Syntheses, Electronic Structures and Dichroic Behavior of Dinuclear Cyclopalladated Complexes of Push-Pull Azobenzenes

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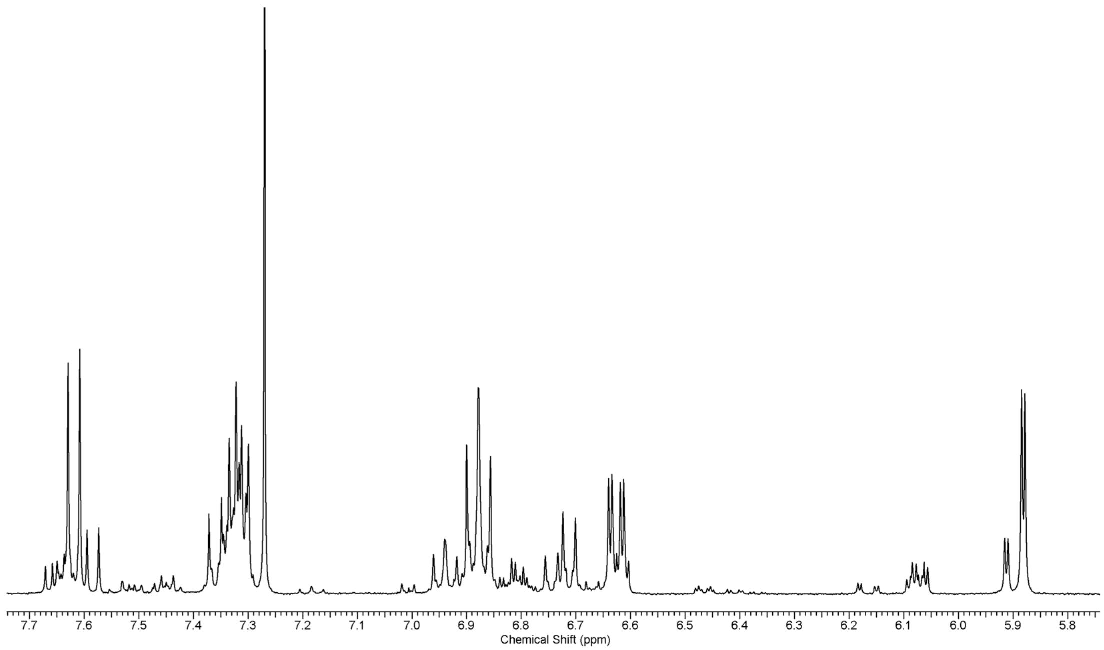
Supporting Information



