Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Fine-tuning of radiative properties by "mild" substituents: In search for a perfectly soft chromophore

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Supporting Information

1. Computational details

Three approaches were used to optimize the geometry and calculate electronic transitions: (a) B3LYP/6-31G(d,p) (as implemented in Gaussian 16[1]); (b) BP86-D/DZP, using version 2023.101 of the ADF package;[2] (c) an INDO/S program, modified to include calculations of MCD parameters. This was an extended version of a program originally created by John Downing and Josef Michl.

Ground state geometry optimizations were done using each of the above methods for each molecule. To ensure whether real minimum was achieved, we checked whether all calculated vibrations had positive values. The optimized geometries served as input for calculations of transition energies. For INDO/S, we found that the best agreement between experiment and calculations was obtained when using B3LYP-optimized structures.

Simulated MCD spectra were obtained using a procedure described in the literature.[3]

For both absorption and MCD simulations (Figures S2-S7), a bandwidth of 1000 cm^{-1} was assumed.

Calculations of FC and HT contributions (B3LYP/6-31G(d,p)) were performed with Gaussian 16 using the procedure described in detail in ref. [4] In this case, geometry optimizations were also performed for S_1, the lowest excited state. Files containing the normal modes parameters for S_0 and S_1 states were used in input. The simulated vibronic spectra (Figures S8-S13) were plotted assuming a gaussian band of 135 cm^{-1} FWHM. This value is lower than that used for electronic absorption and MCD calculated for standard calculations. We decided to use the smaller value in order to make visible the vibronic bands which would be blurred when using 135 cm^{-1} FWHM.

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2. Optimized molecular geometries

2.1 Coordinates of B3LYP/6-31G(d,p) optimized ground state molecular geometry of **Pr**

6	-1.081239144	2.854890668	-0.000108105
7	0.002493650	2.027469238	-0.000711105
6	1.088223014	2.852257921	-0.000059105
6	0.683258466	4.255209162	-0.000094105
6	-0.672869632	4.256854633	-0.000278105
6	-4.261836588	-0.680750489	0.000314895
6	-4.260131119	0.691125612	0.000276895
6	-2.895095867	1.133138171	0.000124895
7	-2.117509202	0.002533823	-0.000029105
6	-2.897897644	-1.126138992	0.000185895
6	2.897895548	1.126138177	0.000031895
7	2.117506101	-0.002536637	-0.000393105
6	2.895093767	-1.133138986	-0.000068105
6	4.260134019	-0.691123426	0.000468895
6	4.261838493	0.680748673	0.000508895
6	2.419184283	-2.443018918	0.000048895
6	1.081230042	-2.854877486	-0.000139105
7	-0.002495748	-2.027467052	-0.000765105
6	-1.088229110	-2.852270738	0.000019895
6	-0.683251565	-4.255210977	-0.000305105
6	0.672878532	-4.256847447	-0.000047105
6	-2.419182383	2.443027104	0.000210895
6	-2.425178062	-2.437185247	0.000340895
6	2.425174966	2.437175431	0.000202895
1	-1.103111130	0.001252473	0.000279895
1	1.103105028	-0.001254288	-0.000560105
1	1.357363806	5.102278991	0.000086895
1	-1.344900385	5.105569923	-0.000216105
1	-5.118610877	-1.340463239	0.000303895
1	-5.115261952	1.352966952	0.000235895
1	5.115265853	-1.352959765	0.000817895
1	5.118609782	1.340461424	0.000857895
1	3.174724069	-3.222689235	0.000244895
1	-1.357335908	-5.102299809	-0.000244105
1	1.344927289	-5.105556736	0.000143895
1	-3.174733166	3.222685419	0.000417895
1	-3.182605386	-3.215018043	0.000617895
1	3.182599290	3.215013228	0.000480895

2.2 Coordinates of B3LYP/6-31G(d,p) optimized ground state molecular geometry of **Pr-1**

6	-0.980200633	-1.202720476	-0.764634936
7	0.343639363	-1.363238023	-0.456766043
6	0.549267151	-2.708929956	-0.398183009
6	-0.680758019	-3.438344564	-0.673340642
6	-1.634503885	-2.503526426	-0.904789398
6	-0.585048688	3.512821975	-0.635810582
6	-1.573574020	2.594422112	-0.878807335
6	-1.002975808	1.281242828	-0.763032719
7	0.325225608	1.466044721	-0.451423551
6	0.627980542	2.801507648	-0.365441963
6	3.002357164	-2.810844346	0.156239518
7	3.297272572	-1.473040614	0.218357971
6	4.622543719	-1.279722131	0.517008210
6	5.209141214	-2.581685551	0.651575978
6	4.224683038	-3.511601312	0.433194764
6	5.228965421	-0.032961027	0.655256359
6	4.592877519	1.206386393	0.517538601
7	3.272958782	1.377324732	0.221428446
6	3.079805943	2.725164982	0.189334832
6	4.321225908	3.441038891	0.474760735
6	5.267171638	2.491177255	0.679047379
6	-1.639182352	0.037149132	-0.923091851
6	1.869530906	3.370000258	-0.077030725
6	1.756351323	-3.364738924	-0.121107751
1	0.968227405	0.692747260	-0.310885968
1	2.647559694	-0.706726805	0.071884604
1	-0.781806230	-4.516148998	-0.686070027
1	-2.674392425	-2.677931605	-1.140702363
1	-0.670957392	4.590725498	-0.641272135
1	-2.605905009	2.806872093	-1.112144709
1	6.249126789	-2.762344796	0.886005183
1	4.316369828	-4.588817777	0.456887983
1	6.287745986	-0.031402274	0.893878472
1	4.430263208	4.517596827	0.508401464
1	6.315061163	2.624542526	0.915797216
1	1.884901288	4.455739367	-0.060847262
1	1.721489930	-4.450137676	-0.121519313
6	-3.127157681	0.046276817	-1.231461055
6	-4.019718338	0.007248803	0.026671550
1	-3.374780989	-0.803654921	-1.873864418
1	-3.378256313	0.933983207	-1.819974071
6	-5.517509133	0.018689521	-0.300707336

1	-3.774360438	-0.888474604	0.611289974
1	-3.773305269	0.864182257	0.666995748
6	-6.413485327	-0.022040150	0.943215355
1	-5.755385313	0.915984995	-0.890231150
1	-5.755478554	-0.838057401	-0.947603616
1	-6.176152718	-0.919328628	1.532282070
1	-6.176279191	0.834650224	1.590049308
6	-7.912752267	-0.011501083	0.620200096
6	-8.800343595	-0.052892573	1.867621645
1	-8.149220783	-0.867783610	-0.026073865
1	-8.149532151	0.885540306	0.031890250
1	-9.862919287	-0.044267287	1.603986667
1	-8.611824729	-0.956505287	2.458380738
1	-8.612013328	0.809672830	2.516927168

2.3 Coordinates of B3LYP/6-31G(d,p) optimized ground state molecular geometry of **Pr-2a**

6	2.789640203	-1.203233084	0.795411059
7	1.479876107	-1.341940099	0.426229030
6	1.252620091	-2.682489192	0.359743026
6	2.456126178	-3.432727247	0.695055049
6	3.414732246	-2.513984180	0.968373072
6	2.368455171	3.492935251	0.649065048
6	3.360209241	2.591389185	0.937046069
6	2.815400202	1.270159089	0.794233058
7	1.500762109	1.432264104	0.421248031
6	1.180219087	2.761745201	0.320753023
6	-1.180283085	-2.761458196	-0.321168023
7	-1.500834109	-1.431971104	-0.421582030
6	-2.815488204	-1.269854092	-0.794478056
6	-3.360312240	-2.591071187	-0.937303070
6	-2.368534172	-3.492635250	-0.649445045
6	-3.451362250	-0.030372002	-0.982879069
6	-2.789743202	1.203534086	-0.795761057
7	-1.479956108	1.342232099	-0.426645030
6	-1.252675089	2.682771190	-0.360194026
6	-2.456170179	3.433023247	-0.695514052
6	-3.414845247	2.514294183	-0.968622071
6	3.451251250	0.030673002	0.982632070
6	-0.050832004	3.315705239	-0.025962002
6	0.050790004	-3.315423240	0.025477002
1	0.892608066	0.633927044	0.255132019
1	-0.892653062	-0.633645045	-0.255518018
1	2.537296184	-4.512139327	0.715195054
1	4.439458319	-2.704111194	1.254106090
1	2.435351177	4.572218328	0.659118045
1	4.377095314	2.819348203	1.219217090
1	-4.377217316	-2.819000205	-1.219427088
1	-2.435427177	-4.571918327	-0.659544049
1	-2.537310181	4.512435322	-0.715721051
1	-4.439599318	2.704459197	-1.254227091
1	-0.070711005	4.401669316	-0.034893003
1	0.070686005	-4.401388318	0.034343002
6	4.924551356	0.038336003	1.349280100
6	5.863012398	0.002985000	0.124663009
1	5.148413373	-0.814233058	1.997269145
1	5.153270373	0.925195066	1.948720138
6	7.348415529	0.019431001	0.504178036
1	5.641376403	-0.893219065	-0.468668034

