2734(10)
Pt-S(1)#1	2.2784(10)
Pt-S(1)	2.2784(10)
S(2)-C(10)	1.751(4)
S(1)-C(1)	1.688(4)
C(10)-C(10)#1	1.390(7)
C(10)-C(11)	1.392(5)
C(4)-C(9)	1.371(6)
C(4)-C(5)	1.386(7)
C(4)-C(3)	1.515(6)
C(1)-N(1)	1.323(4)
C(1)-C(1)#1	1.484(8)
C(12)-C(11)	1.380(6)
C(12)-C(12)#1	1.411(9)
C(12)-C(13)	1.443(6)
N(1)-C(2)	1.467(5)
N(1)-C(3)	1.470(5)
C(2)-C(2)#1	1.424(9)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(11)-H(11)	0.9300
C(13)-N(2)	1.125(6)
C(5)-C(6)	1.395(8)
C(5)-H(5)	0.9300
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(6)-C(7)	1.366(9)
C(6)-H(6)	0.9300
C(9)-C(8)	1.366(7)
C(9)-H(9)	0.9300
C(7)-C(8)	1.338(9)
C(7)-H(7)	0.9300
C(8)-H(8)	0.9300
S(2)-Pt-S(2)#1	89.88(5)
S(2)-Pt-S(1)#1	177.25(4)
S(2)#1-Pt-S(1)#1	90.99(4)
S(2)-Pt-S(1)	90.99(4)
S(2)#1-Pt-S(1)	177.25(4)
S(1)#1-Pt-S(1)	88.27(5)
C(10)-S(2)-Pt	103.73(13)
C(1)-S(1)-Pt	105.76(14)
C(10)#1-C(10)-C(11)	119.7(2)
C(10)#1-C(10)-S(2)	121.33(12)
C(11)-C(10)-S(2)	118.9(3)
C(9)-C(4)-C(5)	119.1(5)
C(9)-C(4)-C(3)	120.8(4)
C(5)-C(4)-C(3)	120.0(4)
N(1)-C(1)-C(1)#1	119.6(2)
N(1)-C(1)-S(1)	120.6(3)
C(1)#1-C(1)-S(1)	119.87(14)
C(11)-C(12)-C(12)#1	119.5(3)
C(11)-C(12)-C(13)	120.4(4)
C(12)#1-C(12)-C(13)	120.1(2)
C(1)-N(1)-C(2)	120.5(3)

C(1) - N(1) - C(3)	121.9(3)
C(2) - N(1) - C(3)	117.2(3)
C(2) #1 - C(2) - N(1)	115.1(3)
C(2) #1 - C(2) - H(2A)	108.5
N(1) - C(2) - H(2A)	108.5
C(2) #1 - C(2) - H(2B)	108.5
N(1) - C(2) - H(2B)	108.5
H(2A) - C(2) - H(2B)	107.5
C(12) - C(11) - C(10)	120.7(4)
C(12) - C(11) - H(11)	119.7
C(10) - C(11) - H(11)	119.7
N(2) - C(13) - C(12)	178.9(6)
C(4) - C(5) - C(6)	119.9(6)
C(4) - C(5) - H(5)	120.1
C(6) - C(5) - H(5)	120.1
N(1) - C(3) - C(4)	113.8(3)
N(1) - C(3) - H(3A)	108.8
C(4) - C(3) - H(3A)	108.8
N(1) - C(3) - H(3B)	108.8
C(4) - C(3) - H(3B)	108.8
H(3A) - C(3) - H(3B)	107.7
C(7) - C(6) - C(5)	118.9(7)
C(7) - C(6) - H(6)	120.6
C(5) - C(6) - H(6)	120.6
C(8) - C(9) - C(4)	120.0(6)
C(8) - C(9) - H(9)	120.0
C(4) - C(9) - H(9)	120.0
C(8) - C(7) - C(6)	120.9(7)
C(8) - C(7) - H(7)	119.5
C(6) - C(7) - H(7)	119.5
C(7) - C(8) - C(9)	121.2(7)
C(7) - C(8) - H(8)	119.4
C(9) - C(8) - H(8)	119.4

