Electronic Supplementary Material (ESI) for RSC Advances.

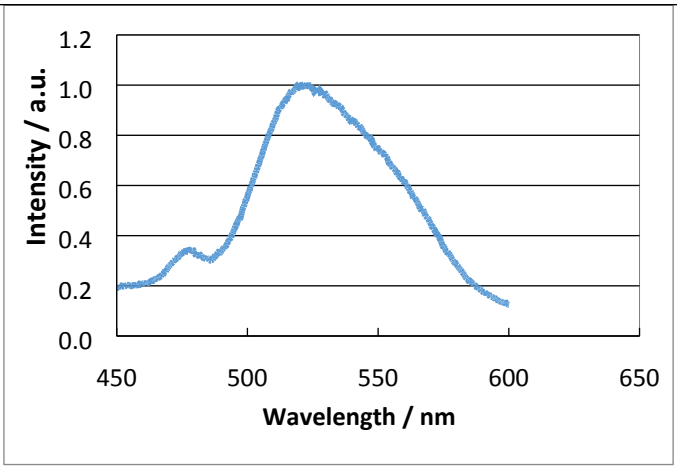


Fig. S1 Fluorescence spectrum of the DAOB dimer with an excitation wavelength of 410 nm.

The protein was dissolved in 0.017 M pyrophosphate buffer (pH 8.3) at 10 μM.

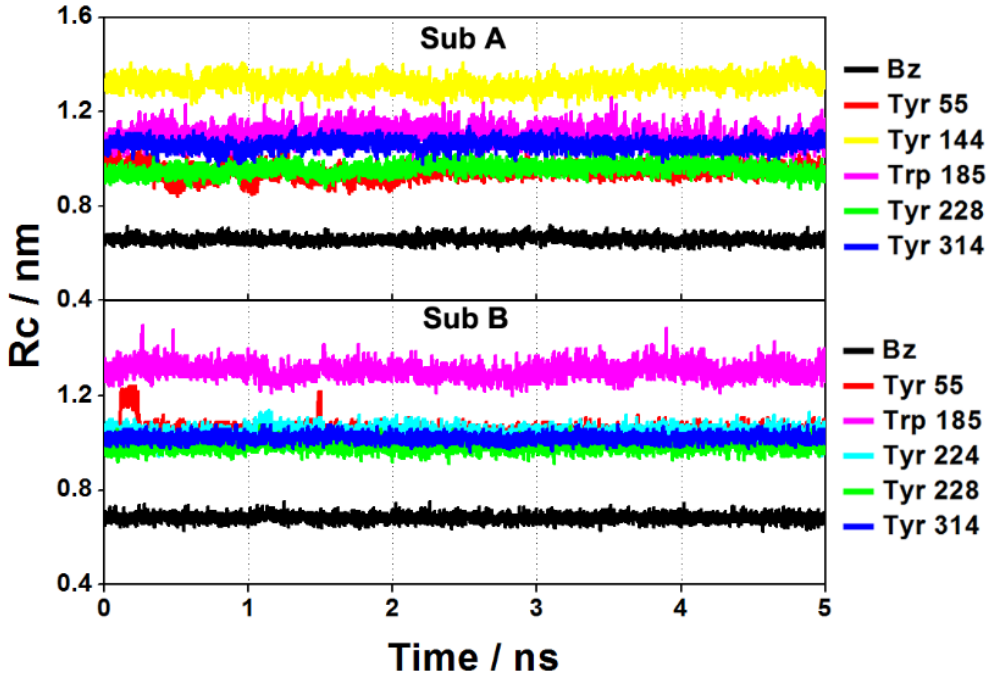


Fig. S2 Time-evolution of the Rc between Iso and the six nearest potential ET donors in the DAOB dimer. Rc denotes centre-to-centre distance.

