Supplementary Material (ESI) for PCCP

Electronic Supplementary Information

Superior *Z* → *E* and *E* → *Z* photoswitching dynamics of dihydrodibenzodiazocine, a bridged azobenzene, by S_1 (nπ*) excitation at λ = 387 and 490 nm

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Table S1. Atomic cartesian coordinates (Å) of the ground state equilibrium structures of **1Z** (**1Z$_{eq}$**, **1Z*$_{FC}$**) calculated by DFT

	x	y	z
N	-0.618886	-0.883112	1.731709
N	0.609782	-1.018485	1.682439
C	-3.149784	0.161082	-1.476635
C	-3.126067	-1.121614	-0.940862
C	-2.268677	-1.401151	0.108970
C	-1.398180	-0.426127	0.604236
C	-1.423557	0.881062	0.096547
C	-2.315554	1.135813	-0.952342
C	-0.617308	2.049069	0.627623
C	0.823679	1.776817	1.115925
C	1.562257	0.759864	0.289180
C	2.438948	1.120736	-0.733271
C	3.104755	0.160800	-1.485427
C	2.920865	-1.189857	-1.205541
C	2.078455	-1.573467	-0.171975
C	1.380794	-0.604192	0.545112
H	-3.818097	0.403014	-2.292443
H	-3.776124	-1.894502	-1.329033
H	-2.252341	-2.382436	0.564684
H	-2.346616	2.136199	-1.367177
H	-1.170931	2.520332	1.446423
H	-0.576530	2.792221	-0.170484
H	0.800661	1.447635	2.155139
H	1.367038	2.722747	1.104189
H	2.601046	2.172258	-0.939281
H	3.776150	0.465143	-2.277520
H	3.445224	-1.942265	-1.779820
H	1.950409	-2.616943	0.084059

Table S2. Atomic cartesian coordinates (Å) of the ground state equilibrium structures of **1E** (**$1E_{eq}$**, **$1E^*_{FC}$**) calculated by DFT.

	x	y	z
N	-0.367763	-0.503565	-1.012256
N	0.367727	0.501058	-1.014376
C	1.699781	0.196441	-0.639281
C	-1.699892	-0.197832	-0.638447
C	-1.806595	0.262669	0.689143
C	-3.094602	0.449760	1.187893
C	-4.220566	0.202705	0.407827
C	-4.081481	-0.272253	-0.891820
C	-2.813034	-0.496315	-1.411644
C	2.813048	0.496483	-1.411925
C	4.081485	0.274404	-0.891468
C	4.220598	-0.200188	0.408333
C	3.094632	-0.448481	1.187906
C	1.806541	-0.263003	0.688663
C	-0.587112	0.516610	1.579363
C	0.587164	-0.518405	1.578669
H	-3.218763	0.794292	2.208638
H	-5.207355	0.363877	0.823612
H	-4.957017	-0.476936	-1.495020
H	-2.678112	-0.883915	-2.413542
H	2.678190	0.883116	-2.414204
H	4.956913	0.479713	-1.494616
H	5.207413	-0.359883	0.824621
H	3.218988	-0.792080	2.208940
H	-0.184377	1.511396	1.372571
H	-0.964360	0.560324	2.603343
H	0.964632	-0.562884	2.602561
H	0.184731	-1.513104	1.371002

Table S3. Atomic cartesian coordinates (Å) of the ground state equilibrium structures of **1Z** (**1Z$_{eq}$**, **1Z*$_{FC}$**) calculated by CASSCF

	x	y	z
N	-0.618886	-0.883112	1.731709
N	0.609782	-1.018485	1.682439
C	-3.149784	0.161082	-1.476635
C	-3.126067	-1.121614	-0.940862
C	-2.268677	-1.401151	0.108970
C	-1.398180	-0.426127	0.604236
C	-1.423557	0.881062	0.096547
C	-2.315554	1.135813	-0.952342
C	-0.617308	2.049069	0.627623
C	0.823679	1.776817	1.115925
C	1.562257	0.759864	0.289180
C	2.438948	1.120736	-0.733271
C	3.104755	0.160800	-1.485427
C	2.920865	-1.189857	-1.205541
C	2.078455	-1.573467	-0.171975
C	1.380794	-0.604192	0.545112
H	-3.818097	0.403014	-2.292443
H	-3.776124	-1.894502	-1.329033
H	-2.252341	-2.382436	0.564684
H	-2.346616	2.136199	-1.367177
H	-1.170931	2.520332	1.446423
H	-0.576530	2.792221	-0.170484
H	0.800661	1.447635	2.155139
H	1.367038	2.722747	1.104189
H	2.601046	2.172258	-0.939281
H	3.776150	0.465143	-2.277520
H	3.445224	-1.942265	-1.779820
H	1.950409	-2.616943	0.084059