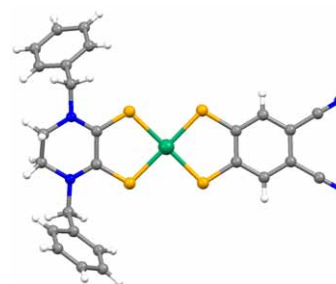
atoms: Symmetry transformations used to generate equivalent
#1 -x+1,y,-z+1/2

Table S2. Cartesian coordinates of the optimized complex [Pt(Bz2pipdt)(dcbdt)] (B3LYP/6-311G(d,p)-SDD).

C	3.34176	6.07453	1.16719
C	3.90209	4.91259	1.69180
C	2.87109	6.08104	-0.14407
C	3.99769	3.76562	0.90721
C	2.96139	4.93185	-0.92439
C	-7.50807	1.36655	-0.49032
C	3.52927	3.76534	-0.40740
C	-6.28788	0.66917	-0.24011
C	-5.07616	1.31168	-0.47031
C	-7.50805	-1.36664	0.49035
C	-6.28788	-0.66925	0.24013
C	-3.85448	0.66407	-0.23828
C	-5.07614	-1.31175	0.47031
C	-3.85447	-0.66413	0.23827
C	4.86461	-0.46050	0.60104
C	3.67751	-2.55108	1.31234
C	2.45559	0.66859	-0.29270
C	3.67747	2.55116	-1.31232
C	2.45560	-0.66854	0.29270
C	4.86460	0.46057	-0.60105
C	3.52937	-3.76528	0.40742
C	2.96154	-4.93181	0.92442
C	3.99778	-3.76554	-0.90719
C	2.87129	-6.08101	0.14410
C	3.90223	-4.91253	-1.69177
C	3.34196	-6.07448	-1.16715
H	3.26323	6.96580	1.77869
H	4.26156	4.89653	2.71440
H	2.42104	6.97683	-0.55615
H	4.42428	2.86315	1.33073
H	2.57586	4.93910	-1.93884
H	-5.07946	2.33139	-0.83517
H	4.95825	0.12080	1.52818
H	2.89564	-2.56757	2.07758
H	4.63738	-2.59693	1.83426
H	-5.07943	-2.33146	0.83518
H	5.71671	1.13858	-0.53914
H	5.71673	-1.13849	0.53912
H	4.63735	2.59703	-1.83422
H	2.89561	2.56763	-2.07758
H	2.57602	-4.93907	1.93887
H	4.95824	-0.12072	-1.52819
H	4.42432	-2.86306	-1.33071
H	2.42128	-6.97682	0.55619
H	4.26170	-4.89646	-2.71437
H	3.26346	-6.96577	-1.77864
N	-8.48118	1.95285	-0.70131
N	-8.48115	-1.95296	0.70135
N	3.63977	-1.25764	0.62217
N	3.63975	1.25770	-0.62217
S	-2.35902	1.52678	-0.54495
S	0.99511	1.49705	-0.57250
S	-2.35900	-1.52682	0.54492
S	0.99514	-1.49704	0.57247
Pt	-0.70800	-0.00001	-0.00001



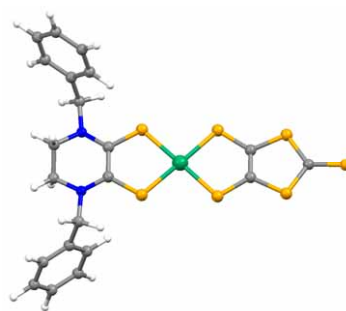
B3LYP/6-311G(d,p)-SDD



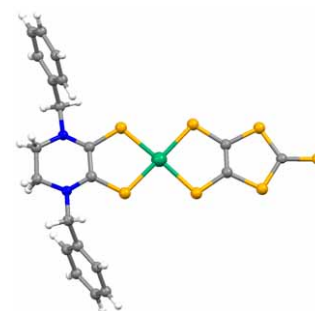
X-Ray

Table S3. Cartesian coordinates of the optimized complex [Pt(Bz2pipdt)(dmit)] (B3LYP/6-311G(d,p)-SDD).