1	5.636438385	0.859405062	-0.523561038
6	8.285261617	-0.017328001	-0.709552050
1	7.562992564	0.917433067	1.101465081
1	7.567670544	-0.836818062	1.158227083
1	8.071553597	-0.916179065	-1.305179092
1	8.064260582	0.837699058	-1.364204099
6	9.773426683	0.001345000	-0.338926024
6	10.699329756	-0.035496003	-1.558527113
1	9.994276744	-0.853610063	0.314564023
1	9.986853710	0.899758066	0.256155018
1	11.753342831	-0.020889001	-1.262708093
1	10.533489734	-0.940425067	-2.153972155
1	10.525674738	0.825772059	-2.213538161
6	-4.924707352	-0.038118003	-1.349337097
6	-5.862968423	-0.003587000	-0.124538009
1	-5.153334372	-0.924680065	-1.949256142
1	-5.148843371	0.814782058	-1.996780143
6	-7.348448550	-0.019705001	-0.503768036
1	-5.636323395	-0.860438063	0.523085038
1	-5.641175421	0.892220063	0.469335034
6	-8.285012586	0.016277001	0.710206050
1	-7.567805537	0.837002062	-1.157178085
1	-7.563199525	-0.917291068	-1.101617077
1	-8.063838563	-0.839167059	1.364255096
1	-8.071167562	0.914749064	1.306356093
6	-9.773271687	-0.002193000	0.339944025
6	-10.698862757	0.035119003	1.559769114
1	-9.987016697	-0.900719067	-0.254851019
1	-9.994120742	0.852636059	-0.313710023
1	-11.752951822	0.020579001	1.264220090
1	-10.525166781	-0.825993059	2.214975158
1	-10.532738778	0.940189070	2.154918155

2.4 Coordinates of B3LYP/6-31G(d,p) optimized ground state molecular geometry of **Pr-2b**

6	2.905148208	1.098133080	-0.553385039
7	2.112906154	2.166282157	-0.197972014
6	2.879086208	3.243221233	0.172078012
6	4.245388304	2.837908206	0.046631003
6	4.264037309	1.540392108	-0.393544028
6	-0.676845049	-1.879062135	-1.486446108
6	0.676681047	-1.879117137	-1.486459109
6	1.093559078	-0.540416037	-1.083159078
7	0.000012000	0.247183018	-0.840780060
6	-1.093606080	-0.540320039	-1.083168080
6	1.083025080	4.890421350	0.721658054
7	0.000176000	4.108813297	0.455006033
6	-1.082606077	4.890481353	0.721758053
6	-0.677538049	6.219539431	1.173451084
6	0.678072047	6.219506463	1.173377084
6	-2.413466173	4.489486323	0.590606044
6	-2.878809205	3.243400232	0.172279012
7	-2.112721153	2.166422156	-0.197853014
6	-2.905054211	1.098351080	-0.553294042
6	-4.263904306	1.540699111	-0.393374029
6	-4.245144306	2.838184204	0.046893003
6	2.453815176	-0.163898012	-0.972780070
6	-2.453826178	-0.163694012	-0.972764068
6	2.413852176	4.489347324	0.590401041
1	5.092962365	3.471455248	0.269022019
1	5.141001372	0.941001066	-0.584299039
1	-1.322045093	-2.710110196	-1.730392126
1	1.321805095	-2.710220196	-1.730413123
1	-1.351317099	7.021559517	1.446930103
1	1.351921096	7.021492523	1.446783103
1	-5.140919371	0.941380068	-0.584124041
1	-5.092663364	3.471775252	0.269368020
6	3.521002251	-1.207620086	-1.271223090
6	3.896118281	-2.072619149	-0.050127004
1	4.421949320	-0.717794050	-1.651273120
1	3.186757232	-1.857116133	-2.084703149
6	4.978426358	-3.113926223	-0.358481026
1	4.234550304	-1.415547104	0.761591055
1	2.994484213	-2.574767183	0.323001023
6	5.351152369	-3.979175285	0.851431059
1	4.637230335	-3.763313270	-1.177727085
1	5.879031440	-2.605824188	-0.732630052

1	5.691829432	-3.330099241	1.670773122
1	4.450693318	-4.487590323	1.224446086
6	6.433421445	-5.023386363	0.550871040
6	6.798149508	-5.883256444	1.764606128
1	7.333366522	-4.514900325	0.178881013
1	6.092803438	-5.672023386	-0.267803019
1	7.569461544	-6.619555468	1.516497110
1	7.179039491	-5.267309377	2.587157186
1	5.925316404	-6.429598457	2.139731154
6	-3.521096254	-1.207322085	-1.271249094
6	-3.896265281	-2.072353147	-0.050194004
1	-3.186889230	-1.856806135	-2.084754152
1	-4.422004317	-0.717414053	-1.651284117
6	-4.978729359	-3.113496224	-0.358559026
1	-2.994679215	-2.574649187	0.322850023
1	-4.234563306	-1.415292104	0.761589055
6	-5.351346365	-3.978922286	0.851260061
1	-5.879344448	-2.605239188	-0.732470050
1	-4.637730334	-3.762771271	-1.177977084
1	-4.450853320	-4.487409323	1.224096088
1	-5.691925425	-3.329972238	1.670743118
6	-6.433646451	-5.023085361	0.550644038
6	-6.798980475	-5.882473421	1.764537129
1	-6.092778461	-5.672064397	-0.267655019
1	-7.333370544	-4.514613326	0.178100013
1	-7.570183554	-6.618858488	1.516339108
1	-5.926341421	-6.428685467	2.140302152
1	-7.180261520	-5.266198380	2.586660188
1	3.178971230	5.217358373	0.841846061
1	-3.178523228	5.217534378	0.842134061
1	1.098753080	2.155818153	-0.207924015
1	-1.098569080	2.155890153	-0.207866015

2.4 Coordinates of B3LYP/6-31G(d,p) optimized ground state molecular geometry of **Pr-3**

6	-2.608597188	-2.686868192	-0.619897047
7	-1.291334095	-2.723251197	-0.256675018
6	-1.035632077	-4.020790287	0.066382005
6	-2.224009161	-4.847729351	-0.094297007
6	-3.207224231	-4.019153288	-0.520763038
6	-2.412364172	1.959621142	-1.505194106
6	-3.347542241	0.960425067	-1.532666110
6	-2.714305196	-0.257677019	-1.124770079
7	-1.402651102	0.063845004	-0.850767063
6	-1.162833084	1.402473102	-1.071576076
6	1.380064097	-3.869808276	0.736446055
7	1.617583114	-2.530108184	0.563133040
6	2.909430210	-2.212589161	0.913450067
6	3.527255253	-3.441500249	1.329761095
6	2.600224186	-4.444208319	1.217978090
6	3.473360249	-0.929485069	0.857038063
6	2.782073201	0.213909016	0.392412028
7	1.484893105	0.259602018	-0.042503003
6	1.255463091	1.557444110	-0.409632030
6	2.456300177	2.363264170	-0.202156014
6	3.397802247	1.532537113	0.302718022
6	-3.304055237	-1.532670111	-1.032343076
6	0.047351003	2.101476153	-0.901586066
6	0.183212013	-4.542674325	0.508770036
1	-0.721061052	-0.619220044	-0.536892039
1	0.949460070	-1.841412131	0.231844017
1	-2.279635162	-5.911536417	0.098848007
1	-4.231576307	-4.282411307	-0.741690054
1	-2.581518188	2.995445215	-1.754772126
1	-4.385422315	1.063398076	-1.809619130
1	4.548743327	-3.543553256	1.663370118
1	2.730799196	-5.492652407	1.448202103
1	2.569002183	3.419041247	-0.398802029
1	4.410201315	1.792020129	0.576059041
1	0.205161015	-5.608299385	0.716302050
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6	-5.695328405	-1.460205107	-0.117192008
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1	-5.424164383	-2.207250160	0.639688049
1	-5.489810408	-0.481485035	0.335665024

6	-8.096381588	-1.405440099	0.777163054
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1	-7.830403556	-2.158306154	1.532742110
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1	-10.344652726	-0.373453027	2.151430157
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6	5.934217430	-0.953240068	0.122864009
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1	5.081340368	0.181715013	1.756952124
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1	5.778695412	-1.930554140	-0.352317025
1	5.718967388	-0.203328014	-0.648965044
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1	11.904940841	-0.961528069	-0.878353063
1	10.772226779	-2.036420144	-1.708539121
1	10.727516752	-0.297311021	-2.018500144
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6	-0.362135026	4.484413323	-0.030597002
1	-0.682780047	3.775027270	-2.049032147
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1	0.347768025	4.306198311	0.786991055
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1	-0.464165034	9.137626674	2.473898178

2.4 Coordinates of B3LYP/6-31G(d,p) optimized ground state molecular geometry of **Pr-4**

6	0.991597074	2.815447204	-0.455424033
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6	-2.695947196	-1.184328084	1.044402073
6	-3.964794285	-0.730749055	1.534958109
6	-3.944357285	0.636615048	1.582769115
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1	-7.287144530	-7.361682532	-2.670126193
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1	3.489520253	-4.349795314	0.841586060
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6	7.916394594	-6.979146490	1.857568135
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1	7.288038522	-7.360741549	2.670345193
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6	-4.141466296	4.002268290	0.306628022
1	-2.659162191	4.346377311	1.843755132
1	-3.824664276	3.131040228	2.260653161
6	-5.094838367	5.108349368	0.773610057
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1	-4.717823337	3.156287227	-0.089779007
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1	-5.697553436	4.739521340	1.616311115
1	-4.507485324	5.949207434	1.170066085
1	-5.426957380	5.981568422	-1.176205087
1	-6.625096483	4.783097346	-0.719775051
6	-6.969728511	6.738632467	0.134423010
6	-7.899737576	7.244891525	-0.972235071
1	-6.372539444	7.575120566	0.522209038
1	-7.570142543	6.378139462	0.980845070
1	-8.556620641	8.042748574	-0.610767046
1	-7.328202546	7.642663533	-1.818550129
1	-8.535763596	6.438594470	-1.354907095

3. Calculated orbital energies and splittings.

Table S1. Calculated orbital energies and splittings (in eV). Three digits after the decimal point are used in cases when the splitting is too small to be analyzed with only two digits.

