Electronic Supplementary Material (ESI) for Dalton Transactions.

A nonlinear optical active polymer film based on Pd(II) dithione/dithiolate second-order NLO chromophore

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Supplementary Material

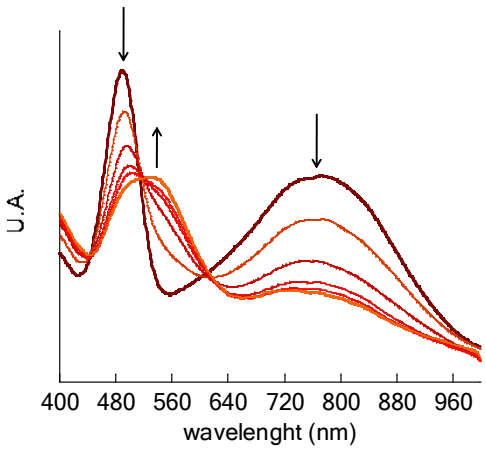

Figure S1. Spectroelectrochemical reduction of [Pd(Bz_2pipdt)(dmit)]. Study carried out in 0.1 M $TBABF_4$/DMF, at –40 °C, with an applied potential of –0.6 V (*vs.* Ag/AgCl).

Table S1. Cyclic voltammetric data. Measured at the Pt electrode in DMF, 0.2 M *n*-Bu_4NClO_4 (reference electrode Ag/AgCl) for **1**. Corresponding data for R= Pr^i and Bz are reported for comparison.

Complex	E_a (V)[a] 0→+1	$E^1_{1/2}$ (V) 0→–1	$E^2_{1/2}$ (V) –1→–2	Ref.
[Pd(Pr^i_2pipdt)(dmit)]	*+0.84*	−0.38	−0.93	21
[Pd(Bz_2pipdt)(dmit)]	*+0.84*	−0.36	−0.81	5c
[Pd(Dod_2pipdt)(dmit)]	*+0.76*	−0.49	−0.99	This work

[a] Irreversible

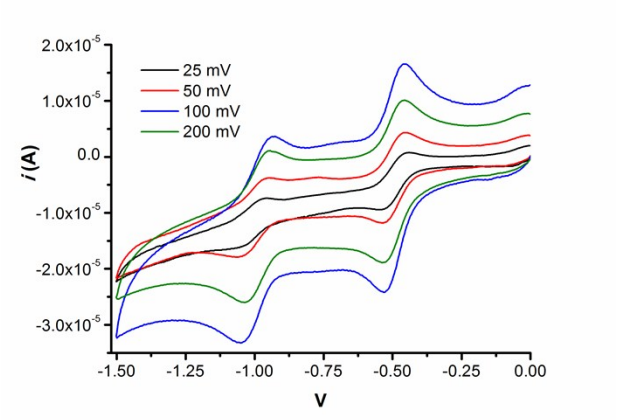

Figure S2. Reduction processes of **1**. Cyclic voltammograms recorded at different scan rates in a DMF solution, containing 0.2 M *n*-Bu_4NClO_4 as supporting electrolyte (V *vs* Ag/AgCl in KCl 3 M).

Figure S3. First reduction process of **1**. Cyclic voltammograms recorded at different scan rates in a DMF solution, containing 0.2 M *n*-Bu_4NClO_4 as supporting electrolyte (V *vs* Ag/AgCl in KCl 3 M).

Computational studies.

Density Functional Theory (DFT)[1] calculations were carried out, using the GAUSSIAN 09[2] software package, with the aim to investigate the electronic structure of the complex [Pd(Me_2pipdt)(dmit)]. In order to reduce the calculation's time, the methyl group was used as substituent instead of the dodecyl. Previous studies on complexes bearing the R_2pipdt ligand, have shown that the substituent at the nitrogen atoms plays a negligible role in determining the frontier orbitals.[3] B3LYP[4] was employed as functional, whereas the basis set 6-31G(d,p)[5] was used for C, H, N, and S atoms and the pseudopotential LanL2DZ for Pd.[6] ArgusLab 4.0 program[7] was employed to input the structure and to visualize the optimized molecular structure and the orbital isosurfaces.

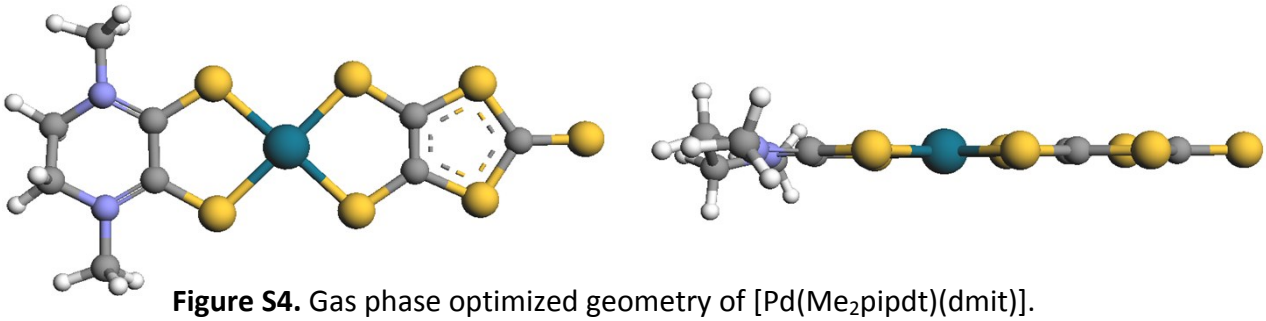

Figure S4. Gas phase optimized geometry of [Pd(Me_2pipdt)(dmit)].

