Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information:

Electrochromic Second-Order NLO Chromophores based on M^{II} (M = Ni, Pd, Pt) Complexes with Diselenolato-Dithione (Donor-Acceptor) Ligands

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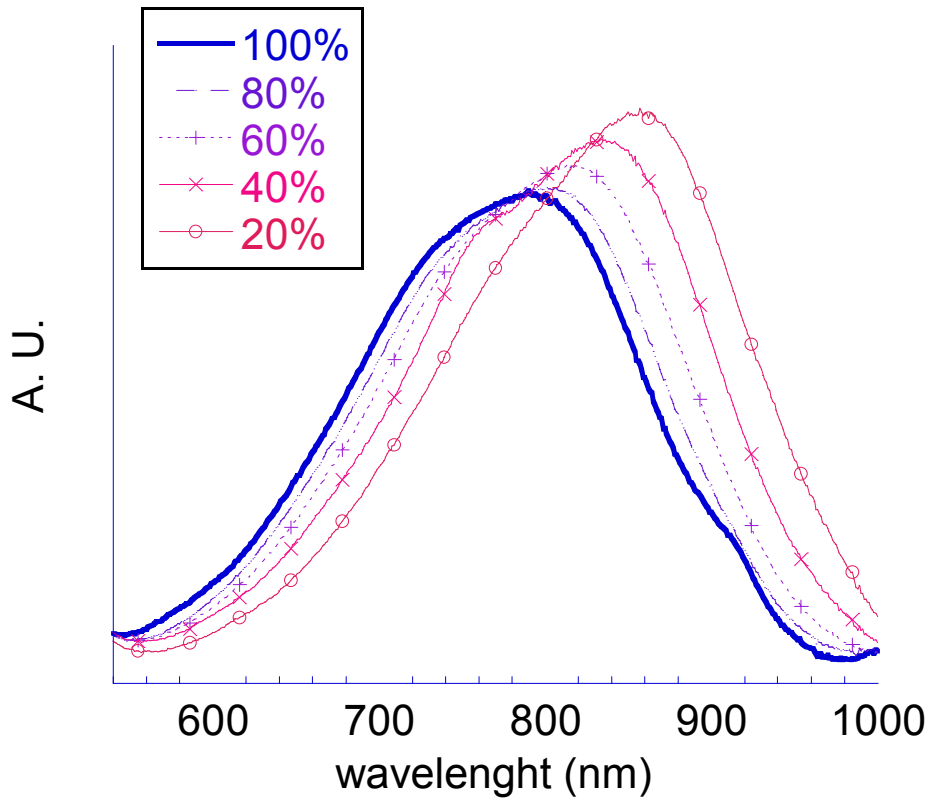


Figure S1. Solvatochromic behaviour of [Pt(Bz_2pipdt)(dsit)] **3** in DMF/CS_2 mixtures ranging from DMF 100% to 20%. The energy of the solvatochromic peak of **3** *versus* the solvent polarity parameter for solutions from DMF 100% to 20% follows a straight line with slope 1.2.