Pt	3.737352	3.974797	2.039873
S	3.897323	-0.69005	7.671681
S	4.435691	6.155474	1.629329
S	4.576006	4.031299	4.213163
S	2.971132	1.806579	2.416007
S	2.965067	3.951645	-0.15434
S	3.118522	-0.00447	4.849784
S	4.561225	1.974996	6.448397
N	4.201067	7.74828	-0.50645
C	3.981668	6.504392	0.011454
C	3.46912	1.531152	4.056056
C	3.354226	5.488123	-0.8125
N	3.08275	5.758624	-2.12275
C	2.451339	4.79758	-3.03791
H	1.643637	5.324837	-3.55613
H	1.9919	4.012509	-2.43888
C	4.827512	8.844009	0.24637
H	5.60235	9.277251	-0.39461
H	5.328469	8.415105	1.113174
C	3.405925	4.207046	-4.0609
C	4.141405	2.458191	4.80483
C	3.855559	9.931976	0.66839
C	2.759183	9.64115	1.489597
H	2.594209	8.626068	1.832767
C	4.536822	3.484996	-3.65998
H	4.741582	3.341786	-2.60503
C	3.861317	0.35955	6.40452
C	5.395486	2.9389	-4.60878
H	6.264875	2.37791	-4.28542
C	2.093795	11.96398	1.457683
H	1.412616	12.74884	1.765763
C	4.055285	11.2491	0.24958
H	4.90351	11.48807	-0.38451
C	3.15547	4.367251	-5.42535
H	2.280176	4.922013	-5.749
C	1.884345	10.65066	1.878553
H	1.042165	10.41332	2.51848
C	5.135355	3.101579	-5.96953
H	5.804143	2.671453	-6.70618
C	4.012303	3.815237	-6.3767
H	3.801868	3.945076	-7.4322
C	3.182352	12.26228	0.643813
H	3.353366	13.28054	0.313471
C	3.65756	6.951444	-2.73853
H	3.0892	7.175931	-3.64289
H	4.69737	6.768077	-3.03422
C	3.573069	8.114411	-1.77293
H	4.104393	8.976384	-2.18037
H	2.529436	8.410194	-1.61292



B3LYP/6-311G(d,p)-SDD



X-Ray

Table S4. MOs diagrams of [Pt(Bz₂pipdt)(dcbdt)] in the gas-phase (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to complexes valence orbitals

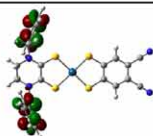
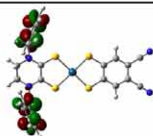
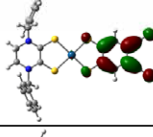
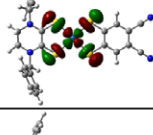
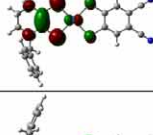
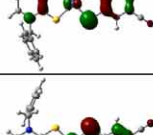
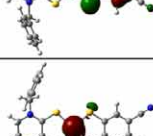
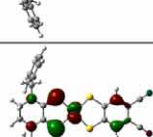
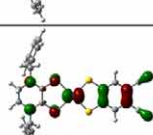
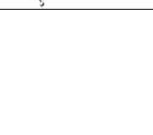
		E (eV)	Fragment composition (%)		
			Pt	Bz ₂ pipdt	dcbdt
LUMO+3		-1.12	1.4	98.4	0.1
LUMO+2		-1.47	1.1	0.0	98.9
LUMO+1		-1.88	33.7	30.0	36.3
LUMO		-3.85	6.3	78.4	15.3
HOMO		-5.47	8.4	23.3	68.3
HOMO-1		-5.91	18.8	4.5	76.7
HOMO-2		-7.01	81.3	4.5	14.2
HOMO-3		-7.10	20.6	54.3	25.2
HOMO-4		-7.16	28.5	29.2	42.3

Table S5. MOs diagrams of [Pt(Bz₂pipdt)(dcbdt)] in the solution phase, DMF, (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to complexes valence orbitals.