	HOMO-1	HOMO	LUMO	LUMO+1	ΔHOMO	ΔLUMO	|ΔHOMO - ΔLUMO|
B3LYP							
Pr	-5.30	-5.16	-2.246	-2.230	0.14	0.016	0.124
Pr-1	-5.26	-5.04	-2.208	-2.187	0.22	0.021	0.199
Pr-2a	-5.22	-4.93	-2.173	-2.145	0.29	0.028	0.262
Pr-2b	-5.22	-4.94	-2.170	-2.158	0.28	0.012	0.268
Pr-3	-5.18	-4.83	-2.140	-2.123	0.35	0.017	0.333
Pr-4	-5.15	-4.74	-2.117	-2.092	0.41	0.025	0.385
BP86-D							
Pr	-5.81	-5.57	-3.611	-3.593	0.24	0.018	0.222
Pr-1	-5.74	-5.43	-3.540	-3.532	0.31	0.008	0.302
Pr-2a	-5.68	-5.29	-3.471	-3.462	0.39	0.009	0.381
Pr-2b	-5.67	-5.30	-3.486	-3.466	0.37	0.020	0.350
Pr-3	-5.61	-5.17	-3.423	-3.406	0.44	0.017	0.423
Pr-4	-5.55	-5.06	-3.389	-3.353	0.49	0.036	0.454
INDO/S [a]							
Pr	-6.96	-6.72	-1.727	-1.714	0.24	0.013	0.227
Pr-1	-6.84	-6.71	-1.704	-1.659	0.13	0.045	0.085
Pr-2a	-6.74	-6.68	-1.695	-1.608	0.06	0.087	-0.027
Pr-2b	-6.72	-6.71	-1.673	-1.615	0.014	0.058	-0.044
Pr-3	-6.70	-6.60	-1.66	-1.578	0.10	0.082	0.019
Pr-4	-6.69	-6.50	-1.643	-1.547	0.19	0.096	0.094

[a] B3LYP-optimized geometry

4. Comparison of main configurations calculated for the $S_1 \leftarrow S_0$ transition.

Table S2. Dominant configurations in the $S_1 \leftarrow S_0$ transition (Q_x band).

	B3LYP/6-31G(d,p)	BP86-D/DZP	INDO/S
Pr	58% (HOMO – LUMO+1)	62% (HOMO – LUMO+1)	99% (HOMO-1 – LUMO)
	41% (HOMO-1 – LUMO)	37% (HOMO-1 – LUMO)	
Pr-1	42% (HOMO – LUMO+1)	50% (HOMO – LUMO+1)	85% (HOMO-1 – LUMO)
	30% (HOMO-1 – LUMO)	26% (HOMO-1 – LUMO)	
Pr-2a	64% (HOMO – LUMO+1)	60% (HOMO – LUMO)	94% (HOMO – LUMO)
	36% (HOMO-1 – LUMO)	26% (HOMO-1 – LUMO+1)	
Pr-2b	64% (HOMO – LUMO)	68% (HOMO – LUMO+1)	94% (HOMO – LUMO+1)
	35% (HOMO-1 – LUMO+1)	31% (HOMO-1 – LUMO)	
Pr-3	59% (HOMO – LUMO)	71% (HOMO – LUMO)	100% (HOMO – LUMO)
	30% (HOMO-1 – LUMO+1)	28% (HOMO-1 – LUMO+1)	
Pr-4	70% (HOMO – LUMO)	74% (HOMO – LUMO)	100% (HOMO – LUMO)
	30% (HOMO-1 – LUMO+1)	25% (HOMO-1 – LUMO+1)	

5. Rates of radiative and nonradiative S_1 depopulation.

Table S3. Rates of radiative and nonradiative S_1 depopulation (estimated accuracy: ±20%).

	k_r [10^6 s^{-1}]	k_{nr} [10^8 s^{-1}]
Pr	3.4	1.2
	4.0	0.9
Pr-1	2.7	1.2
Pr-2a	3.2	1.3
Pr-2b	3.5	1.2
Pr-3	4.5	1.2
Pr-4	5.2	1.2

6. Figures

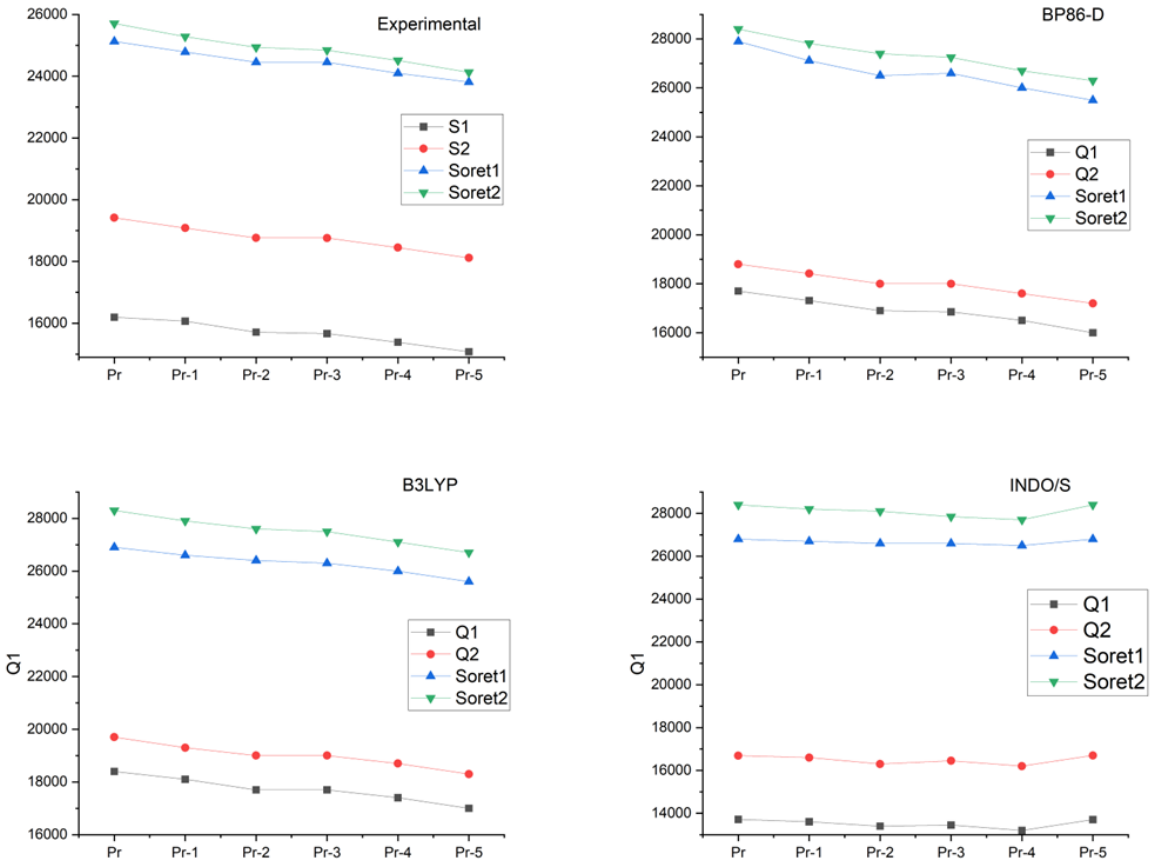

Figure S1. Experimental (absorption in *n*-hexane at 293 K) and calculated energies for Q and Soret transitions. The data for **Pr-2** correspond to **Pr-2a**. The values obtained for **Pr-2b** are practically the same.

