Ultrafast Electronic and Vibrational Relaxations in Mixed-Ligand Dithione-Dithiolato Ni, Pd, and Pt Complexes

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Supplementary Information

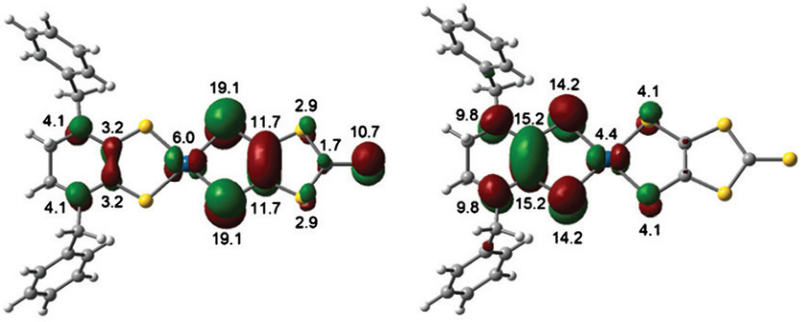

Figure S1. HOMO (left) and LUMO (right) of [Pt(Bz_2pipdt)(dmit)] calculated by DFT in DMF. The numbers show % contributions of the corresponding atomic orbitals. (From: D. Espa, L. Pilia, L. Marchiò, F. Artizzu, A. Serpe, M. L. Mercuri, D. Simão, M. Almeida, M. Pizzotti, F. Tessoree, and P. Deplano, *Dalton Trans.*, 2012, **41**, 3485.

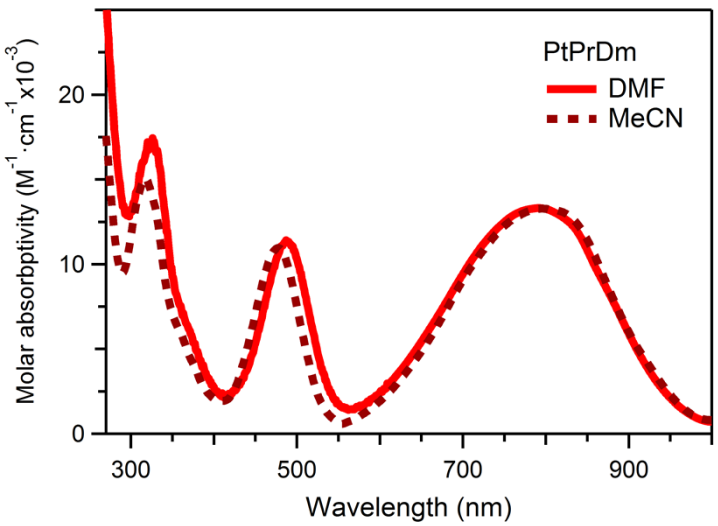

Figure S2. Comparison of steady-state UV-vis absorption spectra of [Pt(^{i}Pr$_2$pipdt)(dmit)] in DMF (solid line) and MeCN (dashed line).

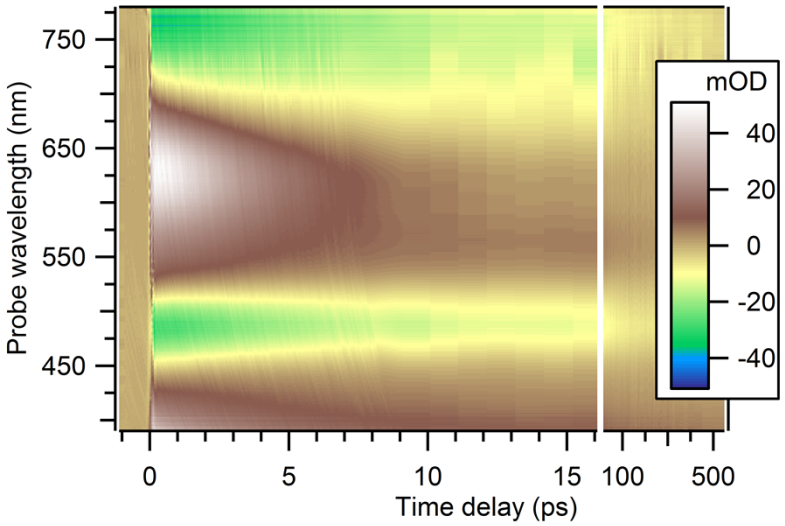

Figure S3. Wavelength-time 2D plot of TA spectra from [Pt(^{i}Pr$_2$pipdt)(dmit)] in DMF. The colour-coded amplitude corresponds to differential absorbance. (Individual spectra at selected time delays are shown in Figure 3.)