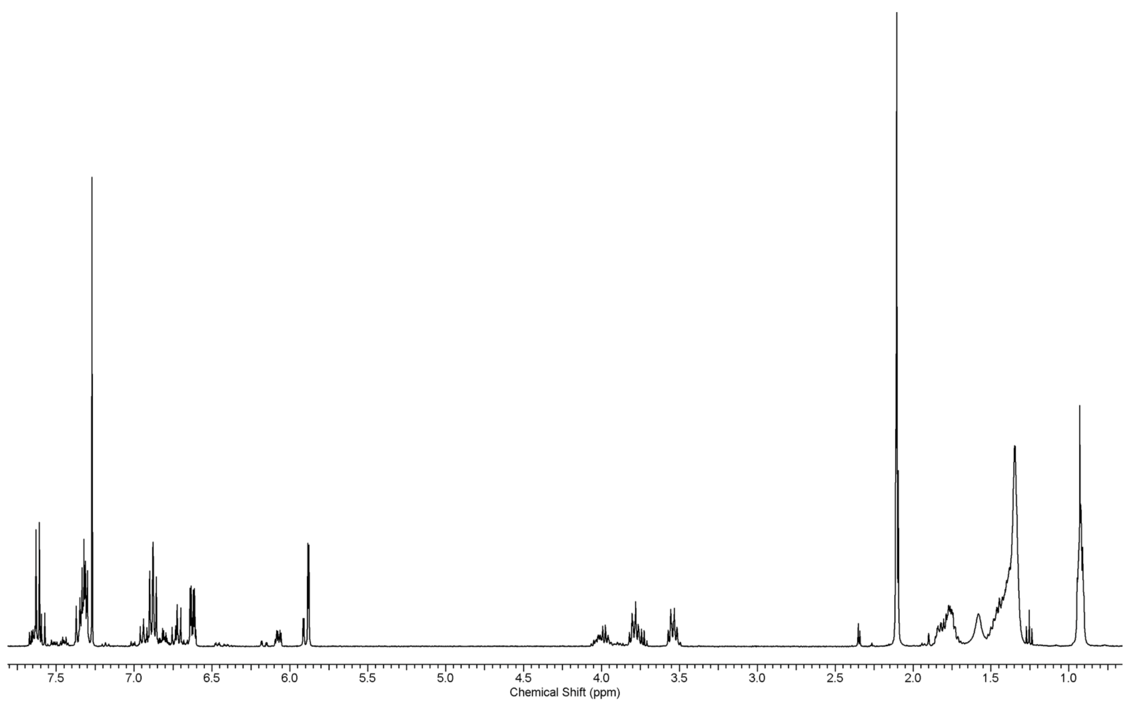


Figure S1. ^{1}H NMR spectra of **3c** recorded in $CDCl_3$ at 293 K showing the aromatic region (top) and the full range (bottom).

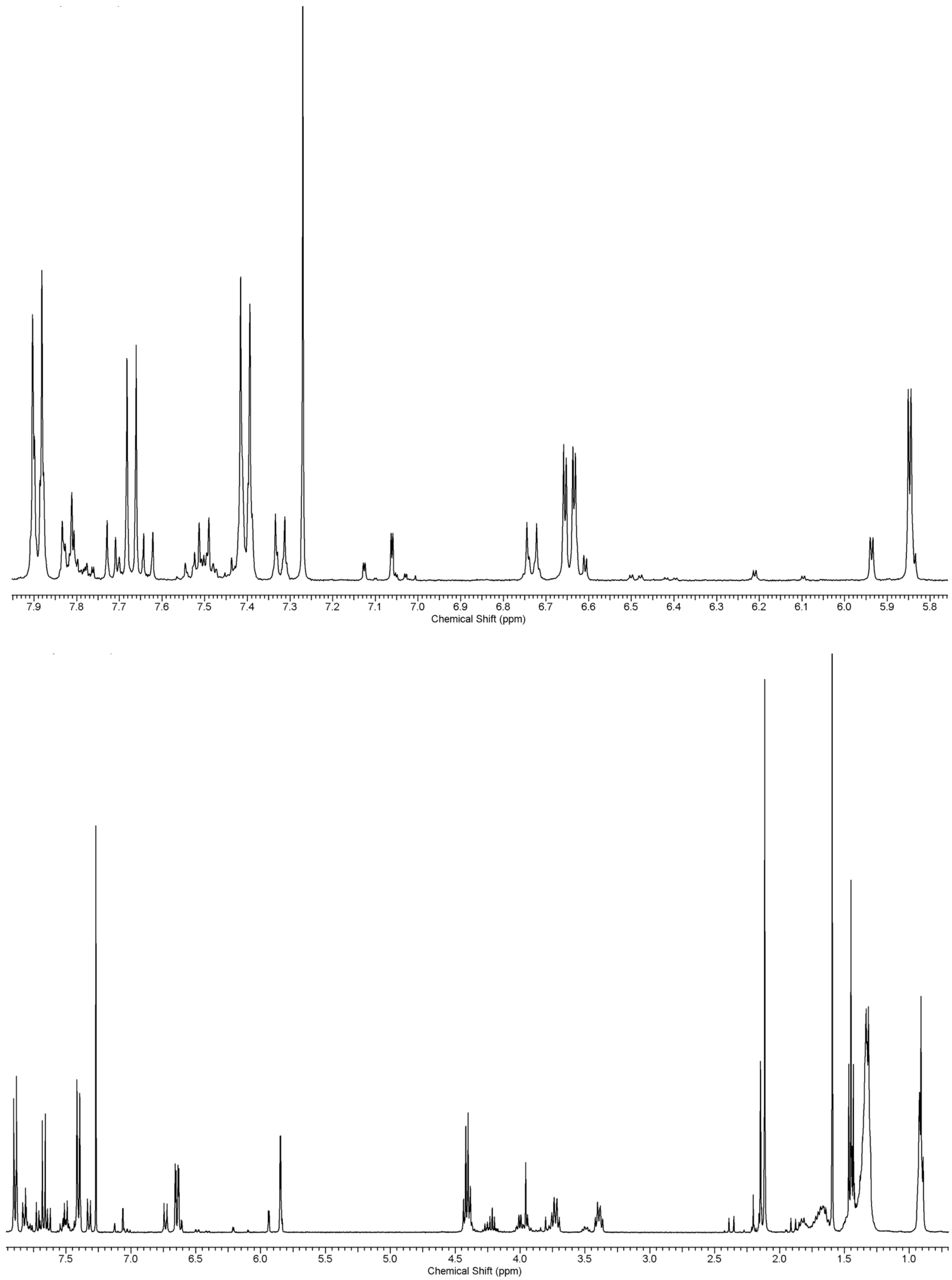


Figure S2. [1]H NMR spectra of **3d** recorded in $CDCl_3$ at 293 K showing the aromatic region (top) and the full range (bottom).