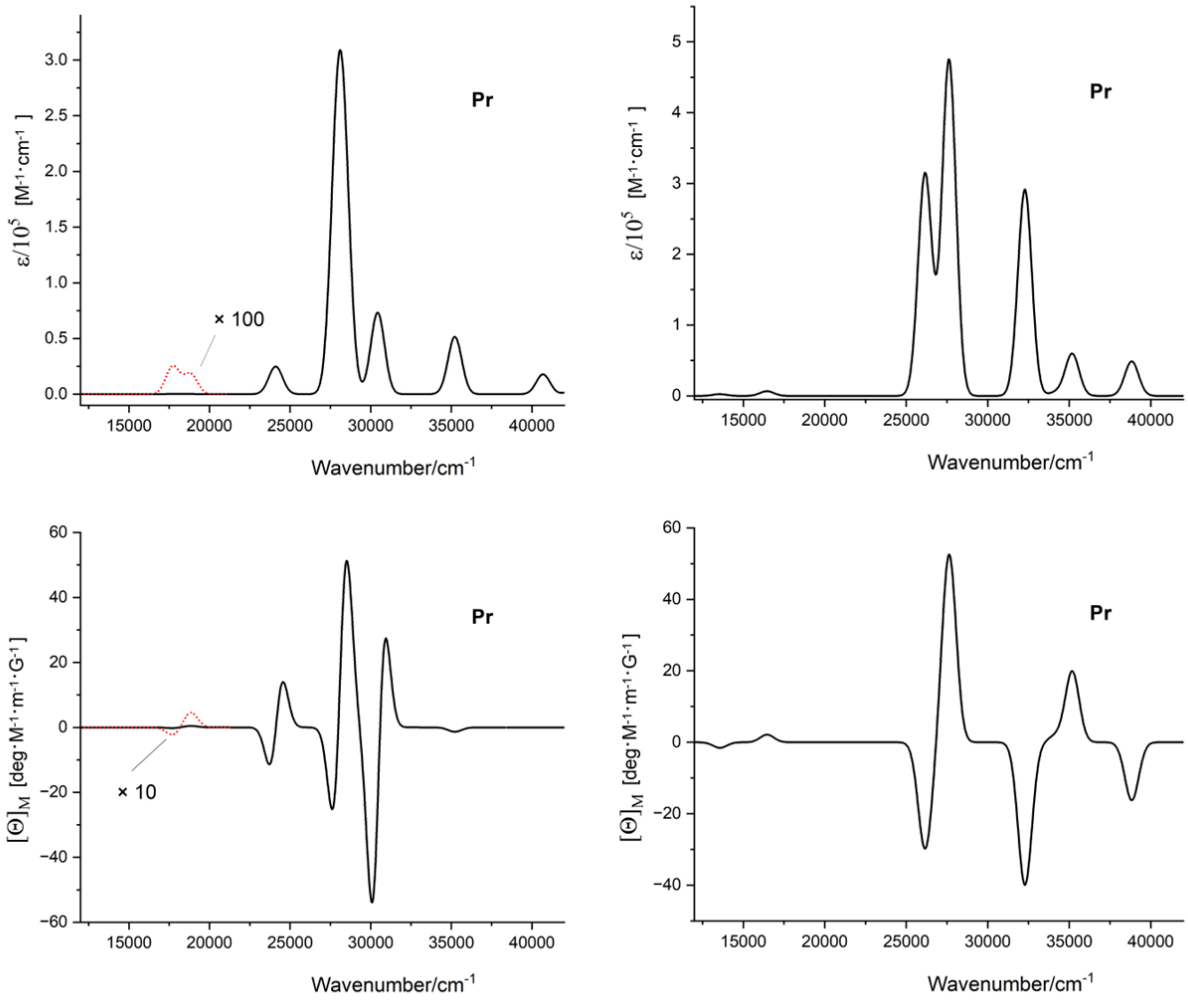

Figure S2. Simulated absorption and MCD spectra of **Pr**. Left, BP86-D, right, INDO/S calculations.

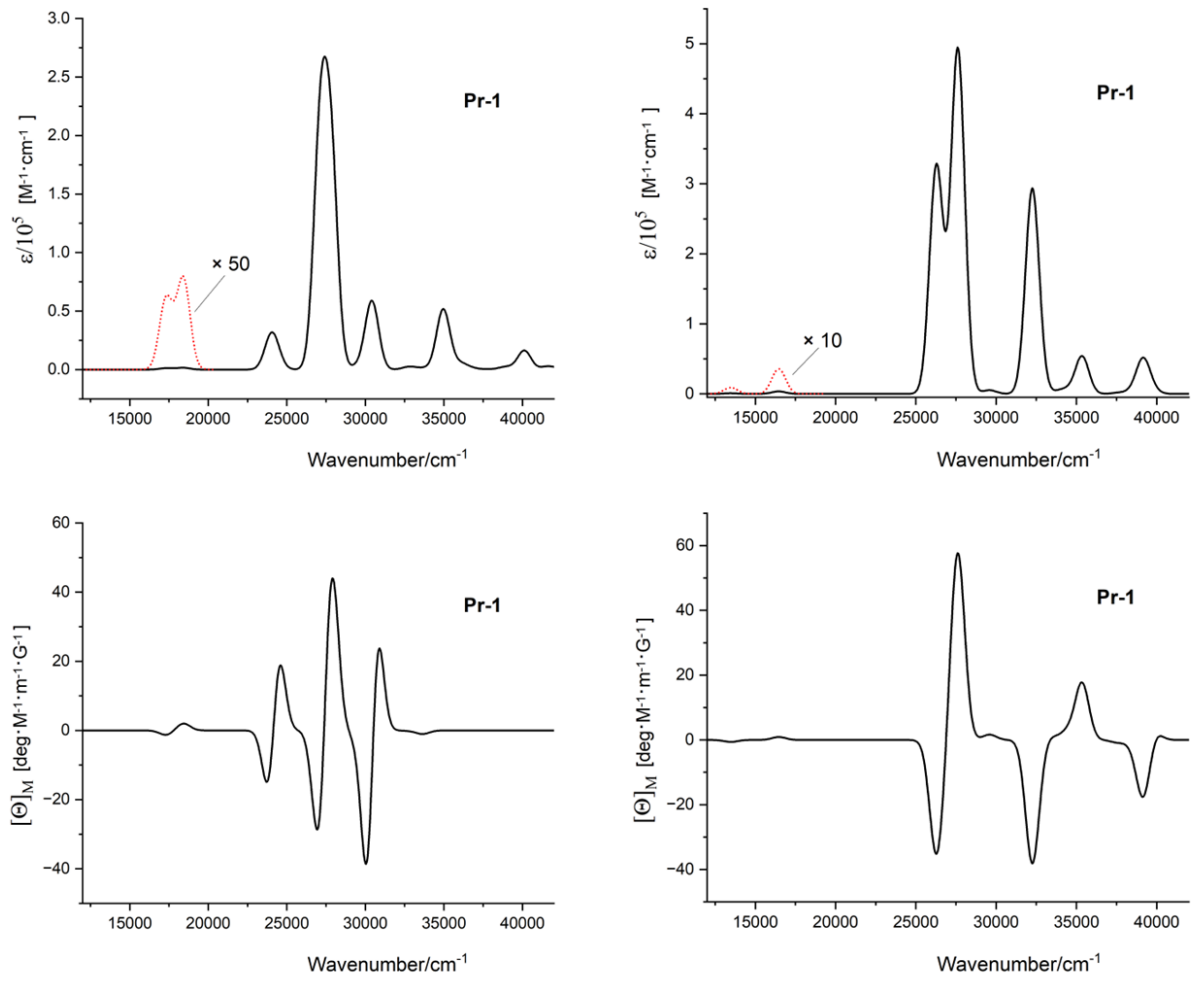

Figure S3. Simulated absorption and MCD spectra of **Pr-1**. Left, BP86-D, right, INDO/S calculations.