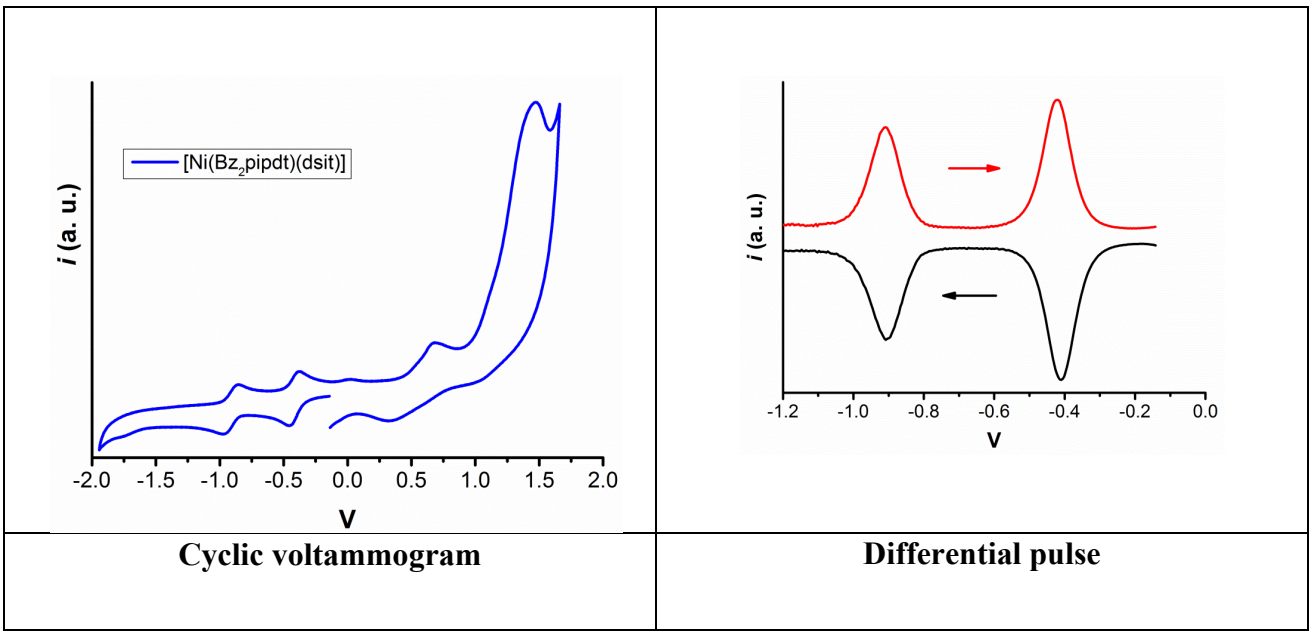


Figure S2. Electrochemical measurements on DMF solution of [Ni(Bz_2pipdt)(dsit