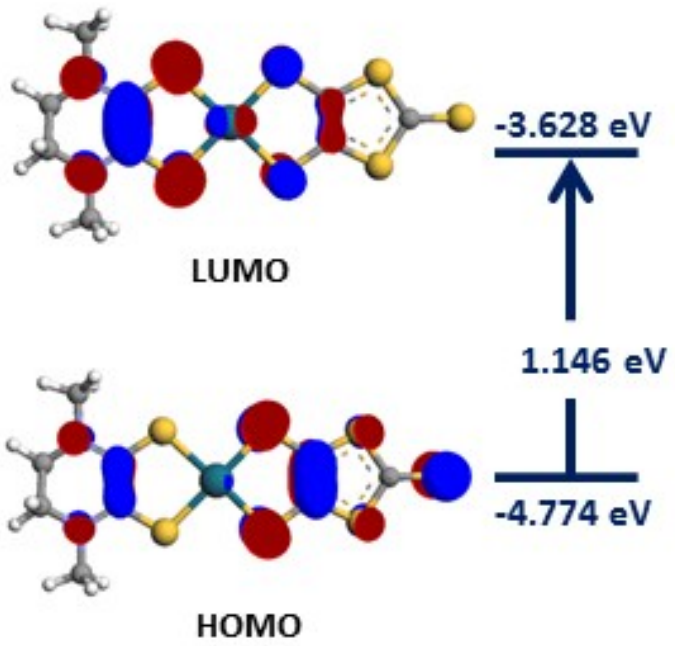

Figure S5. FOs of [Pd(Me_2pipdt)(dmit)] calculated by DFT methods; the contour plot value is 0.040.

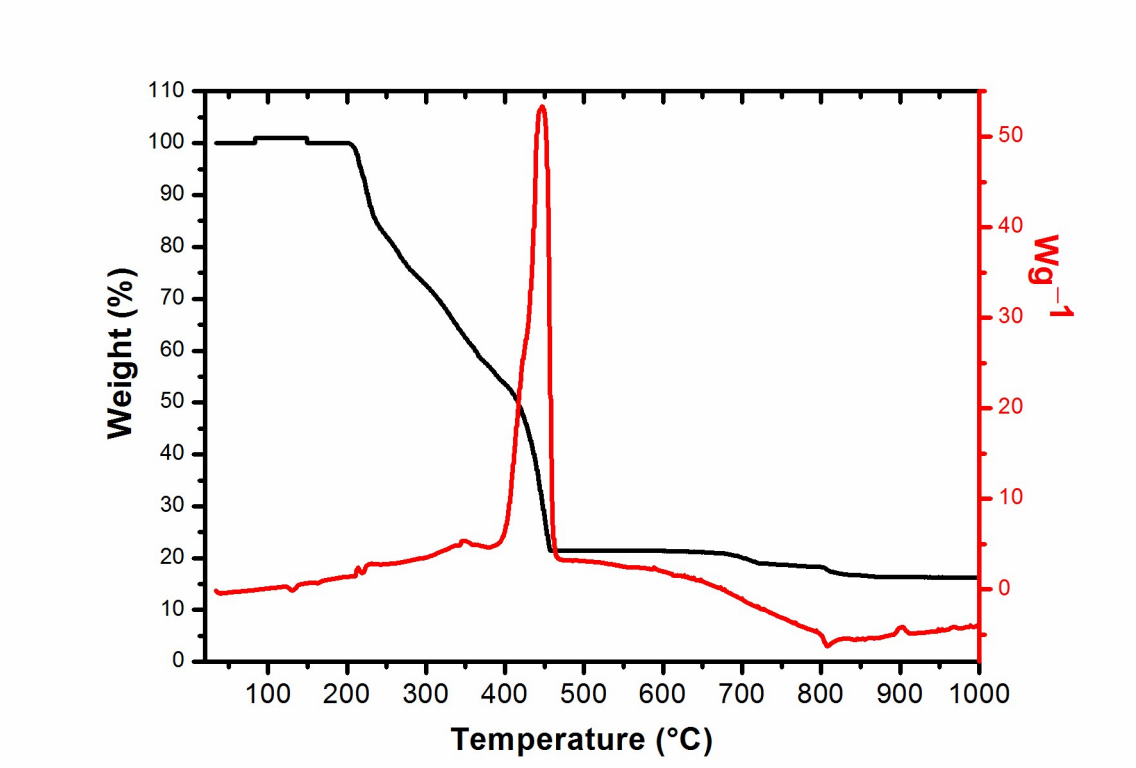

Figure S6. Comparison between TGA (black) and DCS (red) curves of **1**.