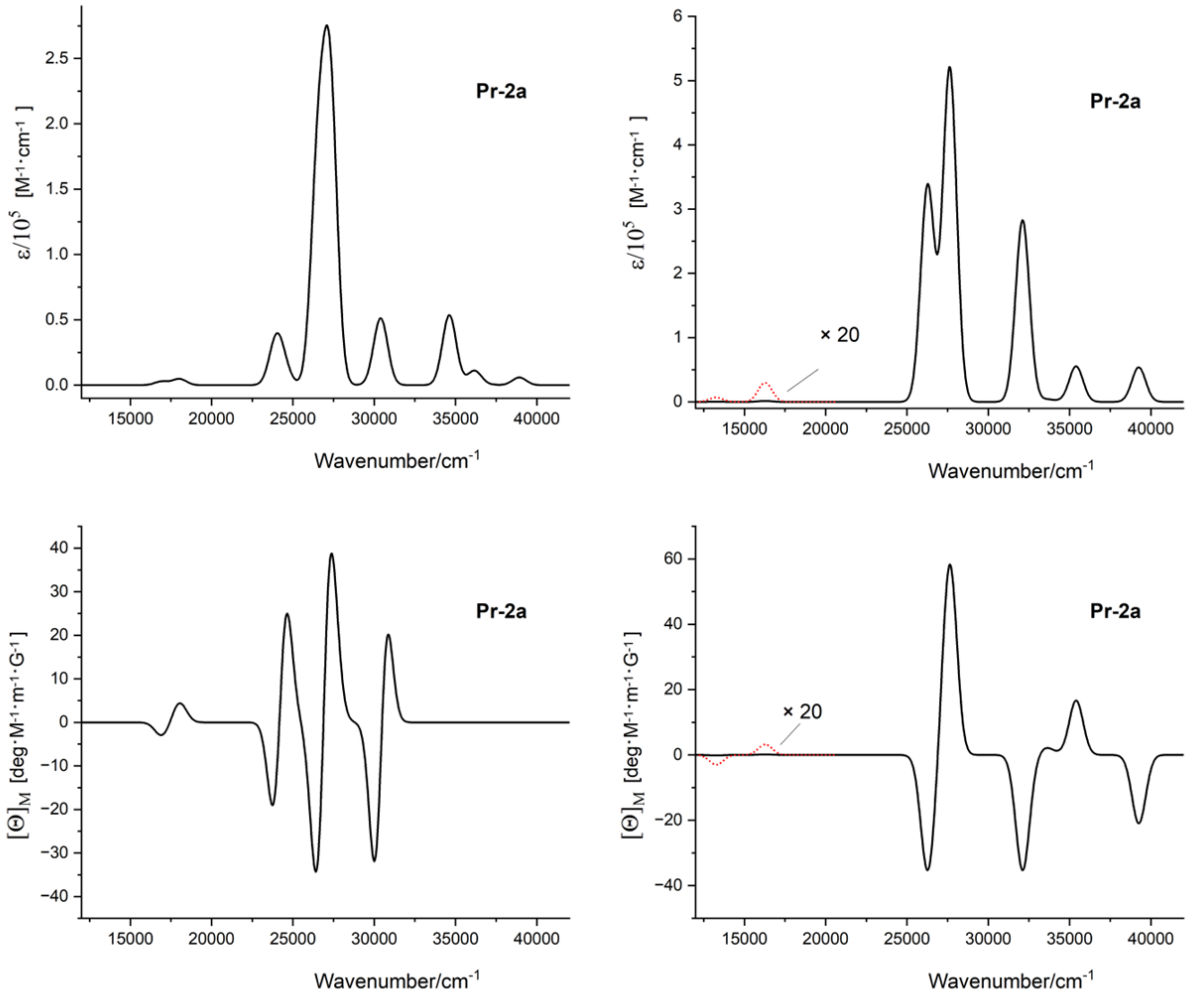

Figure S4. Simulated absorption and MCD spectra of **Pr-2a**. Left, BP86-D, right, INDO/S calculations.

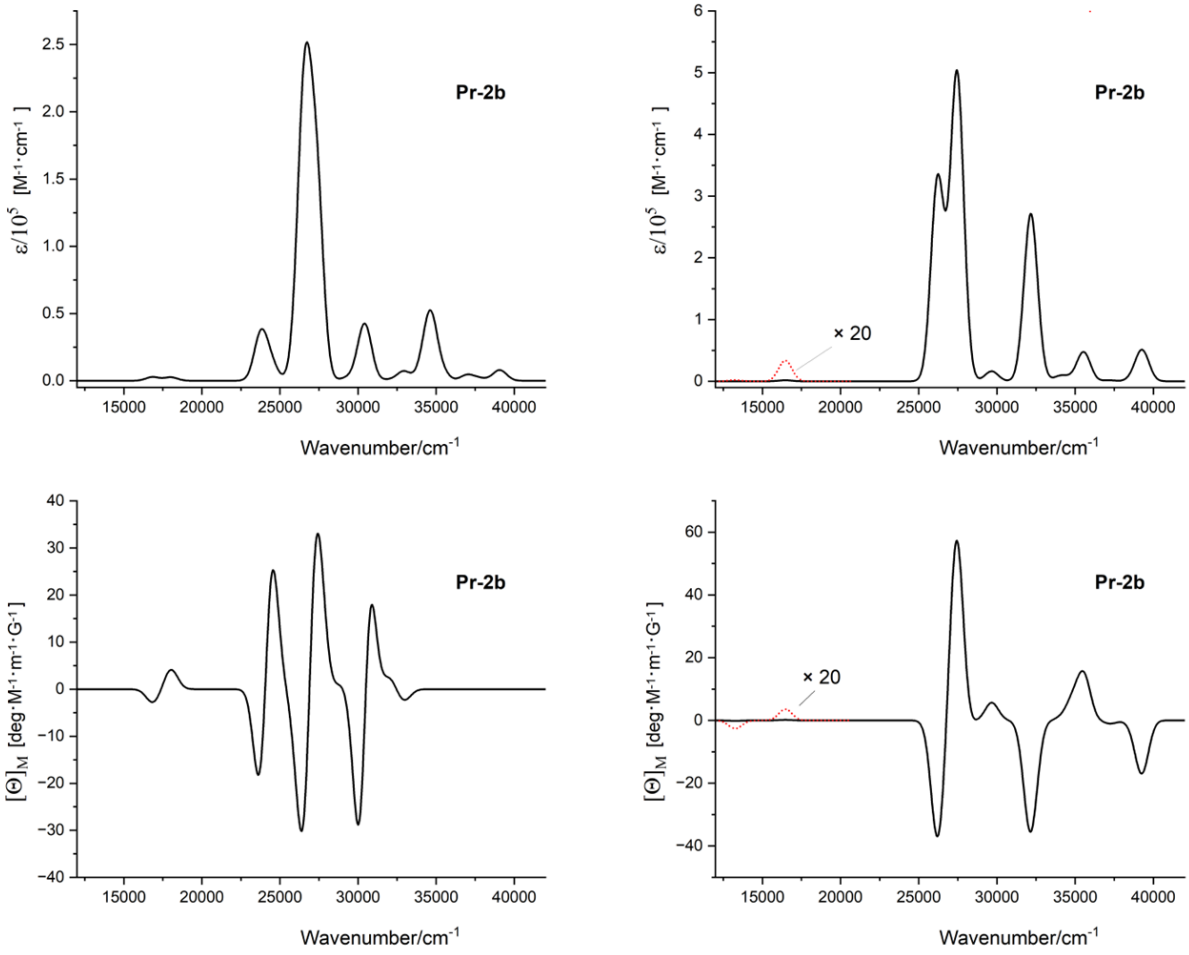

Figure S5. Simulated absorption and MCD spectra of **Pr-2b**. Left, BP86-D, right, INDO/S calculations.

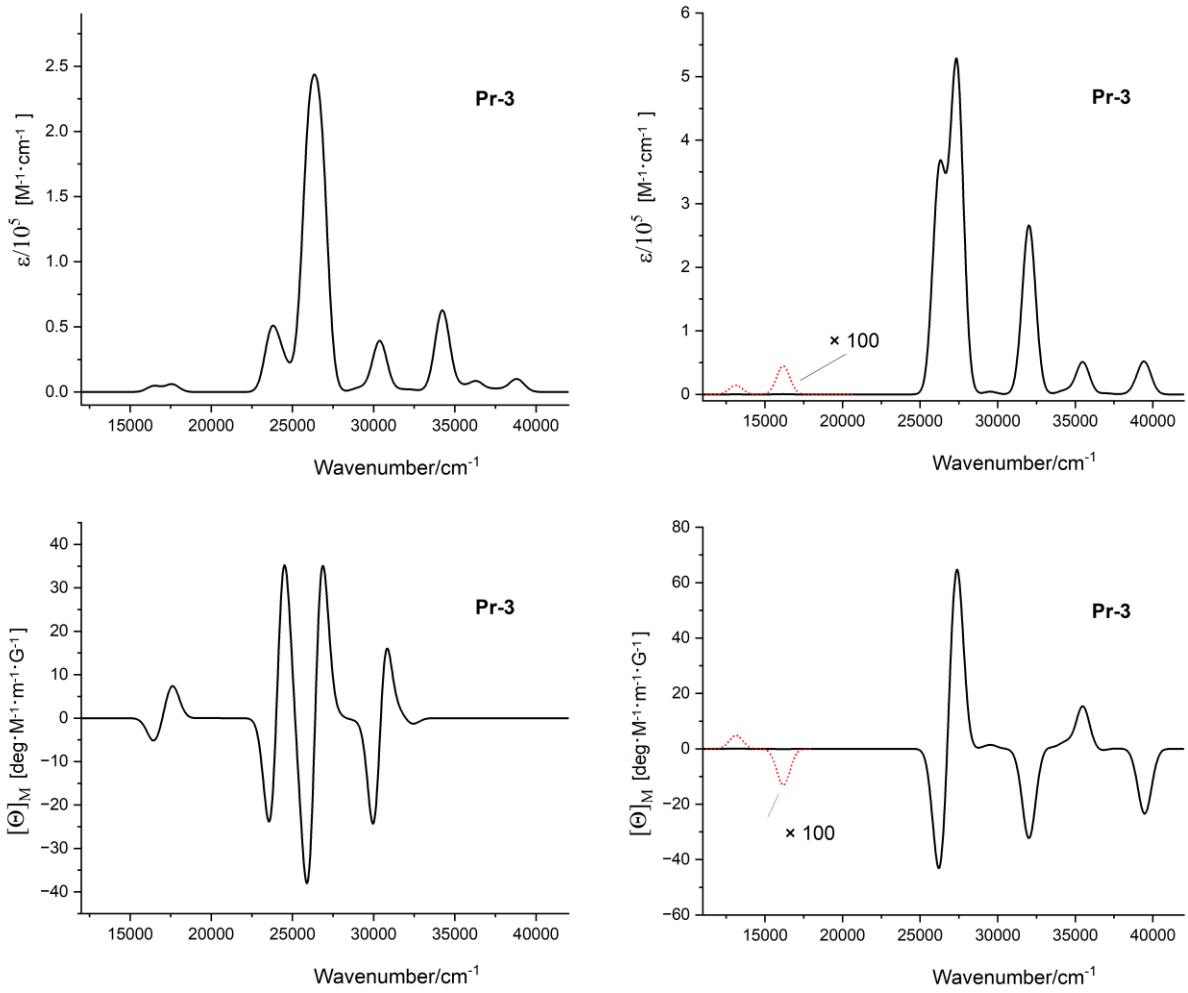

Figure S6. Simulated absorption and MCD spectra of **Pr-3**. Left, BP86-D, right, INDO/S calculations.

