Supporting Information

for

Enhanced charge transport via d(δ)-p(π) conjugation in Mo_2-integrated single-molecular junctions

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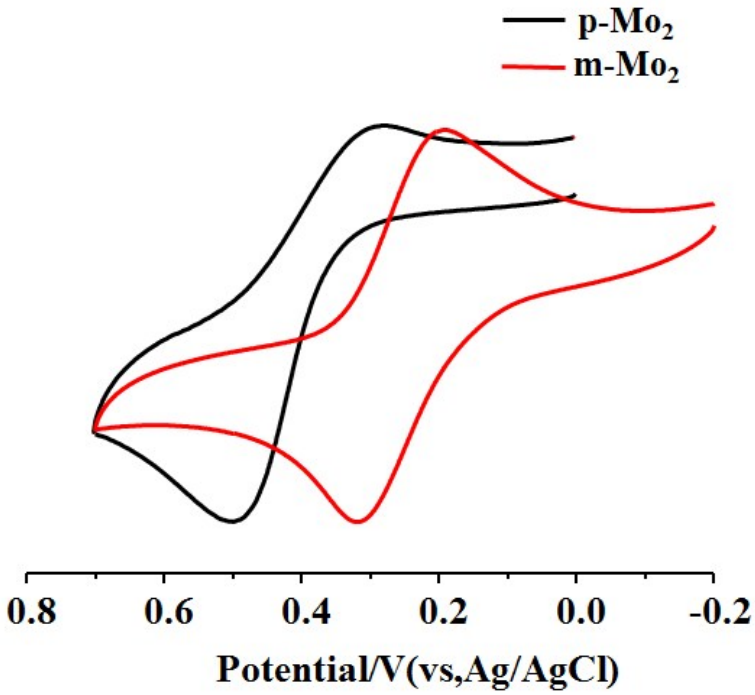

Figure S1 Cyclic voltammograms (CVs) for complexes **p-Mo$_2$** (black) and **m-Mo$_2$** (red).

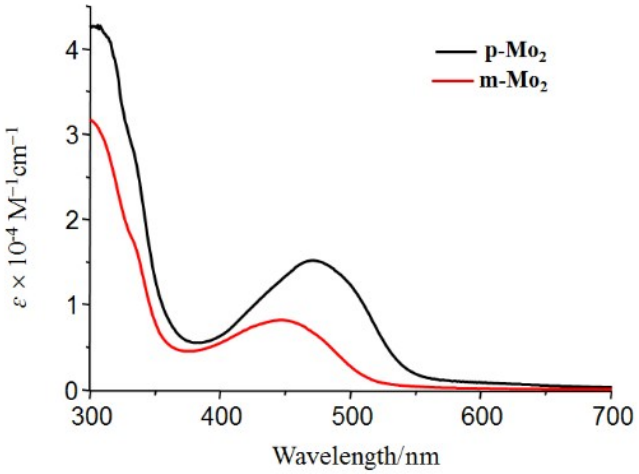

Figure S2. Electronic absorption spectra of **p-Mo$_2$** (black) and **m-Mo$_2$**(red).