)] **1** containing 0.1 M $TBABF_4$

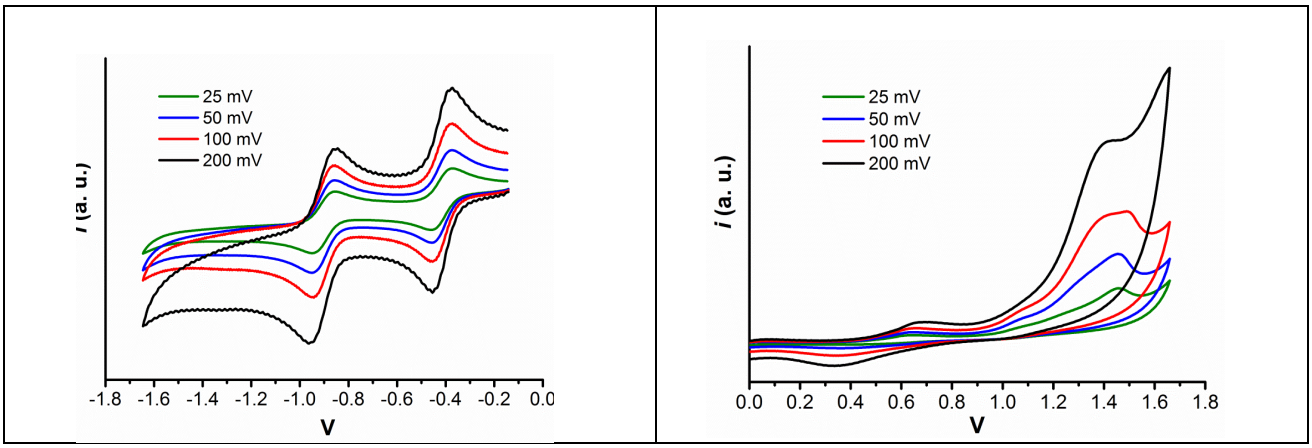
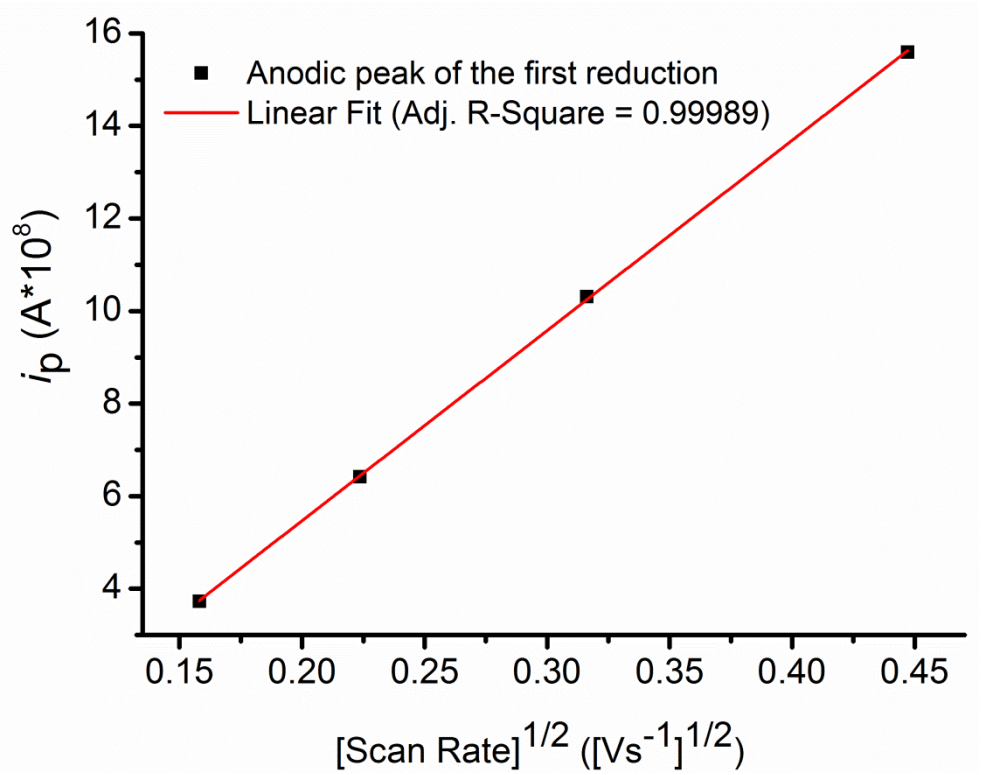


