Supporting information

Computational unveiling surrounding solvent-polarity-dependent ESDPT behavior for typical asymmetric PIQ fluorophore

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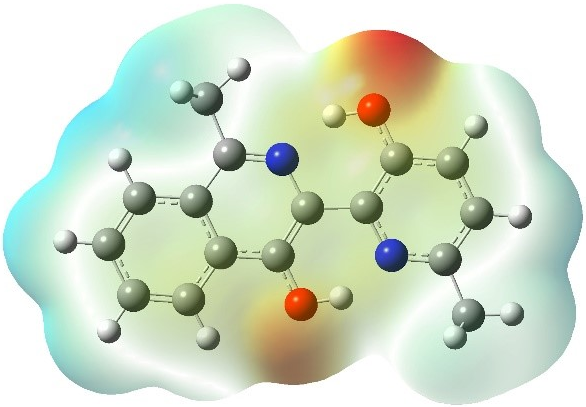

Figure S1. View of the MEP map for PIQ fluorophore in the S_0 state.

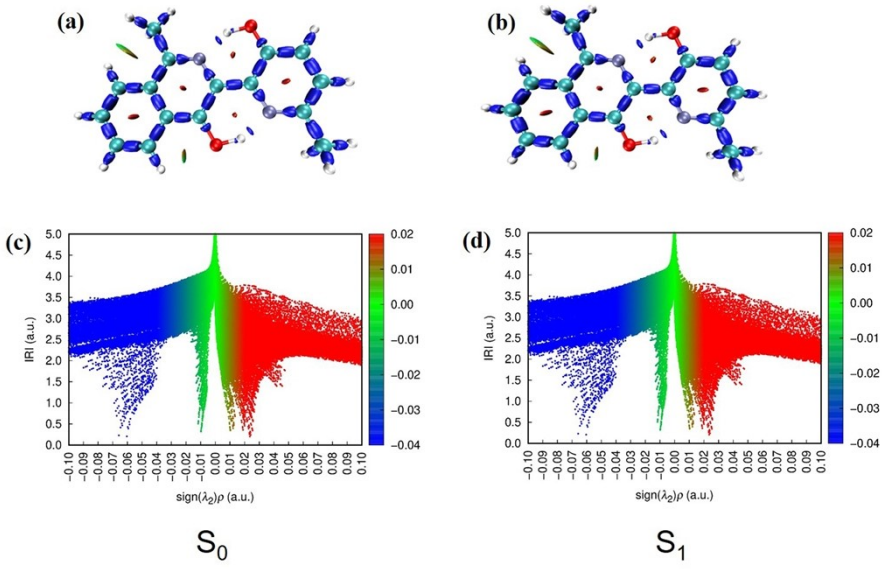

Figure S2. Results of S_0-state and S_1-state IRI isosurface plots and scatter diagrams in acetonitrile solvent using aug-cc-pVTZ.

Table S1. Parameters of bond lengths (Å) and bong angles (Δ°) involved in O1-H2···N3 and O4-H5···N6 for PIQ-T1 form in S_0 and S_1 states in toluene, THF and acetonitrile solvents.

	Toluene		THF		Acetone		Acetonitrile	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O1-H2	1.0020	1.8248	1.4994	1.8356	1.5281	1.8351	1.5337	1.8356
H2···N3	1.6852	1.0196	1.0926	1.0179	1.0827	1.0179	1.0810	1.0179
O4···H5	1.0107	0.9905	1.0183	1.0018	1.0189	1.0009	1.0191	1.0018
H5-N6	1.6455	1.7294	1.6438	1.6705	1.6392	1.6750	1.6381	1.6705
Δ(O1H2N3)	149.06	139.28	149.54	138.13	148.72	138.20	148.56	138.13
Δ(O4H5N6)	149.38	146.20	150.08	147.54	150.12	147.44	150.13	147.54

Table S2. Parameters of bond lengths (Å) and bong angles (Δ°) involved in O1-H2···N3 and O4-H5···N6 for PIQ-T2 in S_0 and S_1 states in toluene, THF and acetonitrile solvents.