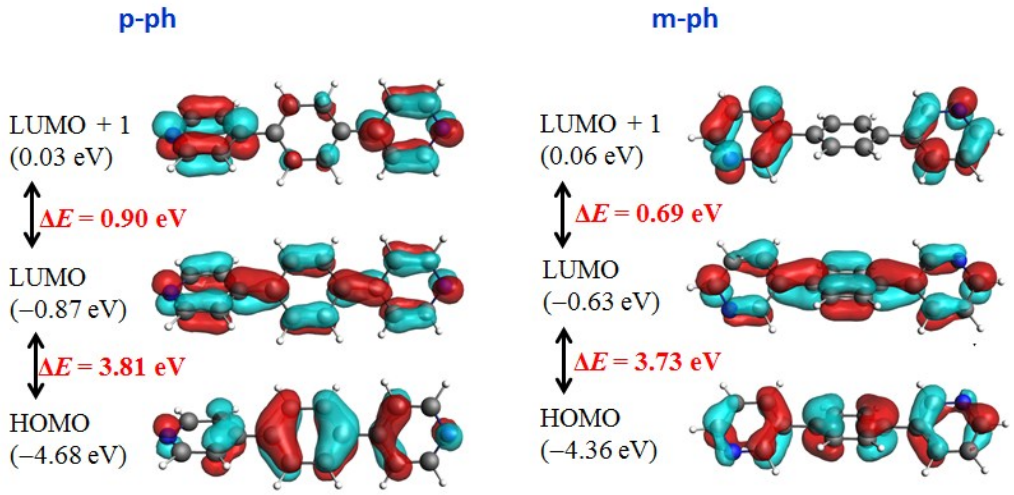

Figure S3 Frontier molecular orbitals (isodensity value 0.04) of **p-Ph** and **m-Ph**, showing the relative orbital energies and the HOMO–LUMO energy gaps.

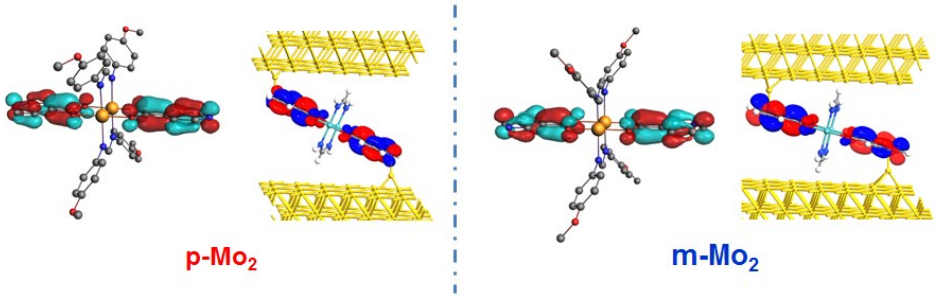

Figure S4 DFT calculated LUMOs (isodensity value 0.04) for **p-Mo$_2$** (left) and **m-Mo$_2$** (right), in comparison with the calculated MPSH plots (isodensity value 0.07) for junction geometries based on the simplified models.

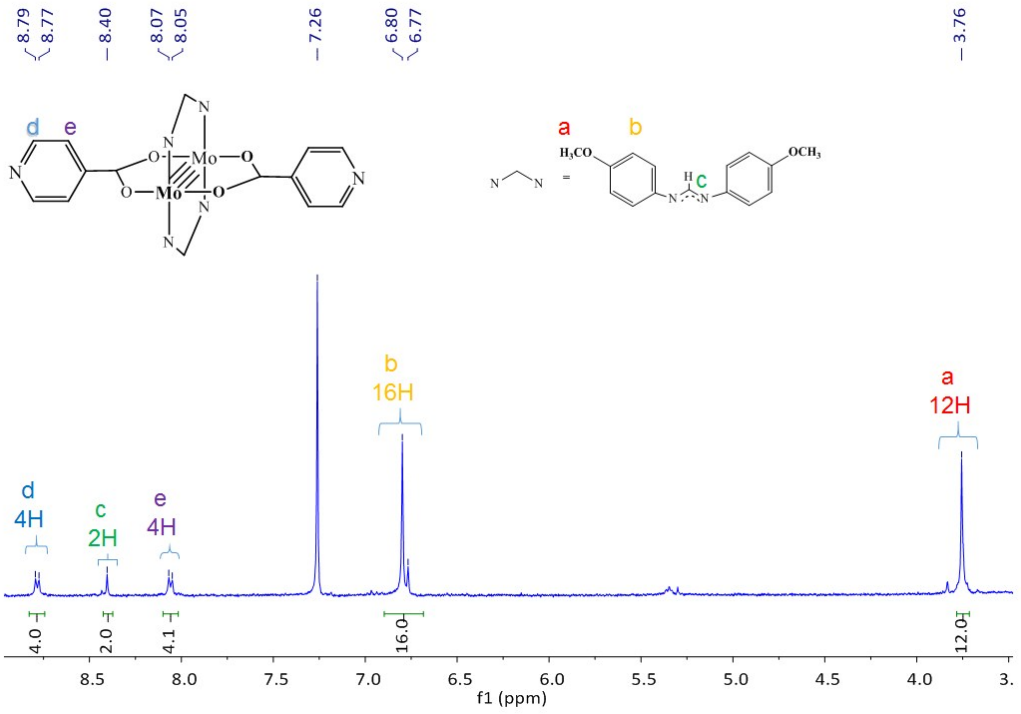

Figure S5 ^{1}H NMR spectrum of compound **p-Mo$_2$** in $CDCl_3$.