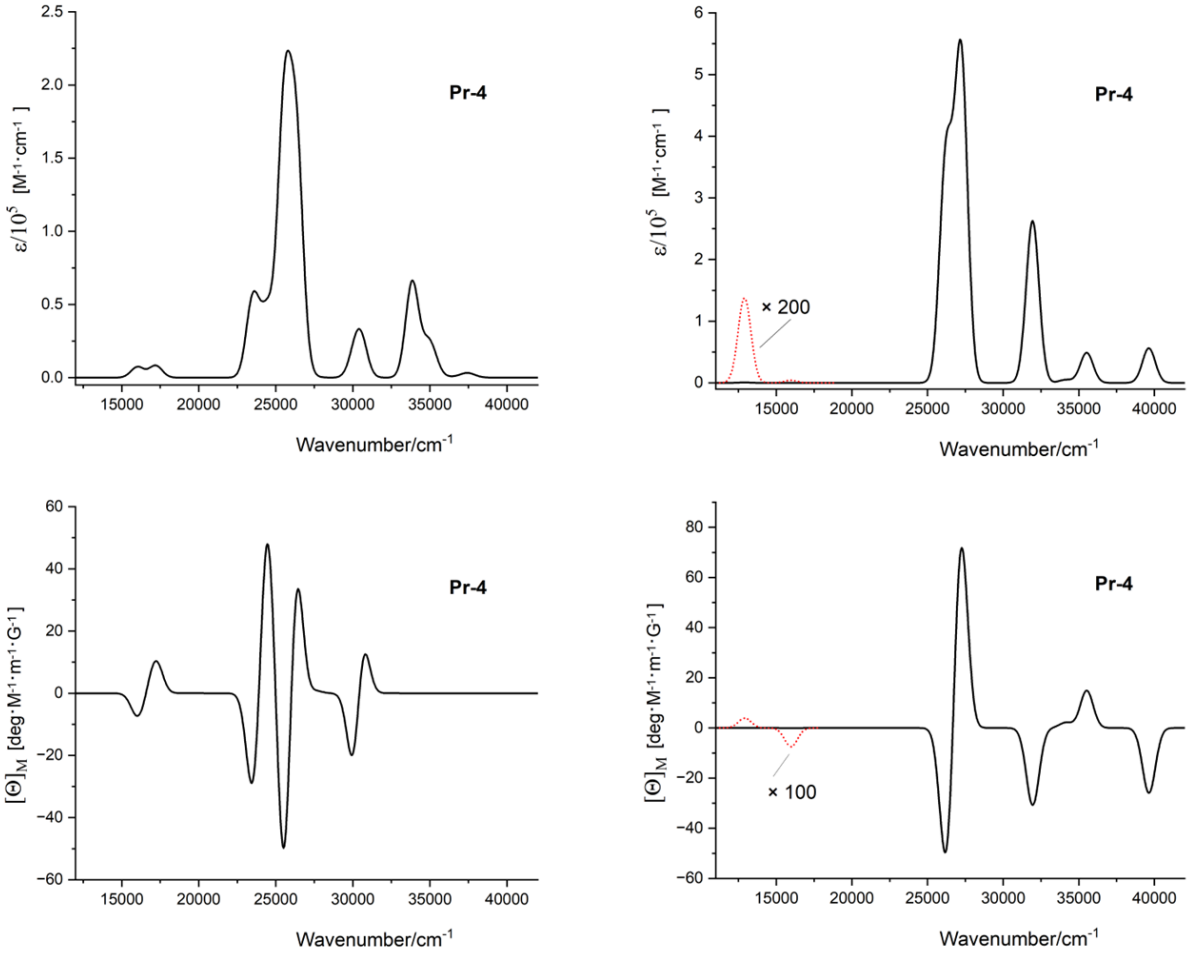

Figure S7. Simulated absorption and MCD spectra of **Pr-4**. Left, BP86-D, right, INDO/S calculations.

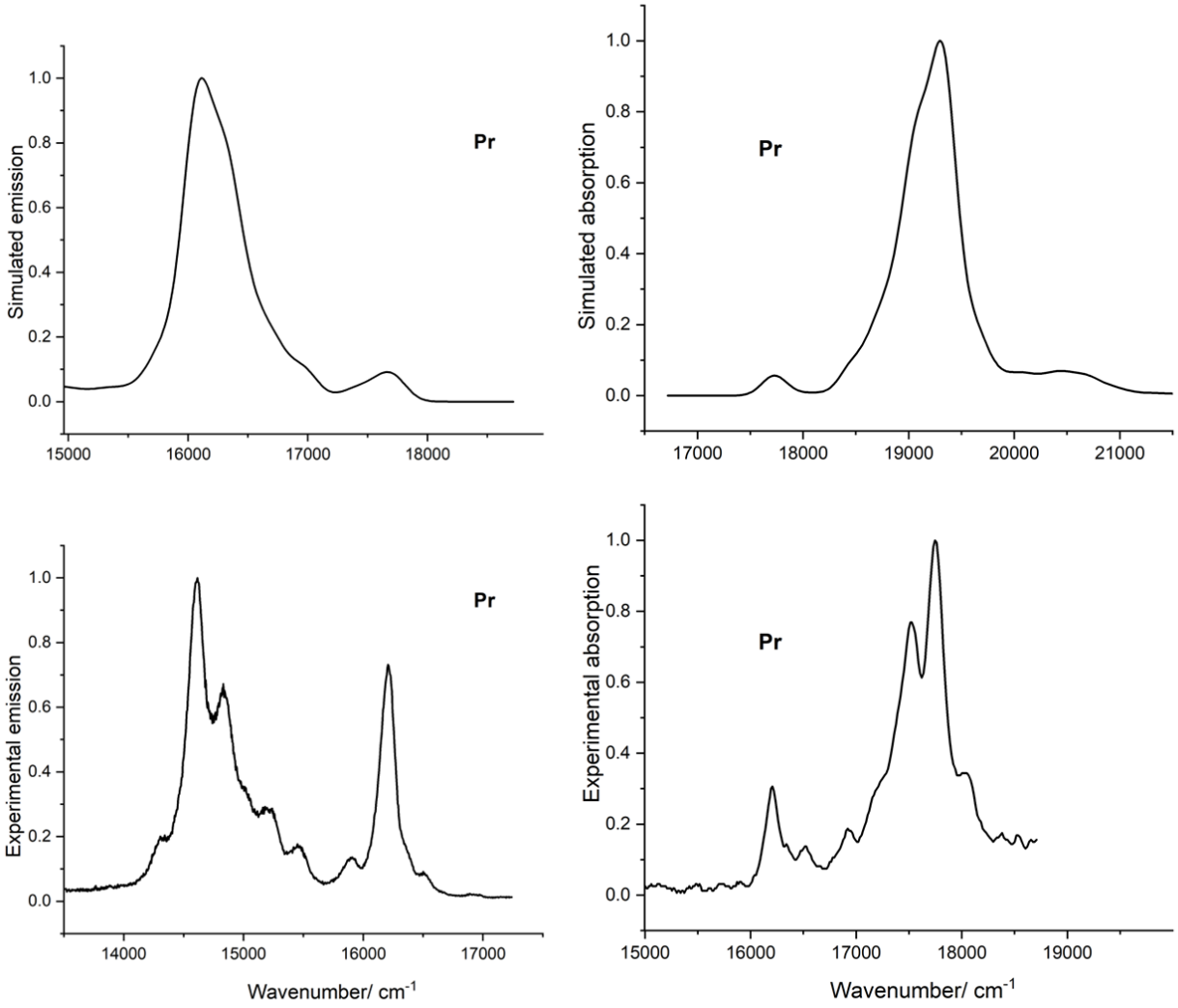

Figure S8. Comparison of simulated (top) and experimental (bottom) absorption and emission spectra of **Pr**. The simulated spectra contain both FC and HT contributions.

