Impact of the Alkyne Substitution Pattern and Metallation on the Photoisomerization of Azobenzene-based Platinum(II) Diynes and Polyynes

Electronic Supporting Information

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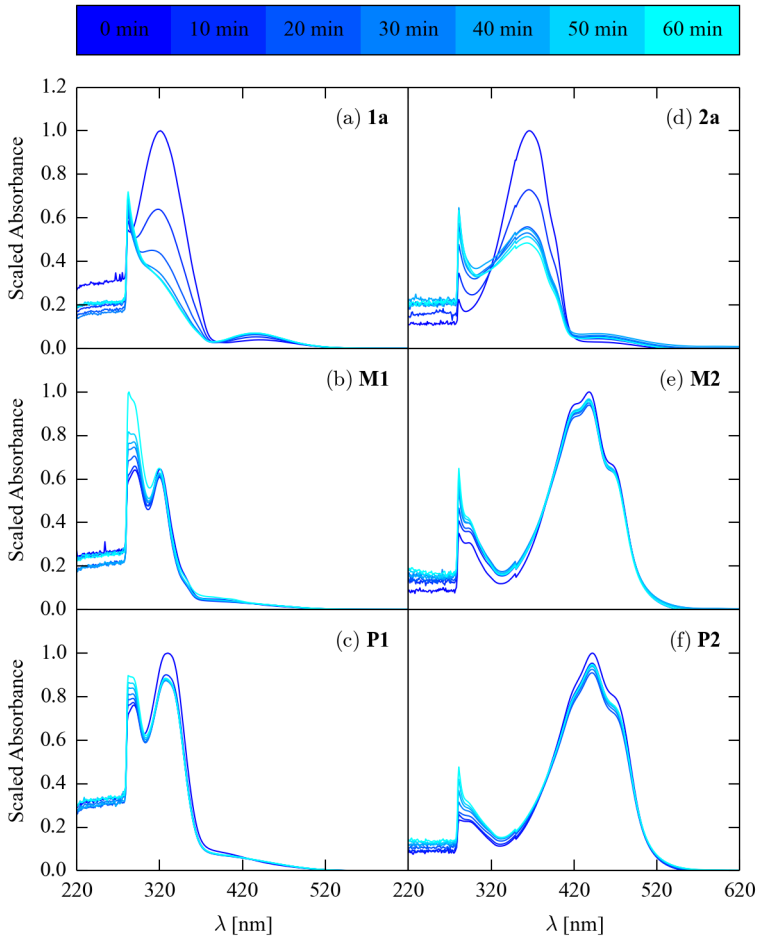

Figure S1 Time evolution of the UV-visible absorption spectra of the trimethylsilyl-protected azobenzene ligands **1a** and **2a** (a, d) and the corresponding Pt(II) diynes **M1** and **M2** (b, e) and polyynes **P1** and **P2** (c, f) in toluene under irradiation with 254 nm UV light. These spectra may be compared to those shown in **Figure 4** in the text. The sharp reduction in absorption below ~280 nm is due to subtraction of the reference spectrum of the solvent, which shows strong absorption in the UV.

Table S1 Electronic transitions in the cis and trans isomers of the meta- and para-substituted azobenzene ligands **1b** and **2b** forming the major long-wavelength features in the simulated spectra in **Figure 6** in the text. Assignment of the transitions to individual orbital excitations is based on the percentage contributions to the sum of the squared coefficients.

		E **[eV]**	**λ [nm]**	**Osc. Str.**	**Assignment**
meta-azo (**1b**)	cis	2.670	464.5	0.044	HOMO -> LUMO (88 %)
		4.155	298.4	0.166	HOMO-3 -> LUMO (88 %)
	trans	3.481	356.2	0.290	HOMO -> LUMO (75 %) HOMO-3 -> LUMO (21 %)
		3.776	328.4	0.596	HOMO-3 -> LUMO (77 %) HOMO -> LUMO (22 %)
para-azo (**2b**)	cis	2.544	487.5	0.102	HOMO -> LUMO (84 %)
		3.707	334.5	0.205	HOMO-2 -> LUMO (82 %)
		3.709	334.3	0.045	HOMO-1 -> LUMO (85 %)
		4.073	304.4	0.037	HOMO-3 -> LUMO (90 %)
	trans	3.230	383.9	1.288	HOMO -> LUMO (99 %)
		3.937	315.0	0.036	HOMO-3 -> LUMO (93 %)

Table S2 Electronic transitions in the *cis*- and *trans*-azo isomers of the Pt(II) complexes **M1** and **M2** forming the major long-wavelength features in the simulated spectra in **Figure 7** in the text. Assignment of the transitions to individual orbital excitations is based on the percentage contribution to the sum of the squared coefficients.

		E **[eV]**	**λ [nm]**	**Osc. Str.**	**Assignment**
meta-azo-Pt (**M1**)	cis	2.648	468.3	0.034	HOMO-4 -> LUMO (45 %) HOMO -> LUMO (31 %) HOMO-2 -> LUMO (12 %)
		2.929	423.4	0.022	HOMO -> LUMO (47 %) HOMO-1 -> LUMO (22 %) HOMO-4 -> LUMO (22 %)
		3.353	369.8	0.013	HOMO-3 -> LUMO (49 %) HOMO-2 -> LUMO (34 %) HOMO-6 -> LUMO (13 %)
		3.975	311.9	0.507	HOMO -> LUMO+1 (69 %) HOMO-1 -> LUMO+2 (14 %)
	trans	2.694	460.2	0.080	HOMO -> LUMO (97 %)
		3.309	374.7	0.021	HOMO-4 -> LUMO (93 %)
		3.657	339.1	1.296	HOMO-9 -> LUMO (94 %)
para-azo-Pt (**M2**)	cis	2.318	535.1	0.394	HOMO -> LUMO (85 %) HOMO-8 -> LUMO (12 %)
		3.117	397.9	0.141	HOMO-1 -> LUMO (82 %)
		3.142	394.7	0.214	HOMO-8 ->LUMO (40 %) HOMO-2 -> LUMO (33 %) HOMO-1 -> LUMO (11 %) HOMO -> LUMO (10 %)
	trans	2.629	471.6	2.128	HOMO -> LUMO (99 %)