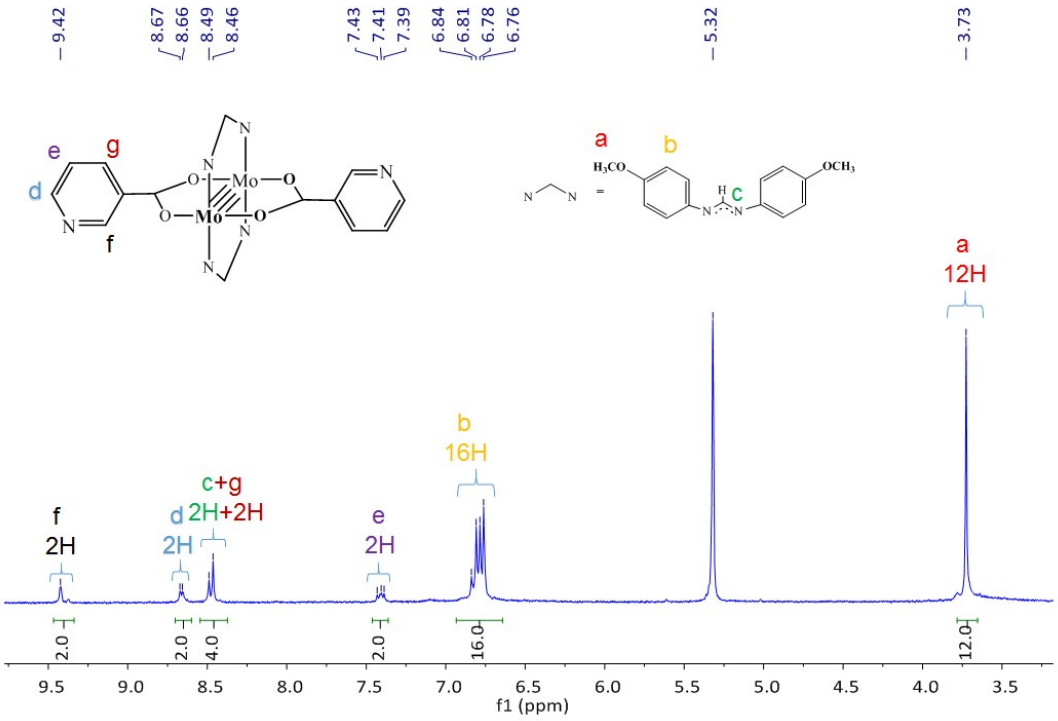

Figure S6 ^{1}H NMR spectrum of compound **m-Mo$_2$** in CD_2Cl_2.