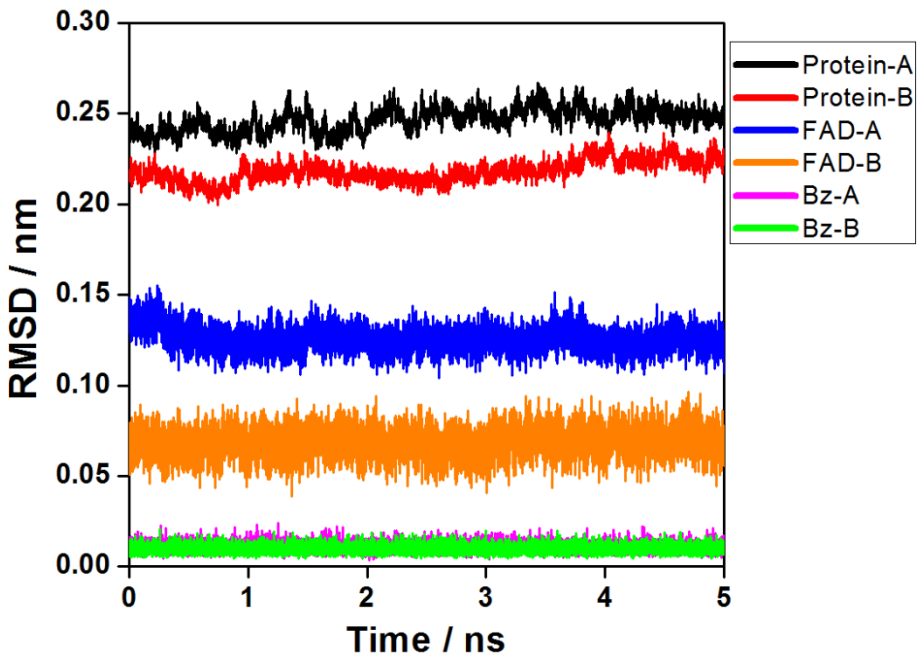


Fig. S3 Time-evolution of root of mean square deviation (RMSD).

The RMSD were obtained by AMBER 10. MDS calculations from the last 5 ns of a 30 ns simulation. Protein-A and protein-B denote Sub A and Sub B in the DAOB dimer. FAD-A and FAD-B denote the FAD in Sub A and Sub B, and Bz-A and Bz-B denote Bz in Sub A and Sub B, respectively. RMSDs of FAD and Bz were steady over the MDS time range of 25–30 ns, whilst the subunits were almost at equilibrium.

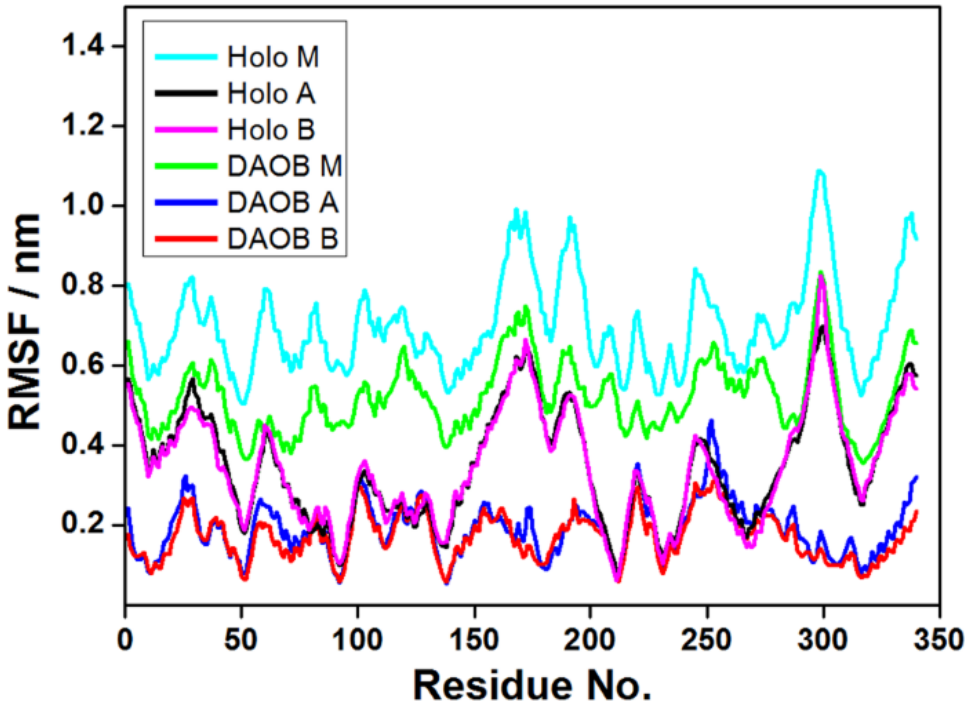


Fig. S4 Comparoson of RMSF in DAOB dimer with other DAAO species.