Figure S3. Cyclic voltammogram in a DMF solution of **1** containing 0.1 M $TBABF_4$ at 298 K at different scan rates.



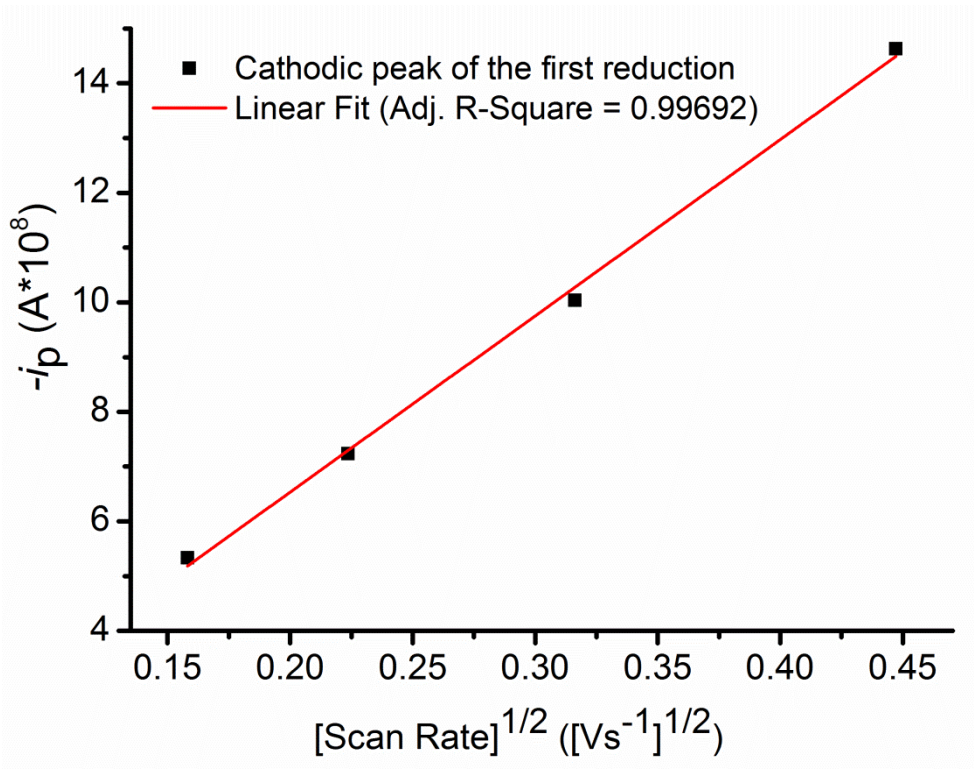
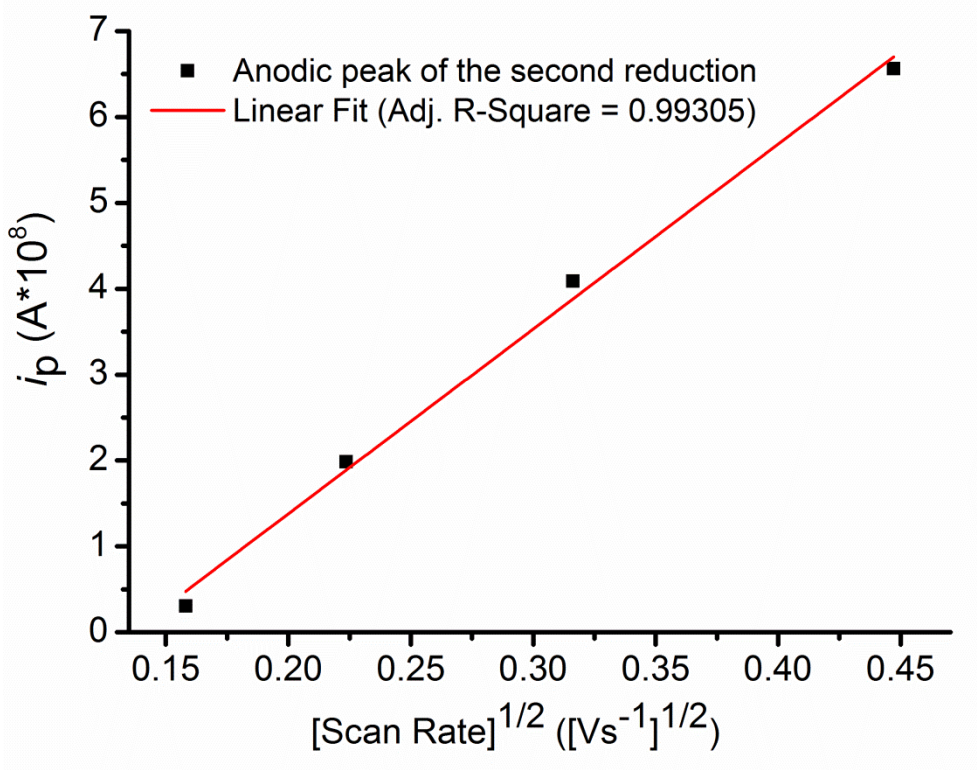