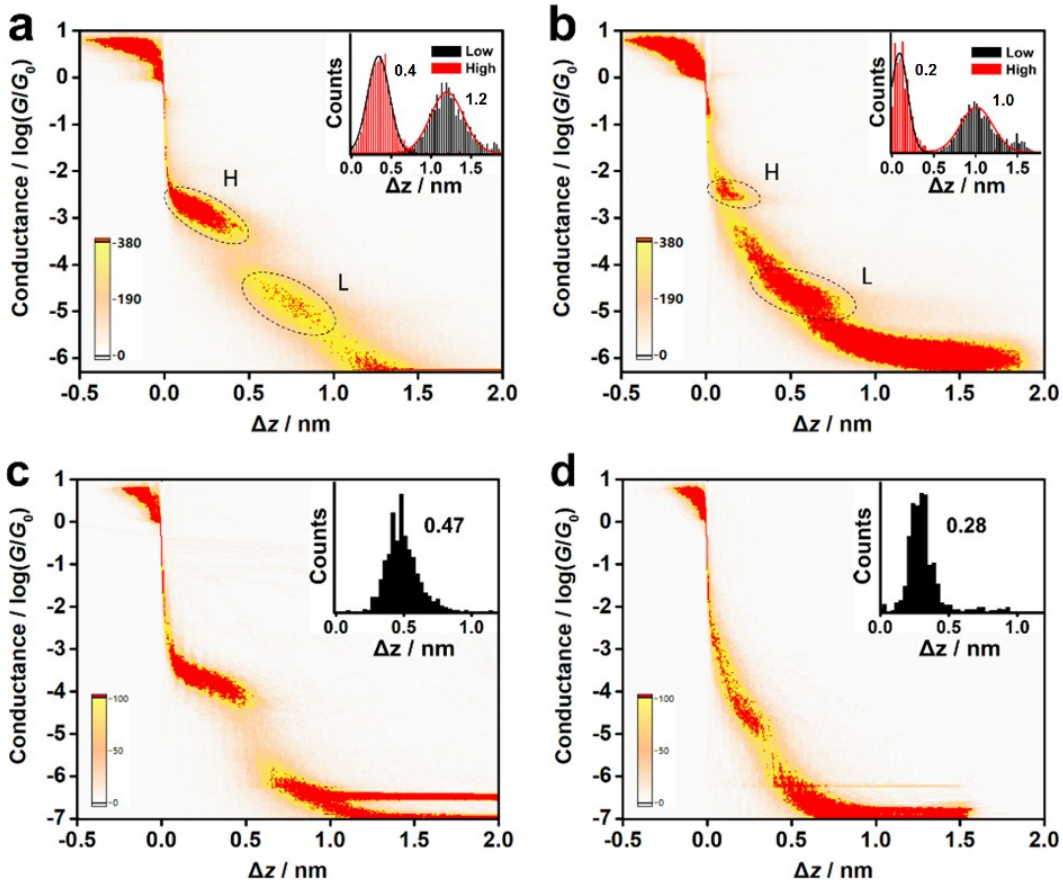

Figure S7 2D conductance-displacement histograms for **p-Mo$_2$** (a) and **m-Mo$_2$** (b) with different molecular plateau regions indicated by dashed circles. H and L refer to high and low conductances, respectively. Inset: Displacement distribution histograms for high-conductance feature (red) and low-conductance feature (black). 2D conductance-displacement histograms for **p-Ph** (c) and **m-Ph**(d).

As shown in Figure S7, both of these 2D conductance-displacement histograms for **p-Mo$_2$** and **m-Mo$_2$** show two separate molecular plateau regions. As no molecular plateau observed in the blank experiments (black curves in Figure 3a), we consider that each molecular plateau region represents a particular configuration. And the displacement distribution histograms show that the probable length of molecular junctions could be very different for every molecular plateau region. According to what we have discussed in the Results and discussion section, the most probable absolute distances z* (determined from z* =Δz + 0.5 nm) is the actual length of the molecular junction we measured. The z* of low-conductance region for **p-Mo$_2$** (1.7 nm) is longer than that of

m-Mo_2 (1.5 nm), and this is consistent with the N···N distances of their molecular lengths in the solid state (the length of N-Au bond is ~2 Å). Therefore, we identified the high-conductance features as the tilted configuration of Mo_2 complexes molecular junctions.

The whole-range 2D histograms of the phenylene bipyridines are shown in Figure S7c and d. In the low-conductance region, the conductance curves were observed to rapidly drop to the tunneling background from the molecular conductance plateau. The molecules with pyridyl anchor should have two conductance features, see Manrique et al., Nat. Commun. 2015, 6, 6389 and Quek et al., Nat. Nanotechnol. 2009, 4, 230. Referring to the literature, the low conductance of OPE-type molecule (p-p-p) is 10^{-7} G_0. Besides, according to the features of Mo_2 complexes, the low-conductance signal is two orders lower than the high-conductance signal. Thus, the low-conductance features of the phenylene bipyridines would probably below 10^{-6} G_0 and be covered by the tunneling background. It is known that the high-conductance feature of molecules with pyridyl anchors corresponding to the tilted configuration and the additional Au-π coupling. As the junction is elongated to a vertical geometry, the high-conductance feature tends to snap to the low-conductance feature after the Au-π coupling breaks. So we can compare the high-conductance features between the Mo_2 complexes and the phenylene bipyridines, as the same tilted configuration and bonding mode of those molecular junctions.