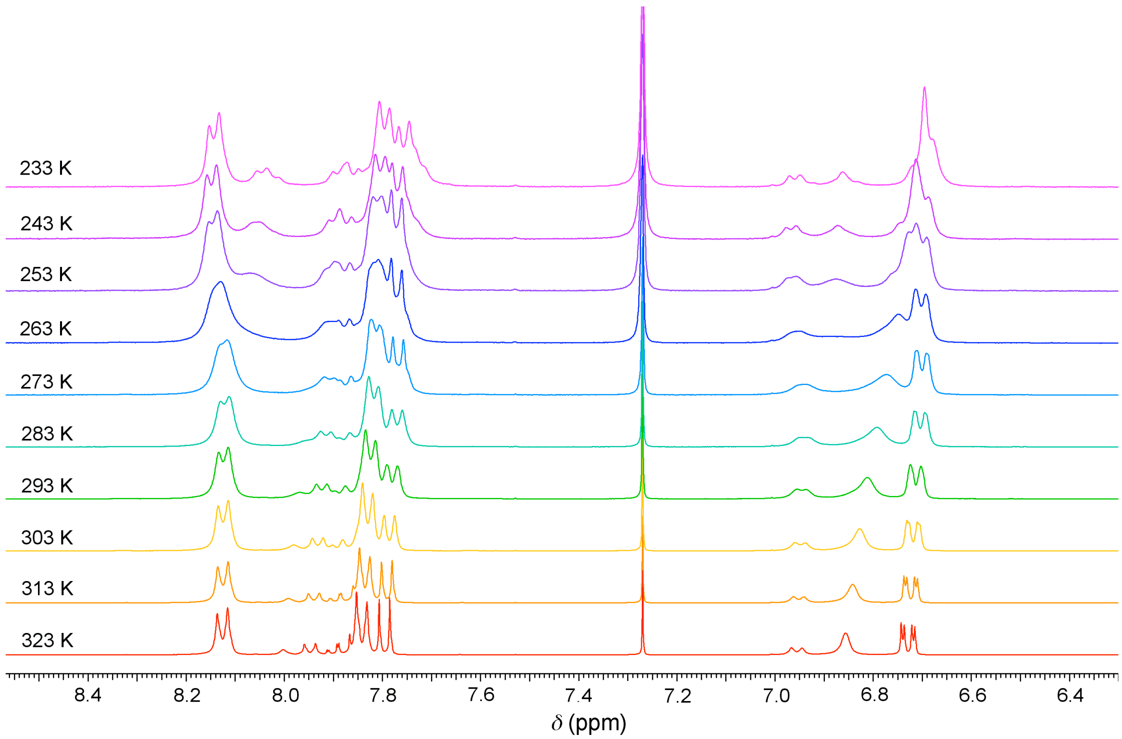


Figure S3. The aromatic region of the ^{1}H NMR spectrum of complex **2d** recorded at 400 MHz in $CDCl_3$ over the range 233–323 K.

Table S1. B3LYP-Optimized Cartesian Coordinates for the Model Chloride-bridged Palladium Complex

	x	y	z
Pd	1.74173	0.35128	–0.00348
Pd	–1.84785	–0.38222	–0.00800
Cl	0.19000	–1.63771	–0.12239
Cl	–0.29287	1.59892	–0.12053
N	4.62440	0.24208	–0.02636
N	3.62420	–0.53227	0.07822
N	–3.72675	0.50796	0.07822
N	–4.72813	–0.26553	–0.02452
O	3.17699	5.54061	–0.20961
O	–3.47789	–5.61190	–0.26718
C	4.29555	1.56993	–0.09384
C	2.91506	1.94105	–0.05604
C	2.58762	3.28416	–0.10122
C	3.60633	4.26502	–0.17840
C	4.96781	3.89388	–0.21816
C	5.30429	2.54587	–0.17555
C	3.91869	–1.92286	0.13641
C	5.01939	–2.45184	–0.56182
C	5.31170	–3.81038	–0.48006
C	4.50463	–4.63113	0.30924
C	3.41317	–4.12548	1.01215
C	3.11542	–2.76635	0.91816
C	–4.01779	1.89917	0.13417
C	–3.20859	2.74510	0.90729
C	–3.50225	4.10545	0.99601
C	–4.59746	4.60970	0.29813
C	–5.41129	3.78659	–0.48185
C	–5.12178	2.42735	–0.55986
C	–4.40408	–1.59317	–0.09751
C	–5.41845	–2.57217	–0.18213
C	–5.07616	–3.91006	–0.23755
C	–3.71313	–4.28791	–0.20974
C	–2.69288	–3.31411	–0.12652
C	–3.02924	–1.96606	–0.06743
H	1.55152	3.62535	–0.08015
H	5.75425	4.64499	–0.28053
H	6.34817	2.22653	–0.20397
H	5.63424	–1.78664	–1.16827
H	6.15288	–4.24671	–1.02205
H	2.80862	–4.79800	1.62324
H	2.26342	–2.35437	1.45793
H	–2.35398	2.33503	1.44422