Root of mean square fluctuations (RMSF), as obtained by AMBER10. Holo M, Holo A and Holo B in insert denote the holoDAAO monomer, Sub A and Sub B of the holoDAAO dimer, respectively. DAOB M, DAOB A and DAOB B denote the monomer of DAOB, Sub A and Sub B of the DAOB dimer, respectively. RMSFs of the holoDAAO monomer were taken from Nueangaudom *et al*. (2012),[31] those for holoDAAO dimer from Nueangaudom *et al*. (2014),[34] and those of DAOB monomer from Nueangaudom *et al*. (2012)[33].

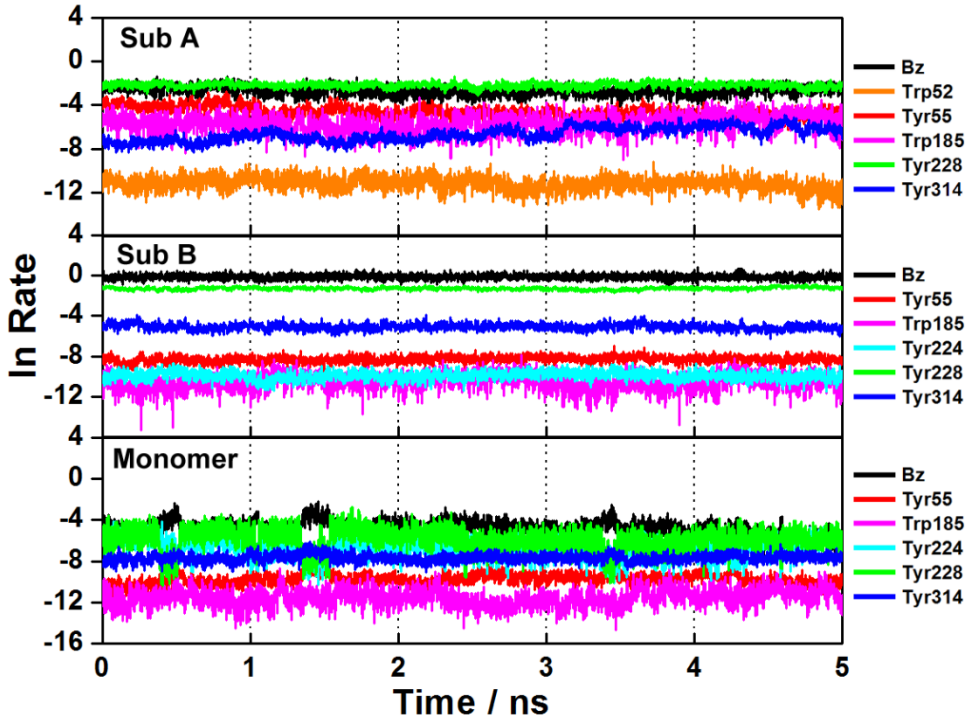


Fig. S5 Dynamics (time-evolution) of the logarithmic ET rate of the six fastest donors. Upper, middle and lower panels show the logarithmic ET rates of Sub A, Sub B and the monomer, respectively. The rates were obtained with Method 2.