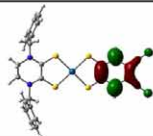
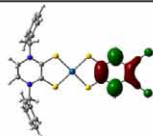
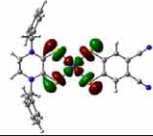
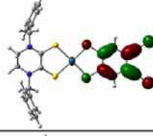
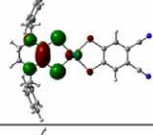
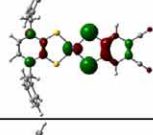
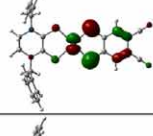
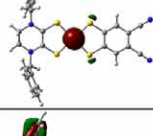
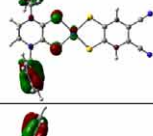
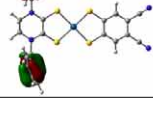
		E (eV)	Fragment composition (%)		
			Pt	Bz ₂ pipdt	dcbdt
LUMO+3		-1.35	0.3	0.0	99.7
LUMO+2		-1.85	34.5	30.1	35.4
LUMO+1		-1.99	1.1	0.0	98.9
LUMO		-3.72	4.6	88.2	7.2
HOMO		-5.64	13.7	17.6	68.7
HOMO-1		-6.10	26.8	10.7	62.5
HOMO-2		-6.87	85.0	6.2	8.8
HOMO-3		-6.99	3.0	87.2	9.8
HOMO-4		-7.05	0.8	96.5	2.7

Table S6. MOs diagrams of [Pt(Bz₂pipdt)(dmit)] in the gas-phase (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to complexes valence orbitals

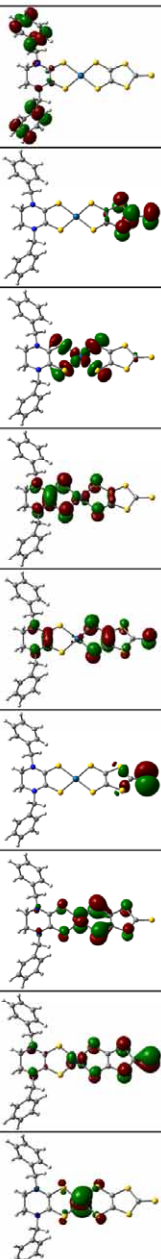
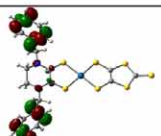
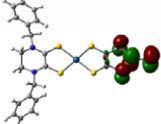
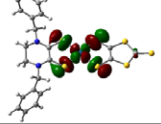
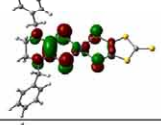
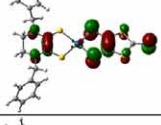
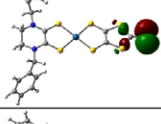
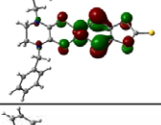
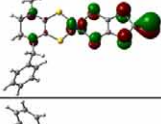
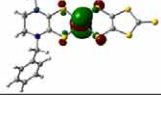
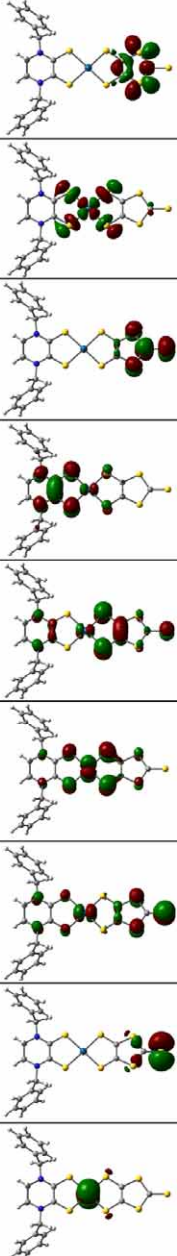
		E (eV)	Fragment composition (%)		
			Pt	Bz ₂ pipdt	dcbdt
LUMO+3		-1.16	0.7	00.0	0.3
LUMO+2		-1.61	0.0	0.0	100
LUMO+1		-1.94	33.3	30.9	35.8
LUMO		-3.70	5.5	70.6	23.9
HOMO		-4.96	3.1	27.2	69.7
HOMO-1		-6.00	0.6	0.9	98.6
HOMO-2		-6.12	28.7	15.5	55.8
HOMO-3		-6.24	15.1	14.7	70.2
HOMO-4		-6.93	74.9	11.1	14.0