Table S4. Atomic cartesian coordinates (Å) of the ground state equilibrium structures of **1E** (**1E$_{eq}$**, **1E*$_{FC}$**) calculated by CASSCF.

	x	y	z
N	-0.367763	-0.503565	-1.012256
N	0.367727	0.501058	-1.014376
C	1.699781	0.196441	-0.639281
C	-1.699892	-0.197832	-0.638447
C	-1.806595	0.262669	0.689143
C	-3.094602	0.449760	1.187893
C	-4.220566	0.202705	0.407827
C	-4.081481	-0.272253	-0.891820
C	-2.813034	-0.496315	-1.411644
C	2.813048	0.496483	-1.411925
C	4.081485	0.274404	-0.891468
C	4.220598	-0.200188	0.408333
C	3.094632	-0.448481	1.187906
C	1.806541	-0.263003	0.688663
C	-0.587112	0.516610	1.579363
C	0.587164	-0.518405	1.578669
H	-3.218763	0.794292	2.208638
H	-5.207355	0.363877	0.823612
H	-4.957017	-0.476936	-1.495020
H	-2.678112	-0.883915	-2.413542
H	2.678190	0.883116	-2.414204
H	4.956913	0.479713	-1.494616
H	5.207413	-0.359883	0.824621
H	3.218988	-0.792080	2.208940
H	-0.184377	1.511396	1.372571
H	-0.964360	0.560324	2.603343
H	0.964632	-0.562884	2.602561
H	0.184731	-1.513104	1.371002

Table S5. Atomic cartesian coordinates (Å) of the excited state structure **1Z*$_{CI}$** calculated by CASSCF.

	x	y	z
C	0.248346	-0.075023	-0.005539
C	0.205767	-0.199785	1.380506
C	1.320843	-0.537075	2.121971
C	2.528369	-0.752634	1.480537
C	2.608225	-0.615937	0.105546
C	1.481210	-0.275333	-0.621611
C	-1.602254	2.437642	1.637681
C	-1.553073	3.677735	2.274650
C	-1.955024	4.814228	1.600361
C	-2.397383	4.726820	0.291106
C	-2.446006	3.491827	-0.338470
C	-2.049413	2.330499	0.305764
N	-1.045146	0.105583	2.055660
N	-1.114448	1.354009	2.326270
H	-2.807651	3.430141	-1.352715
H	-2.715392	5.611438	-0.236188
H	-1.910083	5.770417	2.096408
H	-1.188507	3.727627	3.286789
H	1.560022	-0.157747	-1.691271
H	3.547132	-0.767489	-0.402079
H	3.401158	-1.015031	2.055940
H	1.236810	-0.625349	3.192974
H	-0.571032	0.772549	-1.759149
H	-1.327272	-0.719061	-1.255465
H	-2.824321	1.115414	-1.238061
H	-2.759499	0.322617	0.307204
C	-2.198295	0.977066	-0.356440
C	-0.945303	0.237561	-0.888736

Table S6. Atomic cartesian coordinates (Å) of the excited state structure **1E*$_{CI}$** calculated by CASSCF

	x	y	z
C	0.027654	-0.044299	0.032537
C	-0.137491	0.044053	1.417018
C	-0.163342	1.278726	2.052264
C	-0.062619	2.447031	1.318055
C	0.089703	2.378010	-0.056055
C	0.130606	1.142559	-0.682652
C	-0.974143	-3.287316	1.735923
C	-1.023636	-3.432792	0.349841
C	-0.971464	-4.722671	-0.165726
C	-0.868959	-5.832410	0.657563
C	-0.851867	-5.669608	2.032508
C	-0.909327	-4.395154	2.567926
N	-0.214103	-1.094696	2.253323
N	-1.083361	-2.016860	2.387056
H	-0.104360	3.400860	1.818324
H	-0.265826	1.304246	3.123820
H	0.253567	1.095466	-1.752934
H	0.184202	3.279195	-0.640238
H	-0.905588	-4.240957	3.633962
H	-1.016232	-4.857610	-1.234834
H	-0.801706	-6.525811	2.685419
H	-0.814967	-6.818428	0.224892
H	0.974561	-1.934292	-0.277747
H	0.351638	-1.186790	-1.721433
H	-1.417566	-2.614664	-1.564122
H	-1.992947	-1.623144	-0.254790
C	-1.157697	-2.245667	-0.574294
C	0.127565	-1.374611	-0.673645