Table S1 Selected bond lengths (Å) and torsion angles (°)[a] of **p-Mo_2** and **m-Mo_2**.

	p-Mo_2	**m-Mo_2**
Mo(1)–Mo(2)	2.1312(9)	2.1342(18)
Mo(1)–N(1)	2.143(9)	2.157(10)
Mo(1)–N(2)	2.156(8)	2.149(10)
Mo(2)–N(3)	2.130(8)	2.155(11)
Mo(2)–N(4)	2.136(8)	2.154(11)

Mo(1)–O(5)	2.104(6)	2.110(8)
Mo(2)–O(8)	2.119(6)	2.126(9)
ϕ(1)	11.4	20.4

[a] ϕ(1) refers to C(5)–C(4)–C(3)–O(6).

Table S2 DFT energy-minimized Cartesian coordinates (Å) for compound **p-Mo_2**.

Atom	x	y	z
Mo	-0.753587	-0.874432	-0.347925
Mo	0.681439	0.662735	-0.392670
O	2.264316	-0.712566	-0.462154
O	-0.797628	2.149411	-0.325296
O	-2.337764	0.501192	-0.324636
O	0.727085	-2.360785	-0.367130
N	0.835024	0.724256	1.745862
N	-0.779223	-0.935069	1.794746
C	1.958334	-1.968948	-0.427590
N	-0.871186	-0.970691	-2.487210
C	3.043066	-2.982002	-0.457741
N	5.116596	-4.917980	-0.514908
N	0.669531	0.757297	-2.534565
C	-0.121274	-0.106911	-3.181029
H	-0.154859	-0.107046	-4.286749
C	1.549962	1.594787	-3.271251
N	-5.187617	4.707222	-0.213660
C	4.396925	-2.599199	-0.577069
H	4.665380	-1.538504	-0.652478
C	-2.030268	1.757541	-0.310867
O	4.219516	4.064448	-5.399782
C	-1.794655	-1.808399	-3.168928
O	3.940575	4.594717	4.414619
C	1.721758	2.936425	-2.869543
H	1.129184	3.321247	-2.027630
C	1.623842	1.686302	2.432556
C	3.332651	3.317654	-4.658224
C	2.757033	-4.361769	-0.367892
H	1.719766	-4.704656	-0.271188
C	2.604295	3.794861	-3.548451
H	2.702048	4.832544	-3.208940
C	0.048380	-0.105645	2.440496
H	0.082277	-0.106120	3.546229

O	-4.586830	-4.278625	-5.133163
C	-5.456031	3.388609	-0.283082
H	-6.523326	3.117843	-0.314114
C	-3.657047	-3.531708	-4.446287
C	5.380110	-3.599393	-0.601141
H	6.443646	-3.328452	-0.695397
C	-2.610511	-1.337255	-4.227706
H	-2.550356	-0.284172	-4.533606
C	-3.888545	5.062982	-0.175995
H	-3.689497	6.144845	-0.118124
C	3.822124	-5.274017	-0.400279
H	3.627125	-6.355876	-0.329951
C	2.939338	1.941801	1.991095
H	3.346381	1.352119	1.157636
C	-1.940520	-3.150507	-2.758675
H	-1.297454	-3.535553	-1.954767
C	-2.861960	-4.009212	-3.383404
H	-2.937884	-5.047286	-3.039558
C	2.299346	1.123894	-4.378199
H	2.219732	0.071023	-4.680367
C	-1.524496	-1.899228	2.525428
C	-3.114748	2.770767	-0.277602
C	-4.760283	-5.642316	-4.742696
H	-5.540807	-6.049966	-5.408177
H	-3.826460	-6.228350	-4.874965
H	-5.099363	-5.726833	-3.688632
C	-4.473350	2.388195	-0.316259
H	-4.745991	1.327500	-0.374731
C	-2.823582	4.150520	-0.205965
H	-1.782344	4.493219	-0.171042
C	3.171667	1.974217	-5.065490
H	3.758783	1.609598	-5.918444
C	1.125617	2.434603	3.528208
H	0.088916	2.288294	3.859907
C	3.746648	2.905501	2.620646
H	4.766063	3.067461	2.251649
C	-2.863277	-2.155998	2.161131
H	-3.319529	-1.564464	1.354894
C	3.243659	3.632555	3.719908
C	-3.522382	-2.187782	-4.861320
H	-4.160552	-1.822889	-5.676656
C	-0.961469	-2.649733	3.587627
H	0.092650	-2.502464	3.858393
C	-1.720853	-3.606953	4.268410