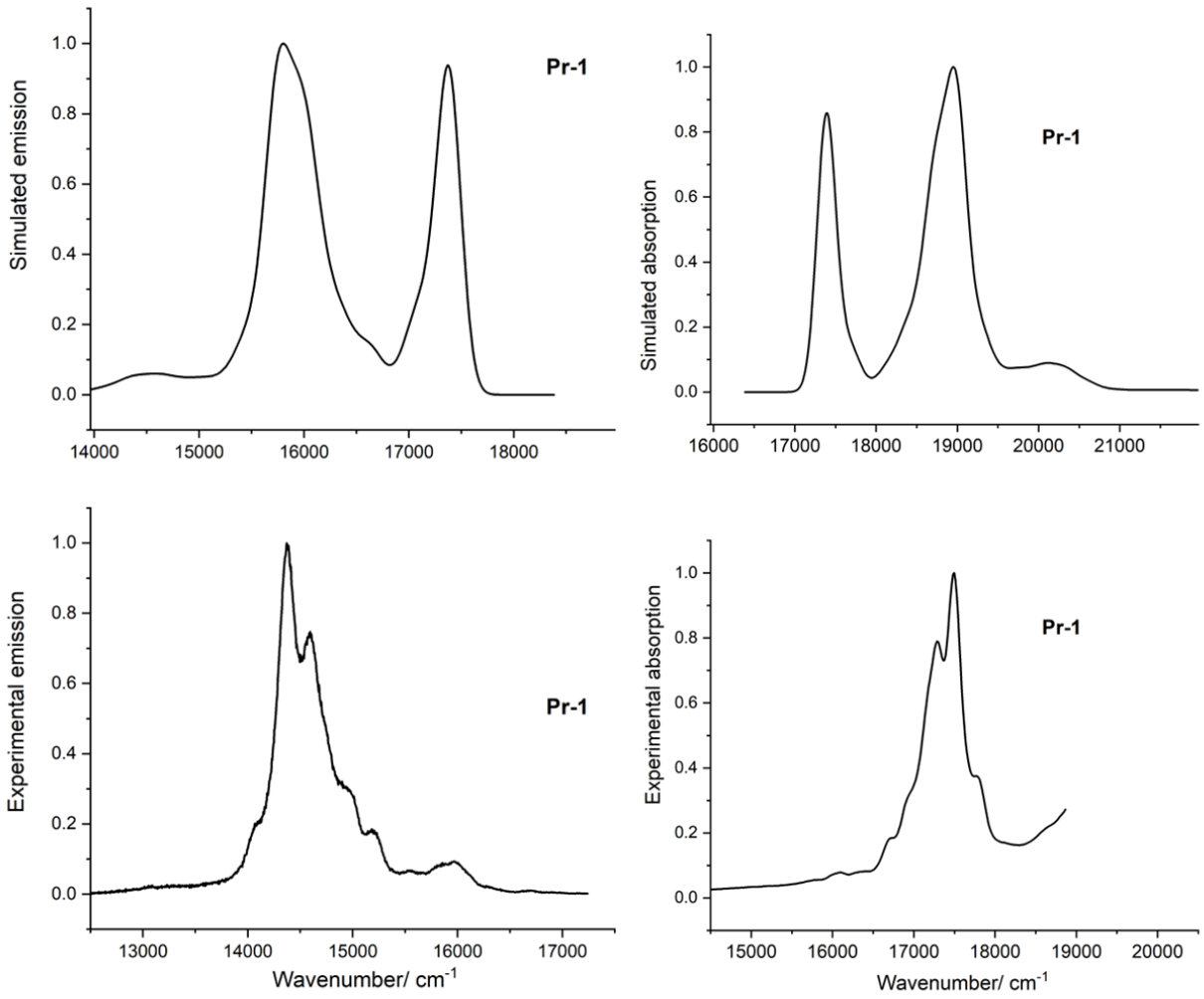

Figure S9. Comparison of simulated (top) and experimental (bottom) absorption and emission spectra of **Pr-1**. The simulated spectra contain both FC and HT contributions.

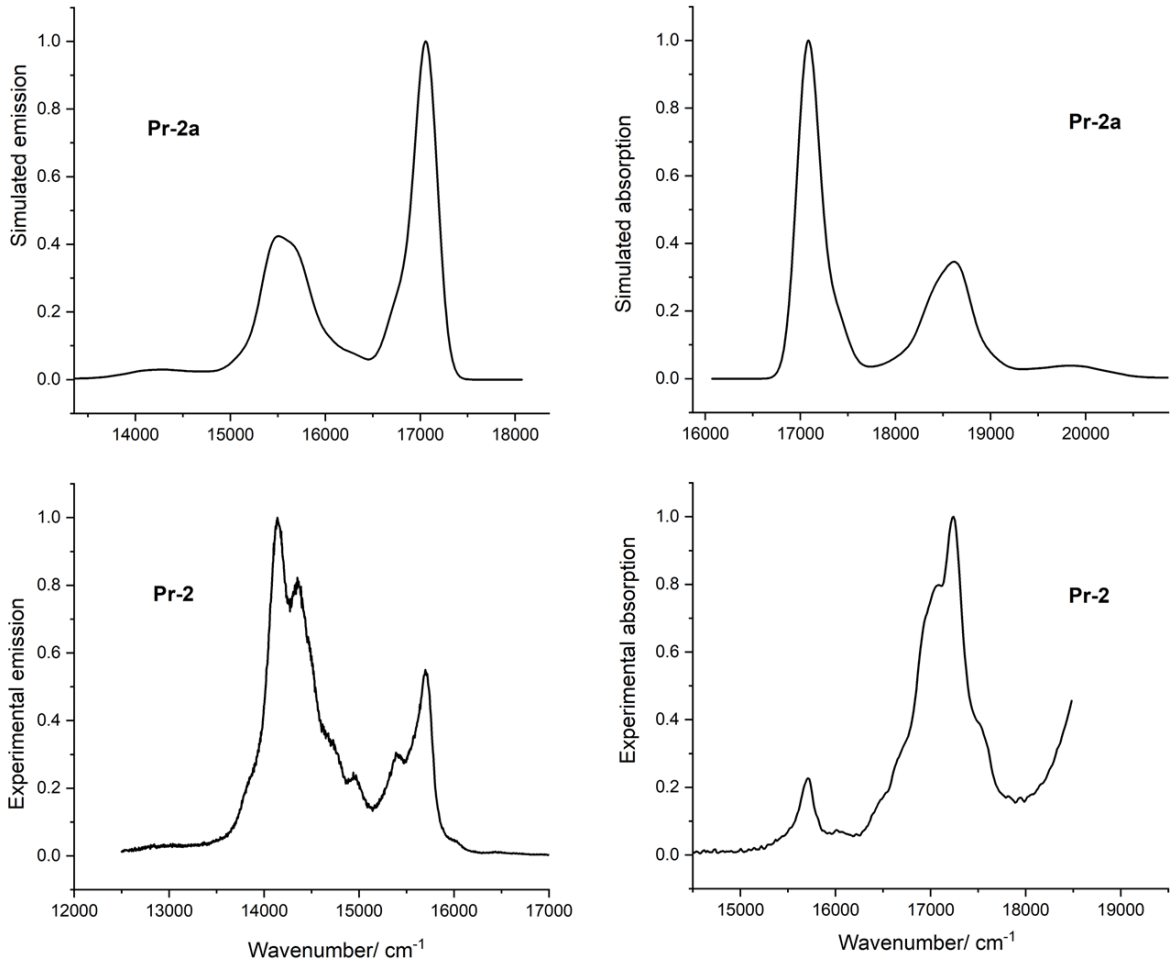

Figure S10. Comparison of simulated (top) and experimental (bottom) absorption and emission spectra of **Pr-2a**. The simulated spectra contain both FC and HT contributions.