Figure S4. Linear dependence of the anodic peak (above) and cathodic peak (below) currents of the first reduction from the square root of the voltage scan rate in the case of complex **1**, [Ni(Bz$_2$pipdt)(dsit)].



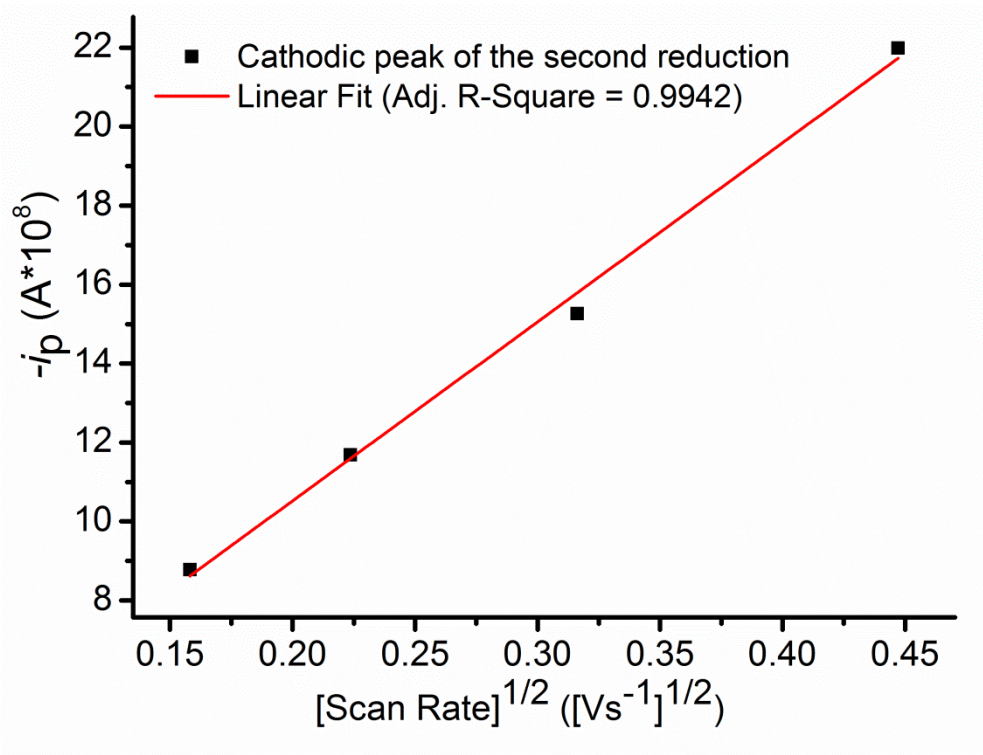


Figure S5. Linear dependence of the anodic peak (above) and cathodic peak (below) currents of the second reduction from the square root of the voltage scan rate in the case of complex **1**, [Ni(Bz$_2$pipdt)(dsit)].

Table S1 Selected Experimental and calculated bond distances (Å) and angles (deg) for [Ni(Bz_2pipdt)(dsit)] (**1**), [Pd(Bz_2pipdt)(dsit)] (**2**), and [Pt(Bz_2pipdt)(dsit)] (**3**).

	[Ni(Bz_2pipdt)(dsit)] (**1**)		[Pd(Bz_2pipdt)(dsit)] (**2**)		[Pt(Bz_2pipdt)(dsit)] (**3**)	
	Exp.	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**
M-Se (dsit)	2.2884(8) 2.2755(8)	2.309 2.309	-	2.427 2.427	2.3939(9) 2.4034(9)	2.436 2.436
M-S (R_2pipdt)	2.151(1) 2.162(1)	2.197 2.197	-	2.335 2.335	2.264(2) 2.276(2)	2.335 2.335
Se-C (dsit)	1.876(5) 1.880(5)	1.883 1.883	-	1.890 1.890	1.896(7) 1.883(7)	1.890 1.890
S-C (R_2pipdt)	1.691(5) 1.673(5)	1.711 1.711	-	1.713 1.713	1.676(7) 1.690(8)	1.715 1.715
C-C (dsit)	1.355(6)	1.367	-	1.365	1.347(9)	1.361
C-C (R_2pipdt)	1.490(6)	1.460	-	1.467	1.491(9)	1.454
C-N (R_2pipdt)	1.323(5) 1.328(5)	1.362 1.362	-	1.363 1.363	1.318(9) 1.353(9)	1.365 1.365
Se-M-Se (dsit)	94.44(3)	94.10	-	91.04	92.21(3)	90.79
S-M-S (R_2pipdt)	91.10(5)	90.66	-	86.85	88.22(7)	86.46
M-Se-C (dsit)	100.4(1) 101.0(2)	100.62 100.62	-	100.75 100.75	99.8(2) 100.0(2)	100.70 100.70
M-S-C (R_2pipdt)	106.4(2) 106.0(2)	105.54 105.54	-	105.93 105.93	106.2(3) 106.0(2)	106.18 106.18
Se-C-C (dsit)	122.7(4) 122.8(3)	122.33 122.33	-	123.73 123.73	123.4(6) 124.5(6)	123.91 123.91
S-C-C (R_2pipdt)	114.6(4) 117.2(4)	119.03 119.03	-	120.48 120.48	119.0(6) 120.3(6)	120.54 120.54

Table S2. Spatial plots of relevant MOs (isovalue= 0.04) of [Ni(Bz_2pipdt)(dsit)] in DMF (B3LYP/6-311G(d,p)-SDD).

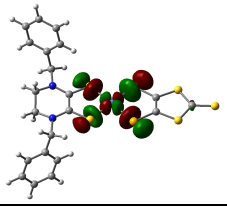
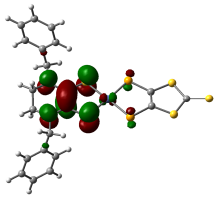
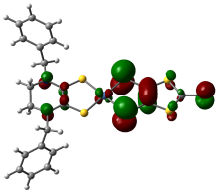
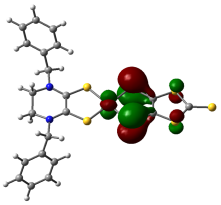
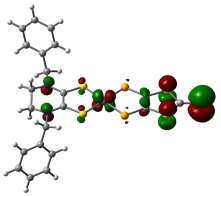
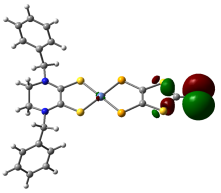
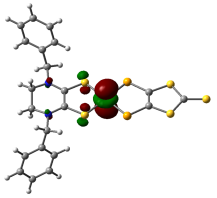
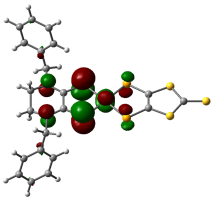
		E (eV)
LUMO+1		**-2.51**
LUMO		**-3.68**
HOMO		**-5.34**
HOMO-1		**-6.26**
HOMO-2		**-6.57**
HOMO-3		**-6.63**
HOMO-4		**-6.80**
HOMO-5		**-6.86**