H	-1.284397	-4.194921	5.086356
C	1.925672	3.387812	4.166581
H	1.539329	3.973849	5.010670
C	4.419271	5.427022	-5.018078
H	3.480338	6.015161	-5.092040
H	4.822146	5.508726	-3.986485
H	5.158545	5.834536	-5.729178
C	5.276572	4.878364	3.994123
H	5.306401	5.253306	2.949267
H	5.645706	5.666741	4.672701
H	5.931885	3.986262	4.081831
O	-3.714891	-4.820386	4.628834
C	-3.630217	-3.123729	2.833326
H	-4.669241	-3.286727	2.524499
C	-3.062072	-3.853624	3.898498
C	-5.071286	-5.108677	4.283363
H	-5.725283	-4.220463	4.411218
H	-5.157883	-5.479961	3.240320
H	-5.397570	-5.901022	4.979052

Table S3 DFT energy-minimized Cartesian coordinates (Å) for compound **m-Mo_2**.

Atom	x	y	z
Mo	6.508920	1.618242	5.646782
C	8.592878	1.803474	7.696968
O	7.560492	1.794931	8.474829
N	5.538948	3.813155	7.575786
O	7.891396	6.238774	0.600898
O	3.859482	6.603695	12.172191
N	6.454580	3.754184	5.448196
C	5.884107	5.677951	9.177316
N	11.320752	2.034590	10.296129
C	10.123724	1.957778	9.694798
C	9.947874	1.887666	8.291104
C	6.284033	6.053689	2.468853
C	5.148571	4.566064	8.715788
C	8.300984	4.692547	2.339412
C	6.779852	4.428663	4.240590
C	5.946475	5.418314	3.678162
C	7.466025	5.692345	1.790468

C	11.106060	1.900184	7.483346
C	5.966925	4.451356	6.480606
C	5.484224	6.391526	10.322270
C	7.962914	4.073771	3.546124
C	4.001115	4.170511	9.447064
C	3.602364	4.867187	10.591147
C	4.338437	5.988151	11.038032
C	7.073090	7.247976	0.005985
C	4.577778	7.737149	12.663417
C	12.359534	1.980319	8.102614
C	12.412939	2.045071	9.507073
O	8.467028	1.739318	6.409448
H	8.632115	3.320127	3.984273
H	9.220370	4.422623	1.803882
H	5.604538	6.810638	2.060085
H	4.999427	5.674491	4.171863
H	3.406506	3.319662	9.086069
H	2.710098	4.565125	11.154646
H	6.088923	7.243739	10.653705
H	6.805122	5.973056	8.656854
H	9.241922	1.950246	10.351882
H	13.381233	2.108641	10.028394
H	13.284262	1.992698	7.510313
H	11.006271	1.847233	6.391910
H	5.917159	5.555455	6.428478
H	7.589759	7.547392	-0.922303
H	6.064063	6.860133	-0.247771
H	6.969314	8.134021	0.667337
H	4.600851	8.561497	11.919653
H	4.031983	8.074691	13.561464
H	5.617656	7.471274	12.947857
Mo	5.672297	1.671373	7.576460
C	3.588339	1.486140	5.526275
O	4.620726	1.494684	4.748414
N	6.642269	-0.523539	5.647456
O	4.289813	-2.949162	12.622340
O	8.321731	-3.314074	1.051046
N	5.726638	-0.464569	7.775046
C	6.297110	-2.388336	4.045926
N	0.860467	1.255016	2.927114
C	2.057494	1.331831	3.528445
C	2.233344	1.401946	4.932138
C	5.897179	-2.764077	10.754388
C	7.032645	-1.276448	4.507454