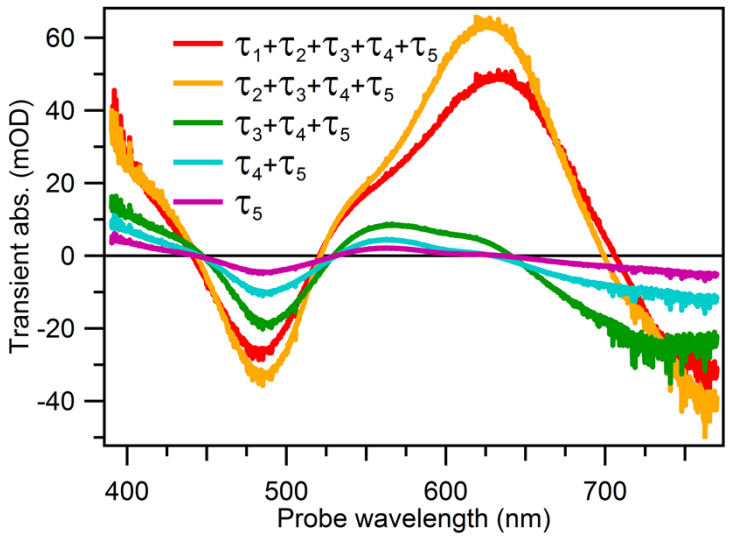

Figure S4. Sums of the DASs of [Pt(^{i}Pr$_2$pipdt)(dmit)] in DMF (Figure 4). The sum of all the DASs (red) can be considered as the time-zero spectrum upon a delta-pulse excitation. Removing each contribution one after the other reveals which kind of dynamics the removed DAS takes into account. However, it should be kept in mind that the observed change is only qualitative since the weight due to the temporal decay is neglected.

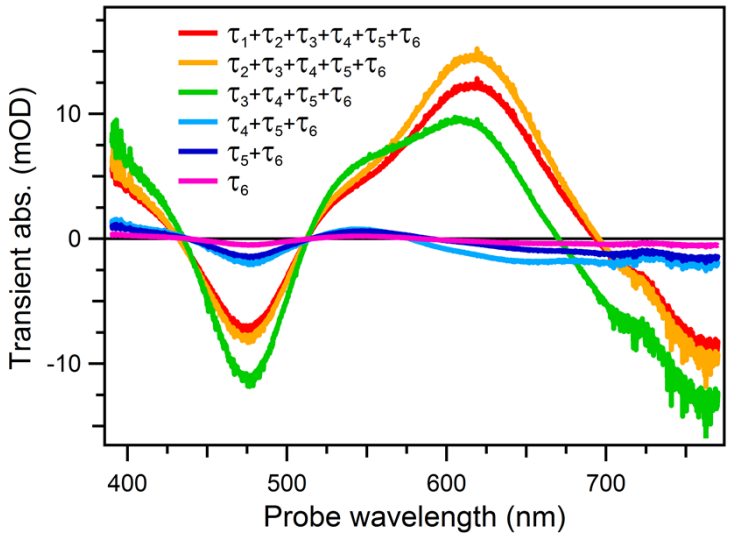

Figure S5. Sums of the DASs of [Pt(^{i}Pr$_2$pipdt)(dmit)] in MeCN (Figure 5). The sum of all the DASs (red) can be considered as the time-zero spectrum upon a delta-pulse excitation. Removing each contribution one after the other reveals which kind of dynamics the removed DAS takes into account. However, it should be kept in mind that the observed change is only qualitative since the weight due to the temporal decay is neglected.