Table S3. Spatial plots of relevant MOs (isovalue= 0.04) of [Pd(Bz_2pipdt)(dsit)] in DMF (B3LYP/6-311G(d,p)-SDD).

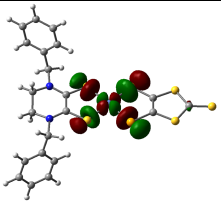
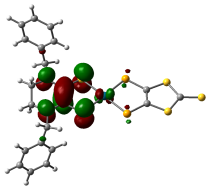
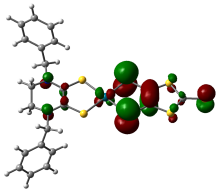
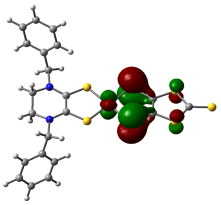
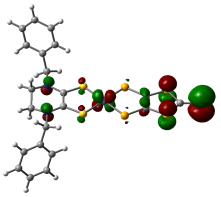
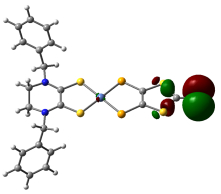
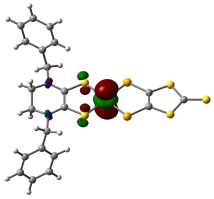
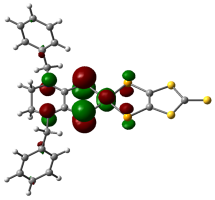
		E (eV)
LUMO+1		**-2.61**
LUMO		**-3.75**
HOMO		**-5.30**
HOMO-1		**-6.22**
HOMO-2		**-6.62**
HOMO-3		**-6.64**
HOMO-4		**-6.91**
HOMO-5		**-6.95**

Table S4. Spatial plots of relevant MOs (isovalue= 0.04) of [Pt(Bz$_2$pipdt)(dsit)] in DMF (B3LYP/6-311G(d,p)-SDD).

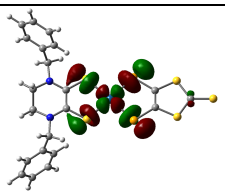
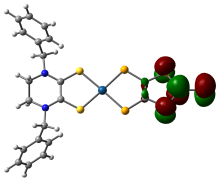
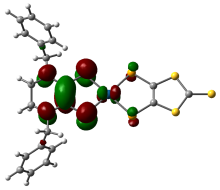
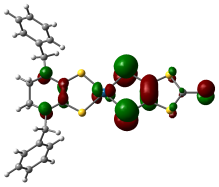
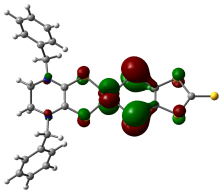
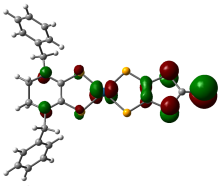
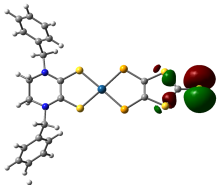
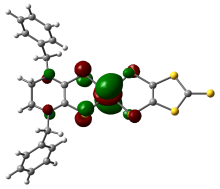
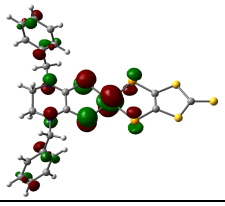
		E (eV)
LUMO+2		**-2.09**
LUMO+1		**-2.14**
LUMO		**-3.74**
HOMO		**-5.32**
HOMO-1		**-6.10**
HOMO-2		**-6.53**
HOMO-3		**-6.62**
HOMO-4		**-6.92**
HOMO-5		**-6.96**

Table S5 TD-DFT calculated energies and compositions of the lowest lying singlet electronic transitions of [M(Bz_2pipdt)(dsit)], (M = Ni, Pd, Pt) complexes in DMF, (B3LYP/6-311G(d,p)-SDD). The principal singlet transition responsible for the main absorption band in the visible region is shown in bold.