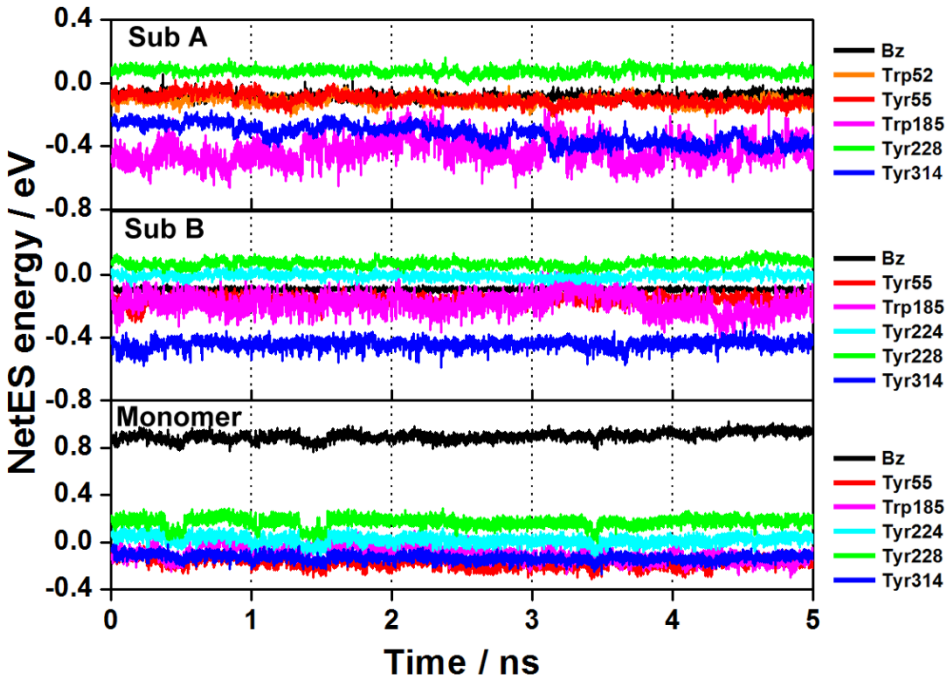


Fig. S6 Time-evolution of the NetES energy between the photoproducts as the Iso acceptor and the six fastest donators (ionic groups) in the DAOB dimer.

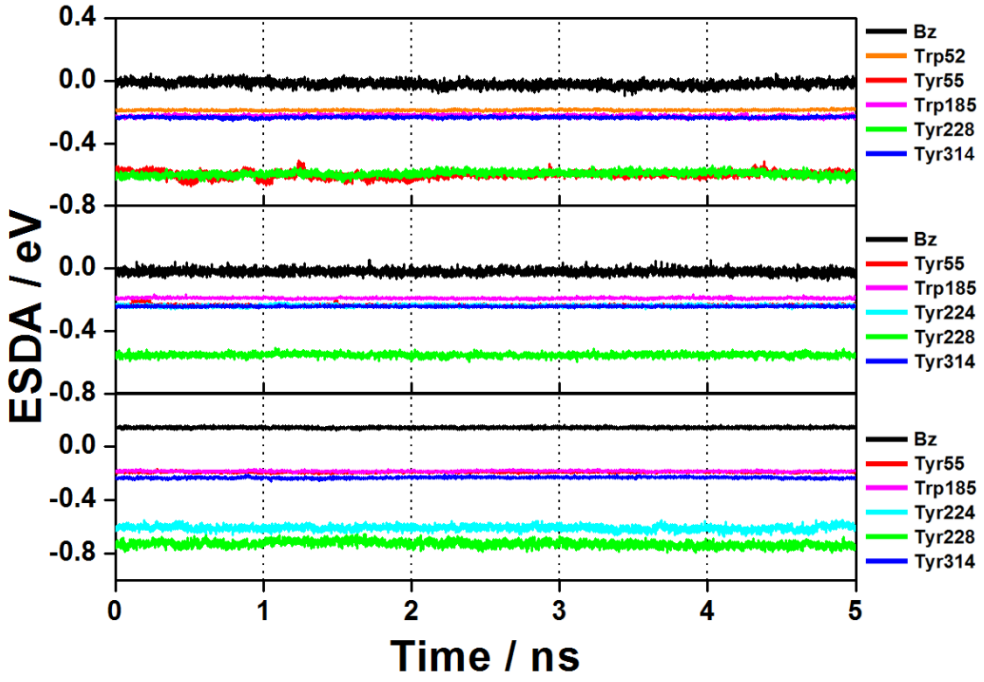


Fig. S7 Time-evolution of the ESDA between the Iso acceptor and the six fastest donators (Bz, Trp or Tyr cations) in the DAOB dimer.