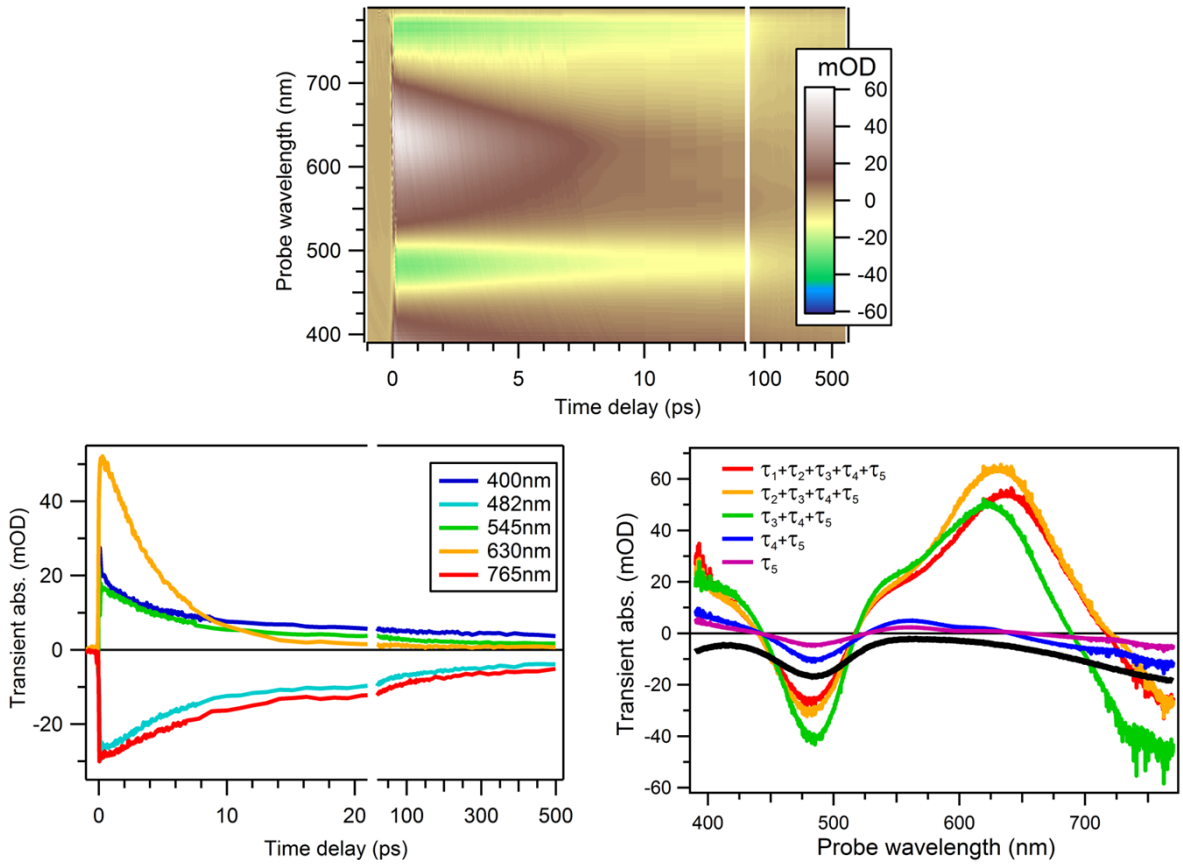

Figure S6. Photodynamics of [Pt(Bz_2pipdt)(dmit)] in DMF. Top: 2D wavelength-time plot of the TA spectra. Amplitude in a colour code. Bottom-left: kinetic traces at the maxima and minima of the TA spectra. Bottom-right: successive sums of the DASs.