C	3.880230	-1.402932	10.883827
C	5.401364	-1.139049	8.982652
C	6.234739	-2.128701	9.545079
C	4.715187	-2.402732	11.432771
C	1.075157	1.389427	5.739896
C	6.214292	-1.161741	6.742637
C	6.696993	-3.101910	2.900970
C	4.218302	-0.784156	9.677117
C	8.180100	-0.880893	3.776176
C	8.578850	-1.577567	2.632092
C	7.842778	-2.698532	2.185206
C	5.108117	-3.958366	13.217253
C	7.603436	-4.447528	0.559819
C	-0.178317	1.309289	5.120627
C	-0.231721	1.244535	3.716168
O	3.714189	1.550296	6.813795
H	3.549103	-0.030511	9.238968
H	2.960844	-1.133008	11.419356
H	6.576672	-3.521028	11.163156
H	7.181787	-2.384879	9.051379
H	8.774708	-0.030042	4.137170
H	9.471114	-1.275503	2.068591
H	6.092294	-3.954123	2.569536
H	5.376097	-2.683443	4.566389
H	2.939297	1.339362	2.871362
H	-1.200015	1.180963	3.194848
H	-1.103044	1.296910	5.712928
H	1.174946	1.442381	6.831332
H	6.264058	-2.265840	6.794764
H	4.591446	-4.257782	14.145540
H	6.117144	-3.570526	13.471009
H	5.211892	-4.844410	12.555900
H	7.580365	-5.271877	1.303583
H	8.149230	-4.785068	-0.338228
H	6.563557	-4.181654	0.275382

Table S4 DFT energy-minimized Cartesian coordinates (Å) for compound **p-Ph**.

Atom	x	y	z
C	-1.401128	-2.319860	-0.574104
C	-1.085104	-3.581915	-0.019994
C	-1.664591	-4.739269	-0.561992

N	-2.521523	-4.737355	-1.599130
C	-2.823372	-3.537977	-2.128623
C	-2.302393	-2.320783	-1.663785
C	-0.818168	-1.061540	-0.040404
C	0.500255	-1.024336	0.473114
C	1.051442	0.162757	0.971036
C	0.306227	1.365950	0.989100
C	-1.014087	1.327533	0.480742
C	-1.561420	0.142915	-0.027250
C	0.889360	2.624376	1.522365
C	2.260325	2.934773	1.368323
C	2.758971	4.138400	1.889569
N	2.008877	5.043495	2.543891
C	0.704317	4.750190	2.692542
C	0.103235	3.577520	2.210250
H	-0.412358	-3.664251	0.849193
H	-1.429692	-5.730613	-0.131055
H	-3.523315	-3.550204	-2.985113
H	-2.577629	-1.380848	-2.169375
H	1.115594	-1.938961	0.463470
H	2.077286	0.150384	1.374513
H	-1.618762	2.249134	0.462883
H	-2.597746	0.148634	-0.403097
H	2.934148	2.256393	0.820017
H	3.828261	4.394283	1.767960
H	0.099909	5.498823	3.238334
H	-0.968018	3.396754	2.396319

Table S5 DFT energy-minimized Cartesian coordinates (Å) for compound **m-Ph**.

Atom	x	y	z
N	-0.707872	4.865060	-1.619832
C	-0.269210	3.642903	-1.283889
C	-1.083296	2.614086	-0.746560
C	-2.453172	2.918951	-0.578201
C	-2.926263	4.189885	-0.931526
C	-2.014498	5.129799	-1.441041
C	-0.518863	1.287689	-0.392690
C	0.781531	1.165592	0.153990
C	1.314330	-0.086822	0.484818
C	0.573513	-1.276548	0.285529

C	-0.726920	-1.154317	-0.261156
C	-1.259840	0.098070	-0.591872
C	1.138053	-2.603101	0.639099
C	0.323644	-3.633953	1.172110
N	0.762505	-4.856128	1.507507
C	2.069886	-5.119058	1.332445
C	2.981976	-4.177243	0.827079
C	2.508863	-2.906221	0.474365
H	0.803454	3.451898	-1.474086
H	-3.139021	2.170029	-0.147643
H	-3.988472	4.455051	-0.801304
H	-2.346269	6.147141	-1.720136
H	1.374628	2.072049	0.358674
H	2.315942	-0.138266	0.943172
H	-1.319958	-2.060708	-0.466235
H	-2.261699	0.149743	-1.049683
H	-0.749799	-3.444909	1.359898
H	2.402727	-6.136527	1.609777
H	4.044644	-4.441996	0.699563
H	3.194558	-2.155651	0.046528

Table S6 DFT energy-minimized Cartesian coordinates (Å) for model compound of **p-Mo_2** used for transmission calculation.