ESDA (electrostatic energy between the iso anion and the donor cation or neutral Bz) was derived as $-e^2 / \varepsilon_{DA} R_j$ from eqn (1) for Trp and Tyr, where the static dielectric constants ε_{DA}^{A} and ε_{DA}^{B} were used for Sub A and Sub B, respectively, or from eqn (11) for Bz.

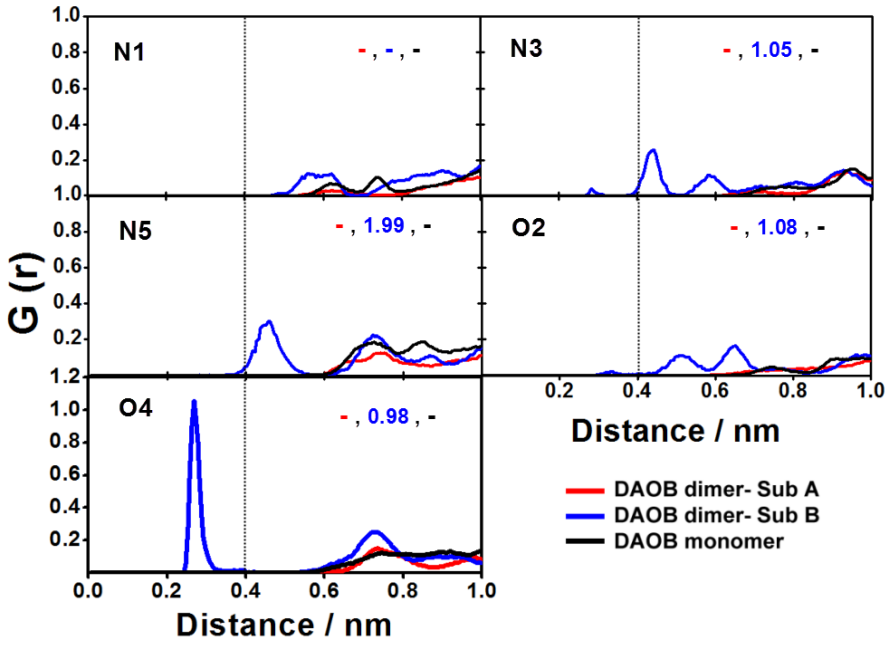


Fig. S8 The radial distribution functions of water molecules near the heteroatoms of Iso.

The radial distribution functions (RDF) were obtained by *ptraj* module of Amber 10 program. Red, blue and black numbers are shown number of mean water molecules of DAOB dimer, Sub A and Sub B and DAOB monomer,[33] respectively.