	Toluene		THF		Acetone		Acetonitrile	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O1-H2	1.0104	0.9908	1.0119	1.0095	1.0122	1.0128	1.0123	1.0136
H2···N3	1.6608	1.7807	1.6528	1.6520	1.6505	1.6378	1.6499	1.6346
O4···H5	1.6205	1.8251	1.6427	1.8013	1.6502	1.8084	1.6524	1.8102
H5-N6	1.0543	1.0284	1.0500	1.0258	1.0488	1.0249	1.0485	1.0247
Δ(O1H2N3)	149.87	146.28	150.09	149.19	150.09	149.53	150.11	149.61
Δ(O4H5N6)	144.32	136.92	143.67	138.42	143.44	137.97	143.38	137.87

Table S3. Parameters of bond lengths (Å) and bong angles (Δ°) involved in O1-H2···N3 and O4-H5···N6 for PIQ-DT in S_0 and S_1 states in toluene, THF and acetonitrile solvents.

	Toluene		THF		Acetone		Acetonitrile	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
O1-H2	1.5562	1.7960	1.5905	1.7677	1.5998	1.7618	1.6021	1.7607
H2···N3	1.0709	1.0257	1.0641	1.0280	1.0618	1.0284	1.0612	1.0285
O4···H5	1.7071	1.6748	1.7125	1.7333	1.7144	1.7467	1.7149	1.7499
H5-N6	1.0427	1.0409	1.0412	1.0319	1.0407	1.0300	1.0406	1.0296
Δ(O1H2N3)	147.65	138.97	147.02	139.85	146.77	140.03	146.71	140.07
Δ(O4H5N6)	142.05	141.80	141.94	139.65	141.89	139.14	141.88	139.02

Coordinates of TS forms for PIQ

TS1 along with I → III in toluene solvent:

	X	Y	Z
C	-1.75799300	1.56913600	-0.00005200
C	-2.59497700	0.39993500	-0.00002400
C	-1.96005100	-0.88862700	0.00004300
C	-0.55169400	-0.96085500	0.00006600

C	0.20768000	0.28283000	-0.00000900
H	-4.48682800	1.43019200	-0.00013000
C	-3.99500400	0.46660700	-0.00007400
C	-2.76947100	-2.05621400	0.00006500
C	-4.14193800	-1.95047700	0.00001900
C	-4.76790500	-0.68828800	-0.00005400
H	-2.28563100	-3.02346500	0.00011500
H	-4.74855900	-2.84806300	0.00003700
H	-5.84768600	-0.61792600	-0.00009000
C	1.63036000	0.27972100	0.00011800
C	2.42795800	1.46629900	0.00009800
C	3.57957700	-1.06976100	-0.00008500
C	3.81603100	1.34729200	0.00002100
C	4.39078400	0.06866900	-0.00006500
H	4.41871800	2.24525400	0.00004400
H	5.46642900	-0.04578600	-0.00012800
N	-0.44016600	1.48219700	-0.00002800
O	0.07570100	-2.11159400	0.00018800
H	1.16839200	-1.84667800	0.00009800
N	2.24706200	-0.96338400	-0.00000200
O	1.86687400	2.68031600	0.00016500
H	0.87027900	2.53856800	0.00011100
C	4.14681700	-2.45784900	-0.00018900
H	5.23586800	-2.44318700	-0.00005000
H	3.80569500	-3.01085600	0.87941200
H	3.80593400	-3.01063200	-0.88002800
C	-2.34314000	2.94873000	-0.00013300
H	-2.97257300	3.10845200	-0.87966300
H	-1.54828800	3.69129900	-0.00002800
H	-2.97282500	3.10846400	0.87921200

TS2 along with III → IV in toluene solvent:

	X	Y	Z
C	1.75167500	1.53388700	0.00030000
C	2.59649300	0.39965200	0.00012400
C	2.00929600	-0.91174300	-0.00022200
C	0.56927700	-1.07124000	-0.00031600
C	-0.20488300	0.16500000	-0.00019800
H	4.47648800	1.48134400	0.00056000
C	4.01263500	0.50370600	0.00030400
C	2.84499500	-2.04105100	-0.00034900
C	4.21746400	-1.90716700	-0.00017400
C	4.80352700	-0.61998900	0.00015600