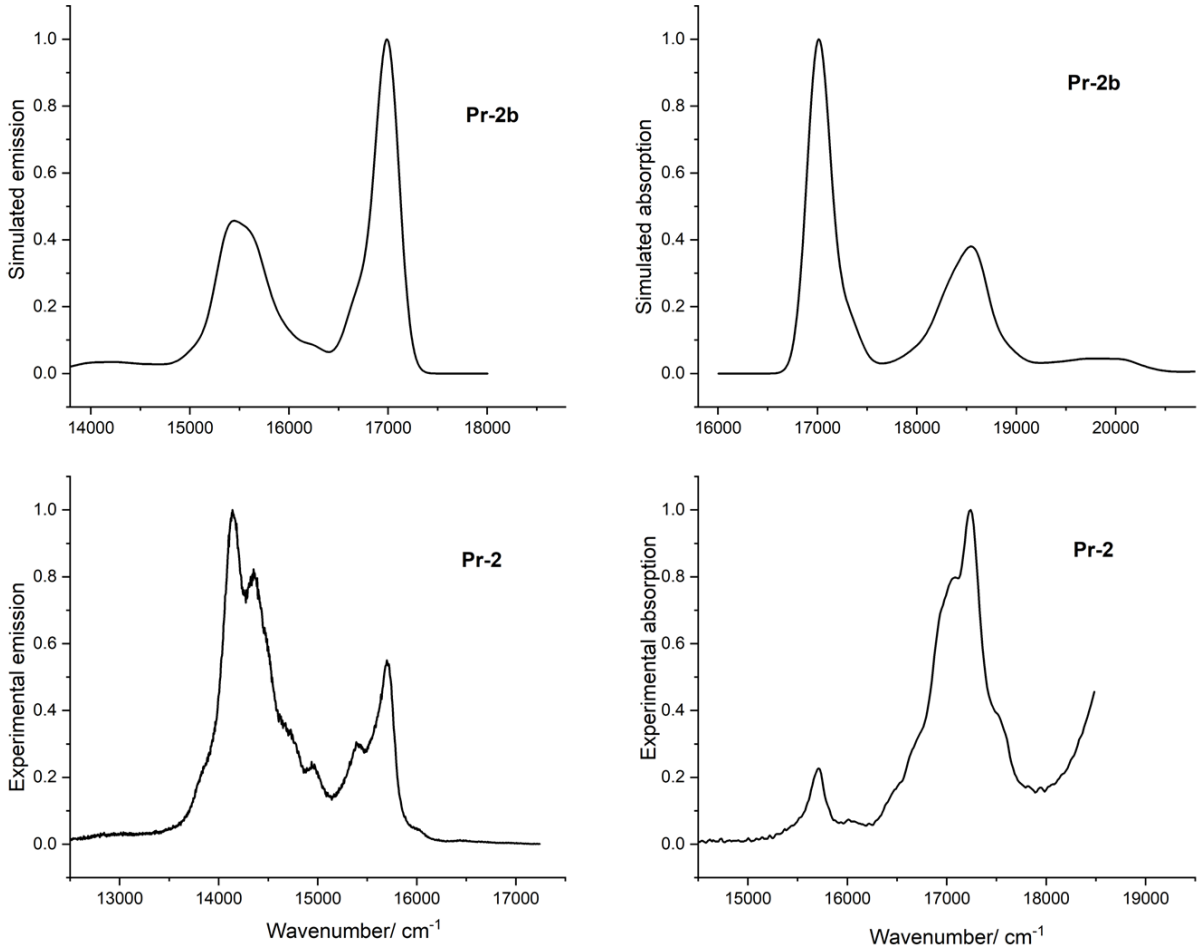

Figure S11. Comparison of simulated (top) and experimental (bottom) absorption and emission spectra of **Pr-2b**. The simulated spectra contain both FC and HT contributions.

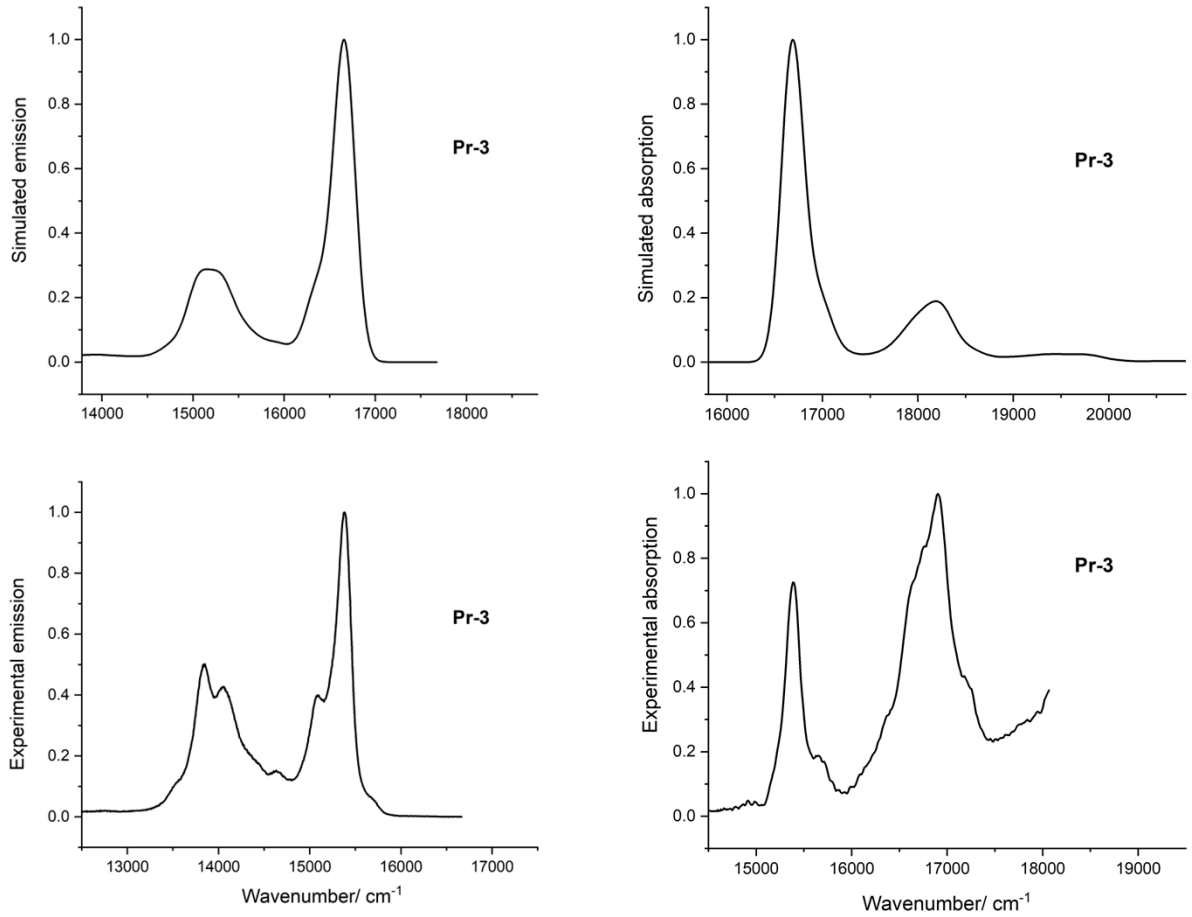

Figure S12. Comparison of simulated (top) and experimental (bottom) absorption and emission spectra of **Pr-3**. The simulated spectra contain both FC and HT contributions.

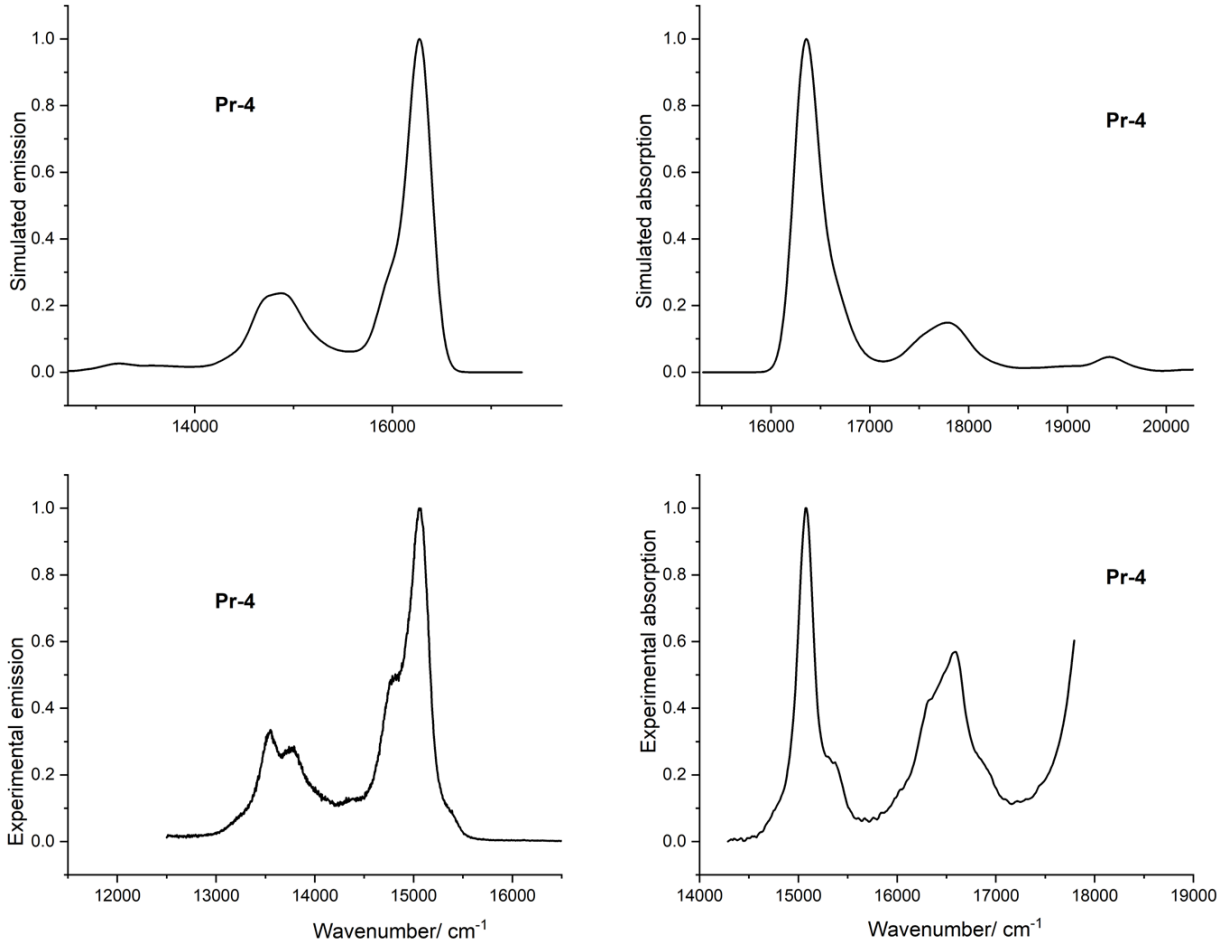

Figure S13. Comparison of simulated (top) and experimental (bottom) absorption and emission spectra of **Pr-4**. The simulated spectra contain both FC and HT contributions.