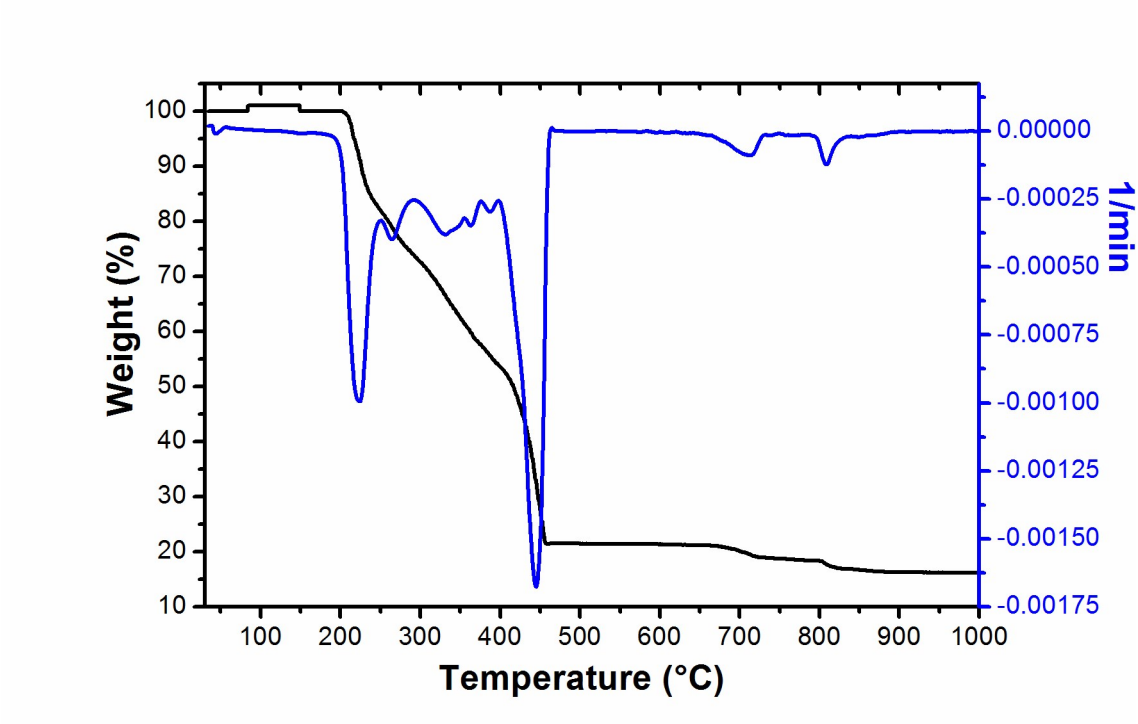

Figure S7. Comparison between TGA curve of **1** (black) and its first derivative.

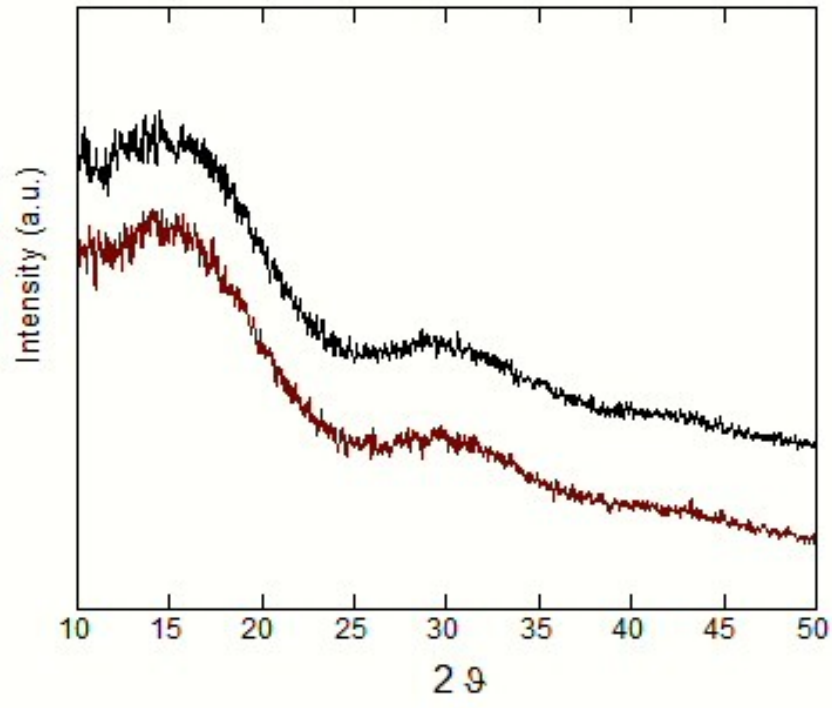

Figure S8. Comparison between the XRD patterns of films of pure PMMA (red-brown) and **1**-PMMA (black).

Wide-angle XRD patterns were recorded with a Panalytical Empyrean diffractometer equipped with a graphite monochromator and a X'Celerator linear detector. The scans were collected within the range 10–50° (2θ) using Cu Kα radiation.

References

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