Compound	State	Composition[a]	ΔE (eV/nm)[b]	*f*[c]	Character
[Ni(Bz_2pipdt)(dsit)]	**1**	**HOMO → LUMO** ***74%***	**1.36 / 914**	**0.3075**	**dsit**/Ni/Bz_2pipdt→ dsit/Ni/**Bz_2pipdt** **(MMLL'CT)**
	2	HOMO → LUMO+1 *60%* HOMO-2→ LUMO+1 *15%*	1.66 / 745	0.0219	
	3	HOMO-1 → LUMO *43%* HOMO-4 → LUMO+1 *22%* HOMO-5 → LUMO+1 *9%* HOMO-1 → LUMO+1 *8%*	1.68 / 737	0.0015	
	4	HOMO-1→ LUMO+1 *35%* HOMO-4→ LUMO+1 *25%* HOMO-4→ LUMO *14%* HOMO-13→ LUMO+1 *7%*	1.77 / 699	0.0001	
	5	HOMO-1→ LUMO *14%* HOMO-4→ LUMO *17%* HOMO-1→ LUMO+1, *15%* HOMO-5→ LUMO+1, *7%*	1.97 / 630	0.0021	
[Pd(Bz_2pipdt)(dsit)]	**1**	**HOMO → LUMO** ***78%***	**1.25 / 989**	**0.2376**	**dsit**/Pd/Bz_2pipdt→ dsit/Pd/**Bz_2pipdt** **(MMLL'CT)**
	2	HOMO → LUMO+1 *93%*	1.80 / 688	0.0125	
	3	HOMO-1 → LUMO *91%* HOMO-4→ LUMO *89%*	1.86 / 668	0.0037	
	4	HOMO-5→ LUMO *8%* HOMO-2→ LUMO *80%*	2.26 / 547	0.0002	
	5	HOMO-3→ LUMO *7%*	2.47 / 502	0.0841	
[Pt(Bz_2pipdt)(dsit)]	**1**	**HOMO → LUMO** ***75%***	**1.35 / 918**	**0.3318**	**dsit**/Pt/Bz_2pipdt→ dsit/Pt/**Bz_2pipdt** **(MMLL'CT)**
	2	HOMO-1 → LUMO *90%* HOMO-4 → LUMO *88%*	1.71 / 723	0.0043	
	3	HOMO-5 → LUMO *10%* HOMO → LUMO+2 *86%*	2.23 / 557	0.0004	
	4	HOMO-2 → LUMO *9%* HOMO-2 → LUMO *81%*	2.35 / 527	0.0000	
	5	HOMO → LUMO+2 *8%*	2.42 / 512	0.0771	

[a] Compositions of electronic transitions are expressed in terms of contributing excitations between groundstate Kohn–Sham molecular orbitals.
[b]Transition energy from the ground state in eV. [c]Oscillator strength.

Table S6. Comparison of HOMO-LUMO energy in eV and energy gap between [Pt(Bz_2pipdt)(dmit)][7b] and [Pt(Bz_2pipdt)(dsit)] in DMF and in the gas-phase (in parenthesis).

dsit	**HOMO**	-5.32 (-4.99)
	LUMO	-3.74 (-3.69)
	Gap	**1.58** (1.30)
dmit	**HOMO**	-5.26 (-4.96)
	LUMO	-3.74 (-3.70)
	Gap	**1.52** (1.26)

Table S7. Calculated ground state dipole moments (μg) and Δμge of [M(Bz_2pipdt)(dsit)], (M = Ni, Pd, Pt) complexes. CPCM (DMF) B3LYP/6-311G(d,p)-SDD. The Δμge (in Debye) was calculated with the finite field approach.

Compound	Ground state	ge (FF)
[Ni(Bz_2pipdt)(dsit)]	18.9550 (void) 32.5138 (DMF)	-8.34 (DMF)
[Pd(Bz_2pipdt)(dsit)]	19.6285 (void) 33.6150 (DMF)	-10.31 (DMF)
[Pt(Bz_2pipdt)(dsit)]	18.8448 (void) 31.8462 (DMF)	-8.66 (DMF)