Atom	x	y	z
Mo	-0.714728	-0.769533	0.025935
Mo	0.722477	0.768978	-0.021826
O	2.306133	-0.607595	-0.066819
O	-0.758174	2.256506	0.020710
O	-2.298366	0.607050	0.071438
O	0.765922	-2.257064	-0.017003
N	0.851822	0.841728	2.101034
N	-0.714291	-0.833965	2.152500
C	1.996757	-1.862978	-0.055468
N	-0.843056	-0.843276	-2.096962
C	3.082111	-2.876555	-0.087639
N	5.156368	-4.812531	-0.149583
N	0.720789	0.834554	-2.148381
C	-0.082093	-0.005687	-2.803130
H	-0.116101	-0.007757	-3.909269
H	1.273587	1.445503	-2.761924
N	-5.148584	4.811981	0.154568
C	4.440250	-2.491853	-0.121011

H	4.711624	-1.429146	-0.123440
C	-1.988996	1.862430	0.059709
H	-1.432356	-1.456420	-2.673215
H	1.441592	1.454440	2.677266
C	2.792382	-4.258430	-0.086198
H	1.751343	-4.602815	-0.060894
C	0.089669	0.005255	2.807239
H	0.123567	0.007413	3.913380
C	-5.415643	3.491210	0.160662
H	-6.482480	3.218381	0.191071
C	5.423572	-3.491775	-0.150377
H	6.490536	-3.218963	-0.176157
C	-3.850035	5.169983	0.117411
H	-3.651905	6.253595	0.113235
C	3.857666	-5.170515	-0.117998
H	3.659416	-6.254113	-0.118239
H	-1.267637	-1.444406	2.766055
C	-3.074339	2.876010	0.092104
C	-4.432322	2.491291	0.131163
H	-4.703576	1.428572	0.137765
C	-2.784761	4.257900	0.085228
H	-1.743841	4.602297	0.055557

Table S7 DFT energy-minimized Cartesian coordinates (Å) for model compound of **m-Mo_2** used for transmission calculation.

Atom	x	y	z
Mo	-0.738126	-0.743119	0.053918
Mo	0.716846	0.776527	-0.005461
O	2.285142	-0.619316	-0.048525
O	-0.747809	2.284769	0.033531
O	-2.306478	0.652742	0.096847
O	0.726468	-2.251339	0.014309
N	0.853537	0.858602	2.116608
N	-0.733006	-0.796820	2.180939
C	1.962186	-1.871195	-0.030265
N	-0.874155	-0.825880	-2.068277
C	3.032681	-2.896818	-0.061630
C	5.101656	-4.713179	-0.123820
N	0.710784	0.831122	-2.132583
C	-0.104557	-0.001931	-2.781359

H	-0.141693	-0.009241	-3.887494
H	1.271911	1.430517	-2.750007
C	-5.123152	4.746580	0.169807
C	4.398410	-2.525242	-0.104671
H	4.668776	-1.459241	-0.114457
C	-1.983509	1.904611	0.078034
H	-5.976180	5.443058	0.195280
H	-1.475080	-1.433122	-2.638807
H	1.456311	1.464079	2.687070
H	5.954601	-5.409742	-0.149782
C	2.728851	-4.275840	-0.050160
H	1.680331	-4.598028	-0.017019
C	0.083078	0.035493	2.829746
H	0.120107	0.042895	3.935879
N	-5.434718	3.435661	0.185422
N	5.413443	-3.402273	-0.135048
C	-3.803406	5.232151	0.124134
H	-3.609508	6.313129	0.112571
C	3.781775	-5.198756	-0.081884
H	3.587975	-6.279793	-0.074919
H	-1.296083	-1.394387	2.798366
C	-3.054047	2.930223	0.108600
C	-4.419677	2.558655	0.155192
H	-4.689905	1.492653	0.168211
C	-2.750448	4.309218	0.093040
H	-1.702129	4.631877	0.058165