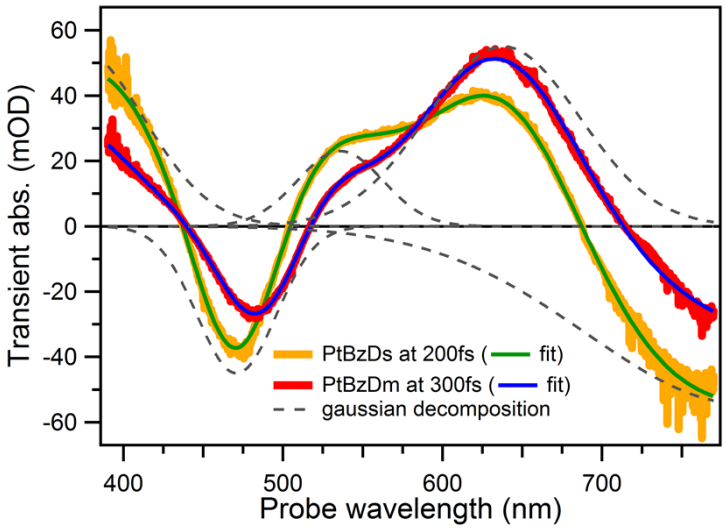

Figure S7. Decomposition of the earliest TA spectra of [Pt(Bz$_2$pipdt)(dmit)] (PtBzDm) and [Pt(Bz$_2$pipdt)(dsit)] (PtBzDs) from Figure 8 into the sum of five Gaussians. Fitting parameters are reported below. Red and blue curves: experimental and fitted spectra of [Pt(Bz$_2$pipdt)(dmit)], respectively. Orange and green curves: experimental and fitted spectra of [Pt(Bz$_2$pipdt)(dsit)], respectively. Dashed curves: individual Gaussians obtained for [Pt(Bz$_2$pipdt)(dsit)].

[Pt(Bz$_2$pipdt)(dmit)]			**[Pt(Bz$_2$pipdt)(dsit)]**		
Amplitude	Centre (nm)	Width (sdv)	Amplitude	Centre (nm)	Width (sdv)
-0.036 ± 0.003	840*	110*	-0.054 ± 0.001	790*	100*
0.056 ± 0.003	636 ± 1	48 ± 2	0.055 ± 0.004	638 ± 1	48 ± 2
0.012 ± 0.001	523 ± 6	28 ±4	0.023 ± 0.001	536 ± 3	34 ±6
-0.033 ± 0.003	485*	25*	-0.045 ± 0.003	471*	25*
0.032 ± 0.001	370 ± 10	42 ± 15	0.055 ± 0.010	370 ± 10	42 ± 15

* Determined independently from ground-state spectra.