H	2.37999800	-3.01837100	-0.00058800
H	4.84952100	-2.78636700	-0.00028500
H	5.88189300	-0.52040300	0.00029000
C	-1.62792500	0.22077900	-0.00048700
C	-2.33857300	1.46614900	-0.00043200
C	-3.72304300	-0.99328200	0.00026300
C	-3.74847600	1.43321400	-0.00041000
C	-4.41972200	0.20607200	-0.00001500
H	-4.28407000	2.37263200	-0.00053000
H	-5.50100100	0.17577800	0.00006300
N	0.42315800	1.38078200	0.00008800
O	0.00420500	-2.19754100	-0.00050000
H	-1.79465000	-1.80606400	0.00023900
N	-2.36982700	-0.95640200	0.00003100
O	-1.67736900	2.59412500	-0.00051900
H	-0.51840100	2.24068900	-0.00009800
C	-4.36393000	-2.34238500	0.00100300
H	-4.06371000	-2.91712300	0.88291200
H	-5.44860000	-2.25483400	-0.00035700
H	-4.06162000	-2.91913800	-0.87886100
C	2.26772900	2.94028500	0.00070600
H	2.88699300	3.13348100	0.88081500
H	1.44230600	3.64994700	0.00054100
H	2.88761200	3.13378100	-0.87889600

TS1 along with I → III in THF solvent:

	X	Y	Z
C	-1.75636400	1.56995700	0.00025400
C	-2.59275300	0.39960600	0.00048000
C	-1.95840400	-0.89105100	0.00036000
C	-0.55219700	-0.96372400	0.00002700
C	0.20934400	0.27975200	-0.00008900
H	-4.48425600	1.43032900	0.00089200
C	-3.99262400	0.46671300	0.00079700
C	-2.77038200	-2.05783200	0.00054000
C	-4.14237400	-1.95124200	0.00085300
C	-4.76654200	-0.68694100	0.00098800
H	-2.28988200	-3.02687100	0.00043300
H	-4.75021600	-2.84787000	0.00099800
H	-5.84619400	-0.61494600	0.00123500
C	1.62657200	0.27579200	-0.00032000
C	2.42477800	1.46771400	-0.00060000
C	3.58144600	-1.06709900	-0.00043100

C	3.81132700	1.35173300	-0.00081700
C	4.39088000	0.07422900	-0.00074300
H	4.41348900	2.25035600	-0.00103200
H	5.46675400	-0.03697900	-0.00090200
N	-0.44003800	1.48303300	-0.00001000
O	0.07774300	-2.11529900	-0.00017000
H	1.16632800	-1.85210000	-0.00017800
N	2.24922600	-0.96552200	-0.00019500
O	1.85672400	2.67817100	-0.00066500
H	0.85727200	2.52919400	-0.00042100
C	4.15443200	-2.45267200	-0.00038700
H	3.81551900	-3.00630100	-0.88030700
H	5.24322600	-2.43352100	0.00007100
H	3.81475100	-3.00657500	0.87905600
C	-2.34269900	2.94888500	0.00030700
H	-2.97257100	3.10726400	-0.87882600
H	-1.54865400	3.69221900	0.00013100
H	-2.97225100	3.10733800	0.87965600

TS2 along with III → IV in THF solvent:

	X	Y	Z
C	1.75076200	1.53294500	-0.00003700
C	2.59761100	0.39920000	-0.00006100
C	2.01126300	-0.91280200	-0.00008900
C	0.57272200	-1.07413300	-0.00005700
C	-0.20592800	0.16340800	0.00000800
H	4.47448400	1.48465200	-0.00005800
C	4.01252300	0.50625900	-0.00008700
C	2.85055800	-2.04074900	-0.00015900
C	4.22292600	-1.90427800	-0.00018800
C	4.80686200	-0.61623300	-0.00014800
H	2.39093700	-3.02058800	-0.00018600
H	4.85634000	-2.78246500	-0.00024100
H	5.88485700	-0.51428100	-0.00016500
C	-1.62637600	0.21759700	0.00008100
C	-2.33903500	1.46351500	0.00011700
C	-3.72790800	-0.99175300	0.00011600
C	-3.74685400	1.43471600	0.00014100
C	-4.42265700	0.20840300	0.00014600
H	-4.28183700	2.37465000	0.00017200
H	-5.50381400	0.18070100	0.00017800
N	0.42314100	1.37939800	-0.00000700
O	0.00811800	-2.20097200	-0.00008100