Table S7. MOs diagrams of [Pt(Bz₂pipdt)(dmit)] in the solution phase, DMF, (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to complexes valence orbitals.

		E (eV)	Fragment composition (%)		
			Pt	Bz ₂ pipdt	dmit
LUMO+3		-0.87	2.8	3.5	93.7
LUMO+2		-2.05	33.9	30.5	35.6
LUMO+1		-2.15	0.0	0.0	100
LUMO		-3.74	4.4	84.6	11.0
HOMO		-5.26	6.0	17.0	77.0
HOMO-1		-6.29	33.8	25.8	40.4
HOMO-2		-6.57	20.7	23.6	55.7
HOMO-3		-6.64	0.6	1.6	97.8
HOMO-4		-6.92	85.8	6.1	8.1

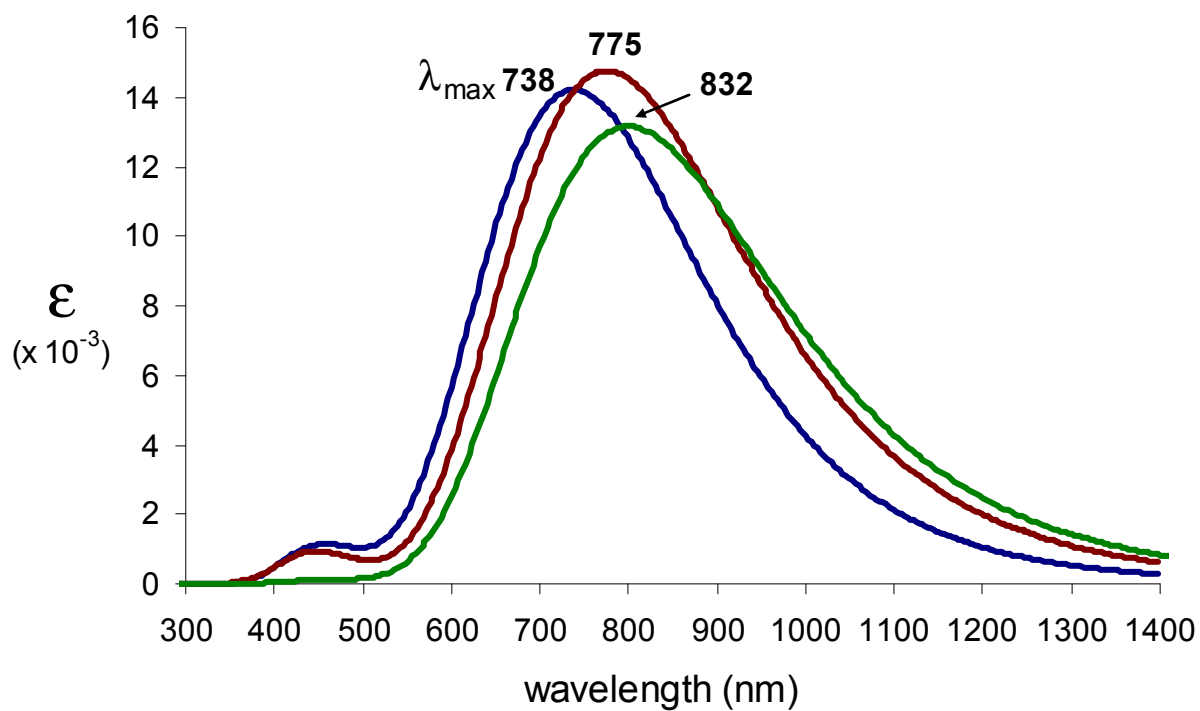


Figure S1. Simulated UV-vis spectrum of [Pt(Bz₂pipdt)(dcbdt)]. Calculation were performed with the CPCM method (DMF, blue; CHCl₃, red) and in Void (green), B3LYP/6-311G(d,p)-SDD.

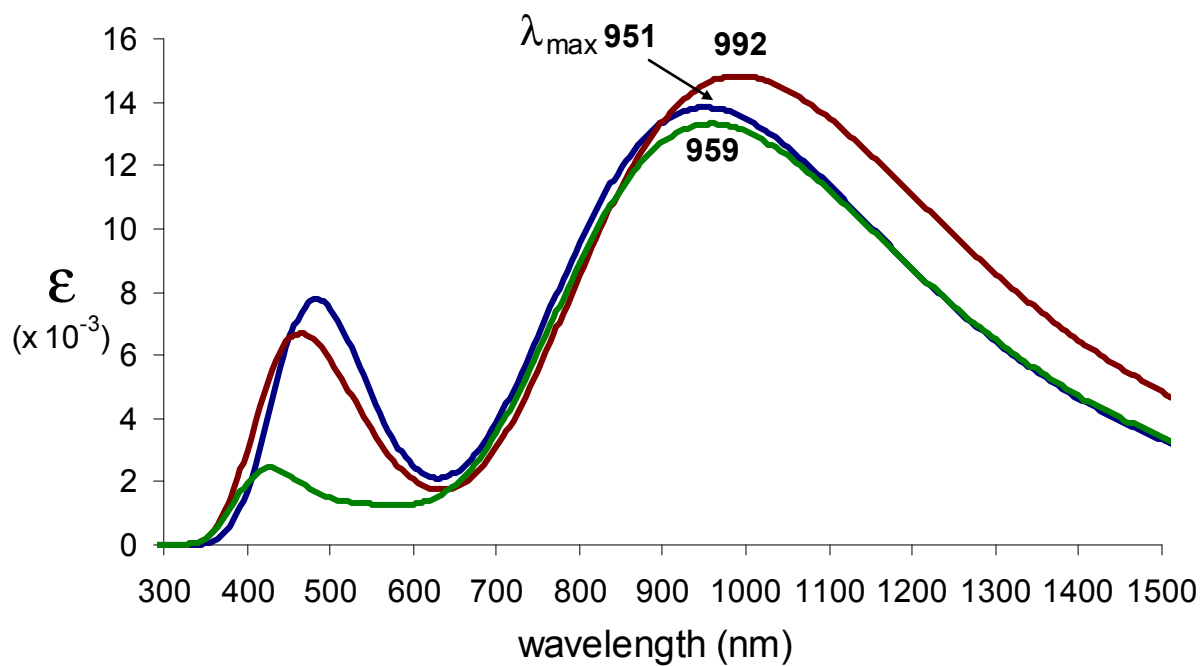


Figure S2. Simulated UV-vis spectrum of [Pt(Bz₂pipdt)(dmit)]. Calculation were performed with the CPCM method (DMF, blue; CHCl₃, red) and in Void (green), B3LYP/6-311G(d,p)-SDD.