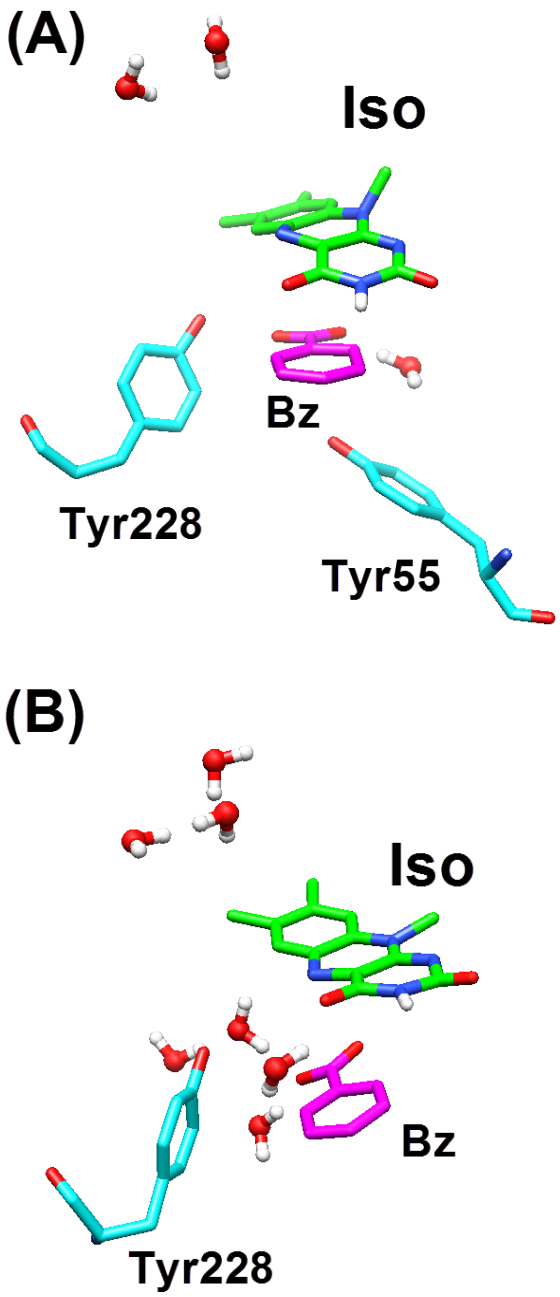
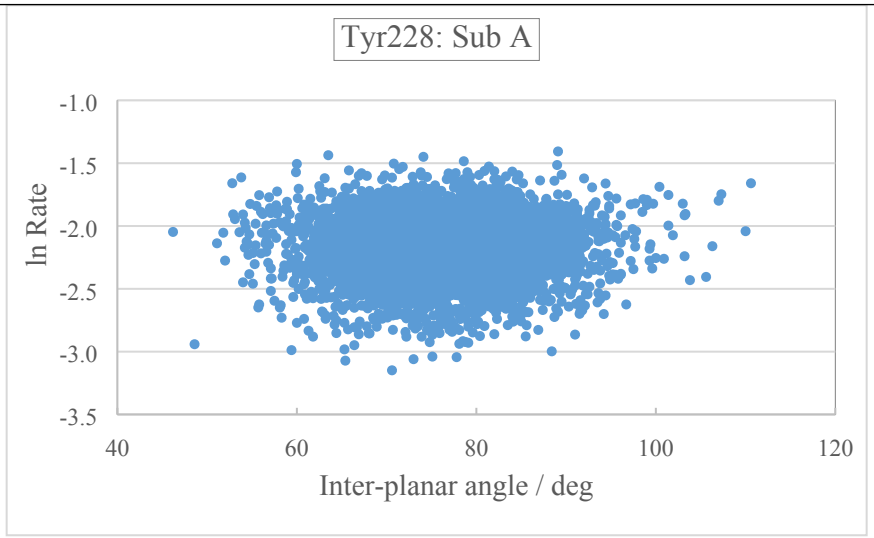
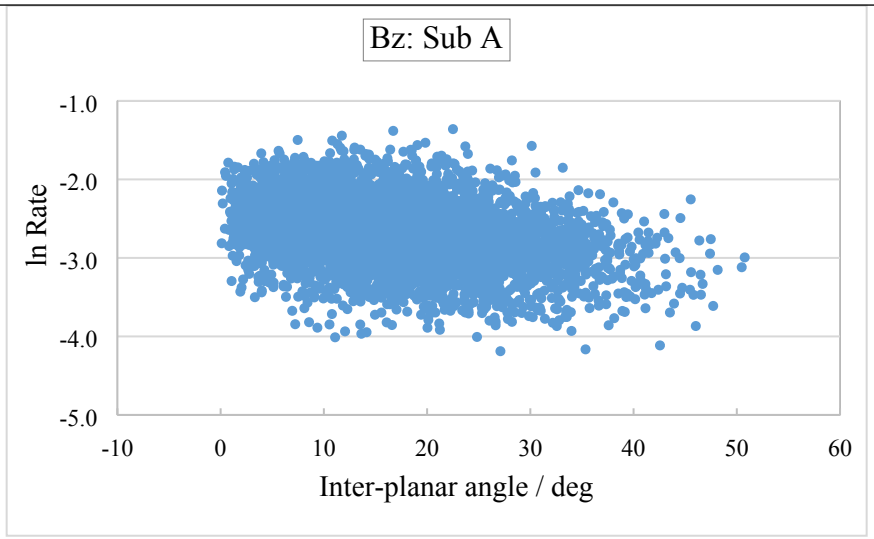