H	-1.80819600	-1.81113900	0.00002300
N	-2.37448200	-0.95816600	0.00008300
O	-1.67575400	2.59355600	0.00011800
H	-0.52867200	2.24506000	0.00005800
C	-4.37314700	-2.33849100	0.00013000
H	-4.07303500	-2.91423200	0.88109500
H	-5.45726400	-2.24663700	0.00011400
H	-4.07301200	-2.91426300	-0.88080800
C	2.26715200	2.93881000	-0.00005400
H	2.88712200	3.13092000	0.87953800
H	1.44245200	3.64899300	-0.00015400
H	2.88727700	3.13084800	-0.87955000

TS1 along with I → III in acetonitrile solvent:

	X	Y	Z
C	-1.75545000	1.57040700	0.00000300
C	-2.59186000	0.39950200	0.00005600
C	-1.95769400	-0.89203600	0.00004600
C	-0.55255700	-0.96494400	-0.00001000
C	0.21015000	0.27854000	-0.00000100
H	-4.48315100	1.43059700	0.00009600
C	-3.99149400	0.46702500	0.00008900
C	-2.77089300	-2.05857000	0.00005100
C	-4.14280500	-1.95138300	0.00008700
C	-4.76606100	-0.68635300	0.00010800
H	-2.29209100	-3.02850900	0.00003200
H	-4.75124200	-2.84755100	0.00009800
H	-5.84563000	-0.61354100	0.00013600
C	1.62491700	0.27418000	0.00006100
C	2.42350800	1.46836200	-0.00005400
C	3.58209300	-1.06615300	0.00000200
C	3.80938100	1.35346000	-0.00012200
C	4.39091100	0.07642700	-0.00009800
H	4.41155200	2.25222300	-0.00018900
H	5.46686200	-0.03344600	-0.00014600
N	-0.43978900	1.48340200	-0.00002000
O	0.07858800	-2.11697400	-0.00010800
H	1.16566000	-1.85427800	-0.00002600
N	2.25004800	-0.96640000	0.00008900
O	1.85263100	2.67738000	-0.00009000
H	0.85188400	2.52551200	-0.00005700
C	4.15740300	-2.45071300	0.00002200
H	3.81882300	-3.00482200	-0.87965300

H	5.24607900	-2.42967800	0.00002700
H	3.81880800	-3.00480500	0.87970100
C	-2.34225300	2.94894400	-0.00003500
H	-2.97215700	3.10658000	-0.87912700
H	-1.54860700	3.69265600	-0.00007200
H	-2.97213200	3.10664000	0.87906400

TS2 along with III → IV in acetonitrile solvent:

	X	Y	Z
C	1.75023700	1.53254600	-0.00018400
C	2.59820100	0.39899200	-0.00006900
C	2.01213500	-0.91333100	0.00010800
C	0.57439800	-1.07537800	0.00016400
C	-0.20648100	0.16275300	0.00002000
H	4.47375900	1.48616500	-0.00024800
C	4.01249300	0.50748200	-0.00011900
C	2.85317400	-2.04072000	0.00021500
C	4.22547700	-1.90299200	0.00015900
C	4.80844100	-0.61453000	-0.00000900
H	2.39624400	-3.02182900	0.00034200
H	4.85954600	-2.78068100	0.00024400
H	5.88624700	-0.51146500	-0.00005100
C	-1.62542000	0.21598900	0.00002600
C	-2.33937100	1.46234400	-0.00017900
C	-3.72996300	-0.99116800	0.00015200
C	-3.74600600	1.43534000	-0.00022700
C	-4.42391100	0.20934400	-0.00005500
H	-4.28084500	2.37545800	-0.00038500
H	-5.50498300	0.18255000	-0.00008700
N	0.42316100	1.37900900	-0.00015900
O	0.00985900	-2.20251400	0.00034100
H	-1.81409300	-1.81361100	0.00030000
N	-2.37643600	-0.95910300	0.00018800
O	-1.67523400	2.59342600	-0.00034100
H	-0.53397500	2.24774800	-0.00028800
C	-4.37773800	-2.33661900	0.00034100
H	-4.07840700	-2.91244000	0.88137300
H	-5.46153400	-2.24194100	0.00042000
H	-4.07855000	-2.91261700	-0.88062400
C	2.26689400	2.93808100	-0.00034800
H	2.88731400	3.12941300	0.87894800
H	1.44257800	3.64858100	-0.00039000
H	2.88724700	3.12923300	-0.87973000