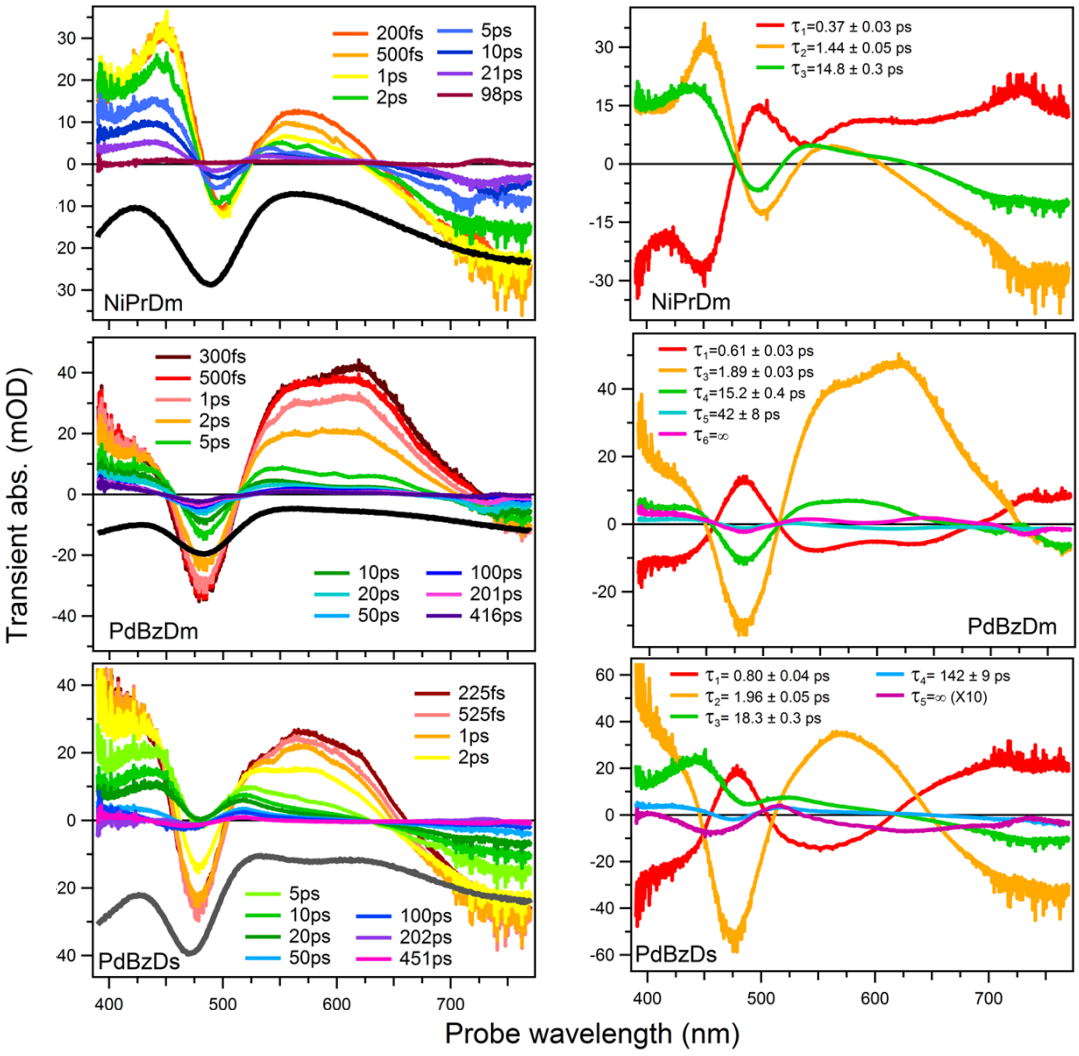

Figure S8. TA spectra (left panels) and respective DASs (right panels) measured in DMF for [Ni(^{i}Pr$_2$pipdt)(dmit)] (top), [Pd(Bz$_2$pipdt)(dmit)] (middle), and [Pd(Bz$_2$pipdt)(dsit)] (bottom).

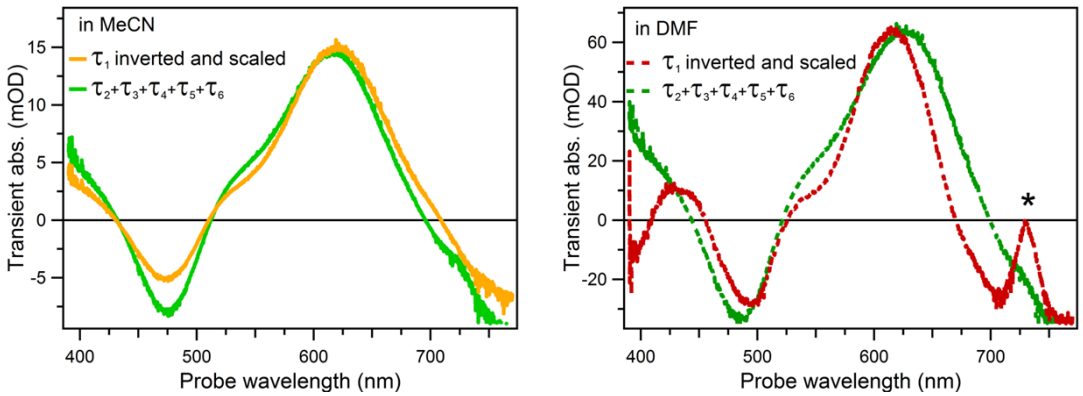

Figure S9. Comparison of the inverted and scaled first DAS (red and orange lines) with the sum of all subsequent DASs (green lines) that corresponds to the spectrum of the decaying S_1 state. Left (solid lines): [Pt(^{i}Pr$_2$pipdt)(dmit)] in MeCN. Right (dashed lines): [Pt(^{i}Pr$_2$pipdt)(dmit)] in DMF. * an SVD fitting artefact.