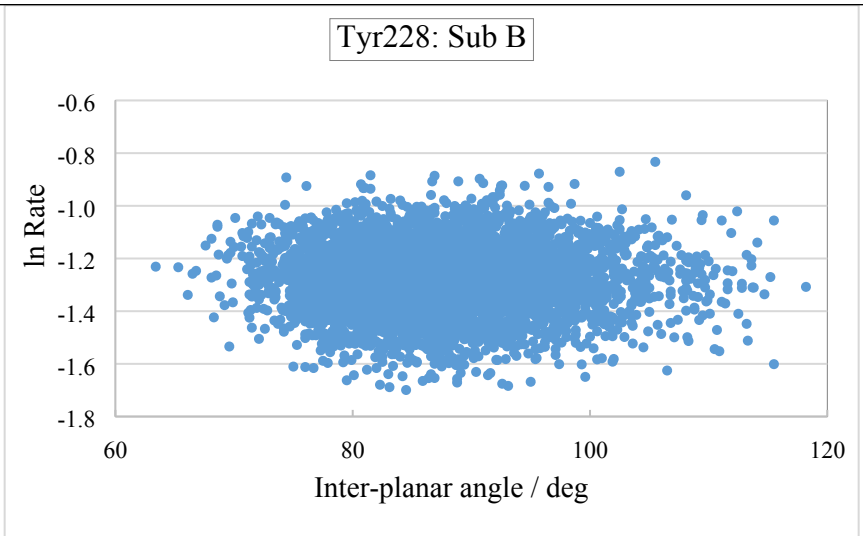
Fig. S9 Presence of water molecules near Iso and ET donors in a snapshot.

Panel (A) shows Sub A and (B) Sub B. ET donors are shown with Rc shorter than 1 nm.

Water molecules selected are shown with the distance from IsoN5 shorter than 0.7 nm.


Tyr228: Sub A
ln Rate
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
40
60
80
100
120
Inter-planar angle / deg


Bz: Sub A
ln Rate
-1.0
-2.0
-3.0
-4.0
-5.0
-10
0
10
20
30
40
50
60
Inter-planar angle / deg



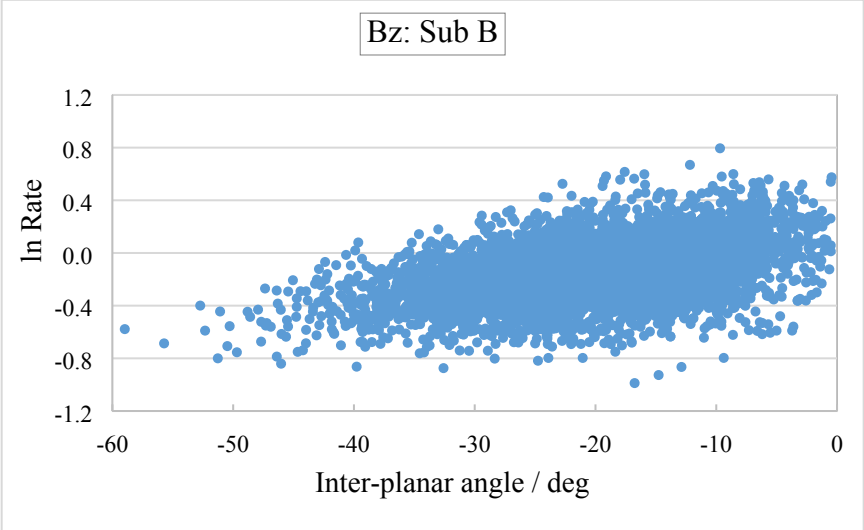
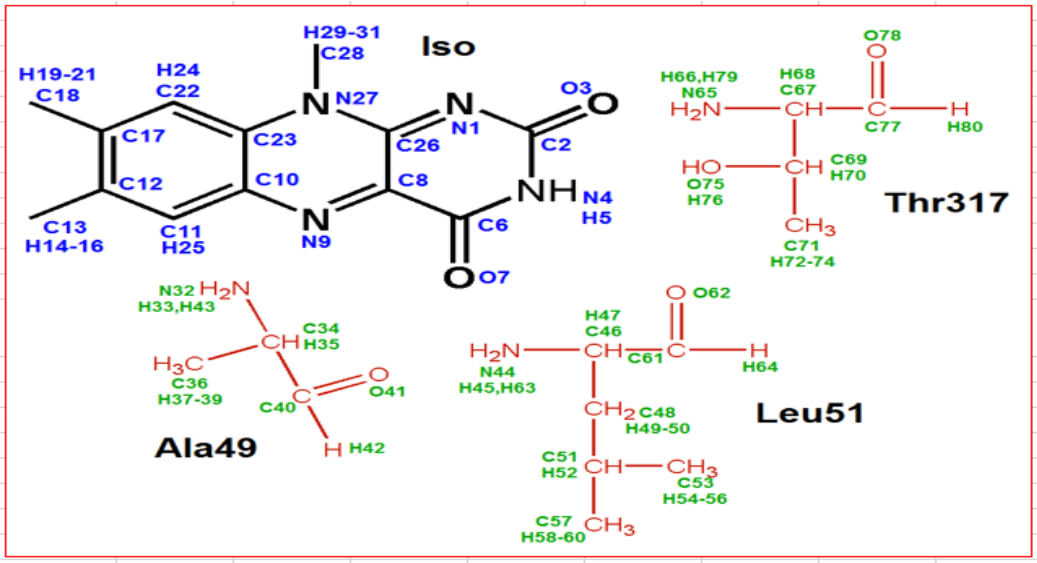