H	–2.89024	4.77982	1.59748
H	–6.25508	4.22198	–1.02053
H	–5.74138	1.76076	–1.15989
H	–6.46238	–2.25268	–0.20349
H	–5.82989	–4.69612	–0.30351
H	–1.64400	–3.60719	–0.10918
C	4.10764	6.60210	–0.28642
H	3.51950	7.52889	–0.29745
H	4.78348	6.61492	0.58645
H	4.71135	6.54827	–1.20916
C	–2.14778	–6.09695	–0.26144
H	–1.57448	–5.72011	–1.12546
H	–1.61970	–5.82188	0.66758
H	–2.21891	–7.19055	–0.32476
F	–4.87543	5.91720	0.37263
F	4.78492	–5.93791	0.38831

Table S2. B3LYP–Optimized Cartesian Coordinates for the Model Acetate–bridged Palladium Complex

	x	y	z
Pd	–0.233576	1.444510	1.012254
Pd	0.240770	–1.774119	0.874390
O	1.556931	–1.298000	2.394187
O	–1.370832	–1.465028	2.261646
O	1.402269	0.950572	2.322425
O	–1.558330	0.774299	2.452332
N	0.825353	2.427517	–0.474826
N	–0.825742	–2.333966	–0.818501
C	–2.239082	–2.378461	–0.971828
C	–1.834900	–0.417843	2.779684
C	1.834341	–0.126122	2.800683
C	1.209618	–2.512519	–1.677595
C	–1.700241	2.142795	–0.099785
C	2.089022	–2.800482	–2.735574
C	–1.210776	2.931111	–1.186179
C	3.071747	–2.177197	–0.172448
C	2.237447	2.570334	–0.571183
C	–3.036172	–2.763078	0.117188
C	–2.839744	–2.062824	–2.204525
C	2.811299	3.773431	–1.019327
C	1.702183	–2.184478	–0.377980
C	2.802886	–0.028486	3.965236
C	3.463823	–2.769381	–2.524693
C	3.957049	–2.457137	–1.239388
C	–4.421404	–2.845181	–0.026108
C	3.060440	1.485545	–0.238777
C	–3.069218	2.015853	0.061326
C	–4.997298	–2.526167	–1.253838
C	–2.844464	–0.593963	3.900170
C	–3.466424	3.417376	–1.918934
C	–2.092797	3.559057	–2.082816
C	–4.222492	–2.133142	–2.346303
C	4.444778	1.587261	–0.371184
C	–3.956840	2.643723	–0.843693
C	4.994407	2.789231	–0.812548
C	4.194649	3.886822	–1.134254
H	1.678158	–3.046903	–3.717002
H	3.497727	–1.956709	0.808015
H	–2.565323	–2.992856	1.072081
H	–2.209573	–1.759278	–3.040338
H	2.161981	4.612518	–1.269865
H	3.118884	–1.020866	4.309423

H	3.680618	0.559962	3.656134
H	2.320598	0.519581	4.788952
H	4.141405	–2.986449	–3.349545
H	–5.061324	–3.153520	0.802755
H	2.609743	0.553622	0.094356
H	–3.494845	1.443025	0.886357
H	–3.141340	0.372061	4.326308
H	–2.413041	–1.237032	4.681935
H	–3.732419	–1.112374	3.505009
H	–4.146295	3.906259	–2.615705
H	–1.683926	4.157368	–2.899930
H	–4.712998	–1.882750	–3.288926
H	5.097208	0.741246	–0.146459
H	4.665440	4.813762	–1.467379
N	–0.148336	–2.573805	–1.865993
N	0.145816	3.064916	–1.338725
F	–6.328152	–2.592555	–1.390376
F	6.325002	2.896286	–0.931397
O	–5.268390	2.448646	–0.599354
O	5.270548	–2.390466	–0.934853
C	–6.241242	3.039167	–1.436377
H	–6.155284	2.681436	–2.477487
H	–7.218383	2.739424	–1.035561
H	–6.171893	4.141159	–1.428168
C	6.241579	–2.676771	–1.922369
H	6.183071	–1.969598	–2.768055
H	7.219560	–2.571461	–1.434963
H	6.139457	–3.706869	–2.305849

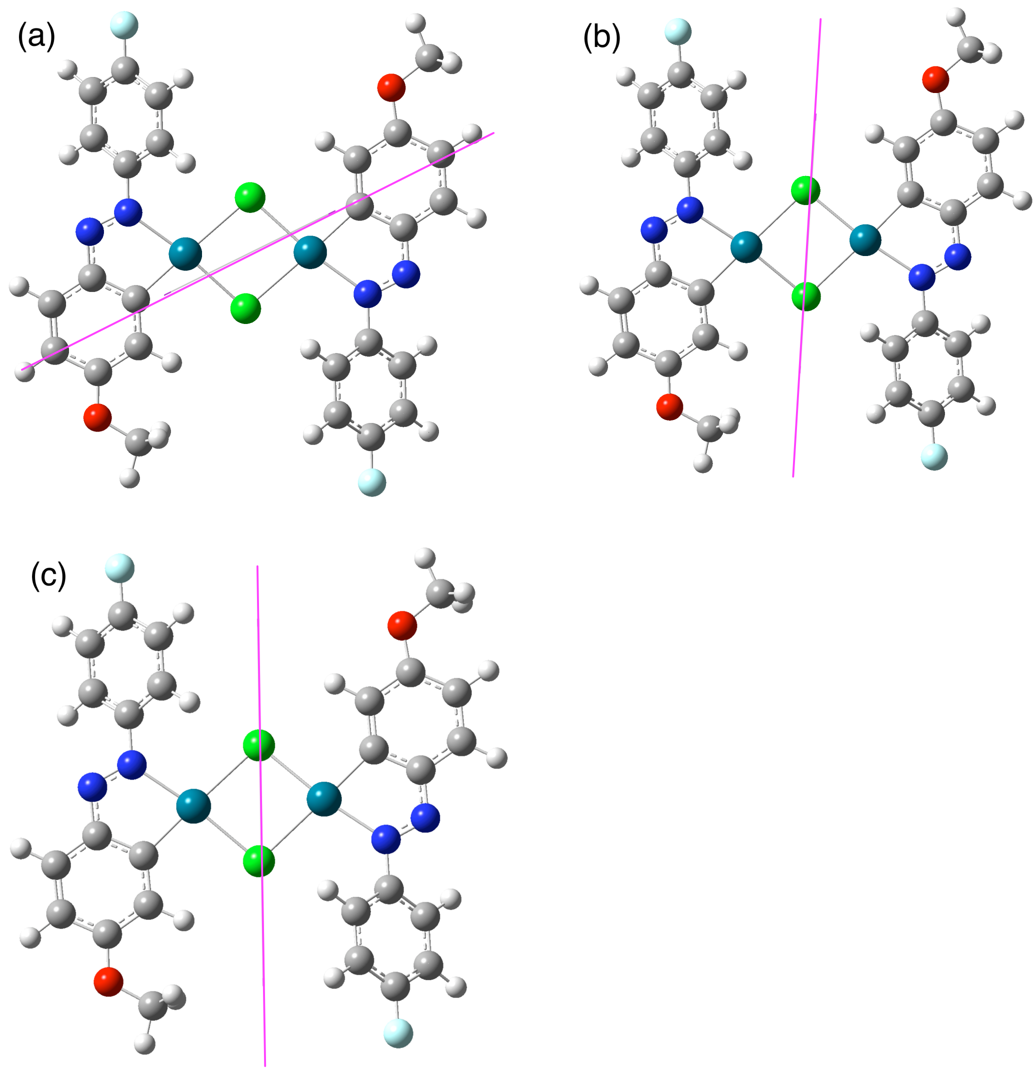


Figure S4. Calculated μ_{12} vectors (scaled to show direction) of the chloride-bridged model system for the transitions with (a) ΔE = 3.16 eV, (b) ΔE = 3.39 eV and (c) ΔE = 3.44 eV.