Figure S10 Relationship between logarithmic ET rates and inter-planar angles between Iso and main donors.

Sub A


Iso
H29-31
C28
H19-21
C18
H24
C22
C17
C23
C26
C12
C10
C8
C13
H14-16
C11
H25
N9
N27
N1
O3
C2
N4
H5
C6
O7
Thr317
O78
H66,H79
N65
H68
C67
C77
H80
C69
H70
O75
H76
C71
H72-74
Ala49
N32
H33,H43
C34
H35
C36
H37-39
C40
O41
H42
Leu51
O62
H47
C46
C61
H64
N44
H45,H63
C48
H49-50
C51
H52
C53
H54-56
C57
H58-60

Sub B

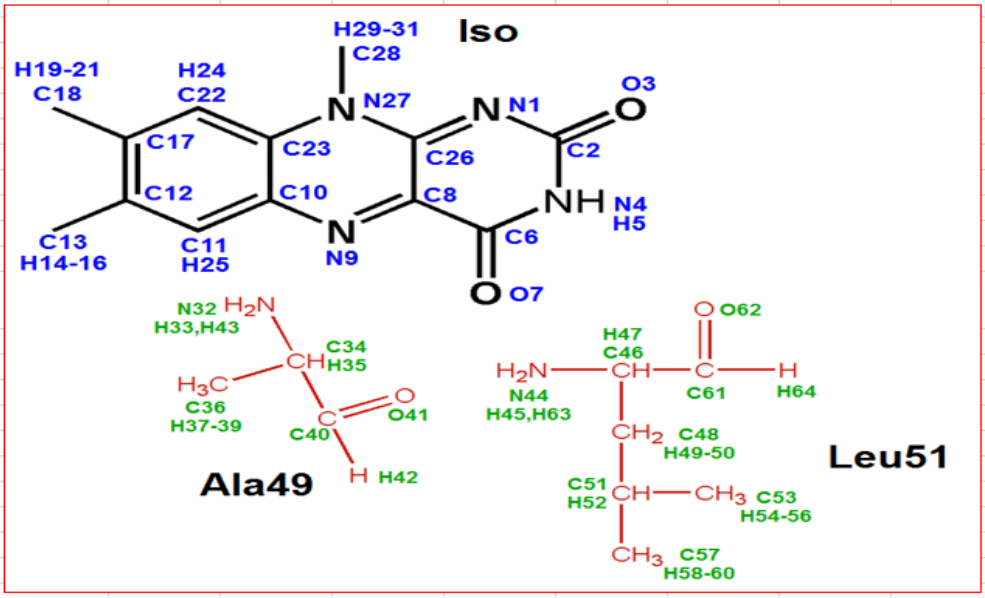
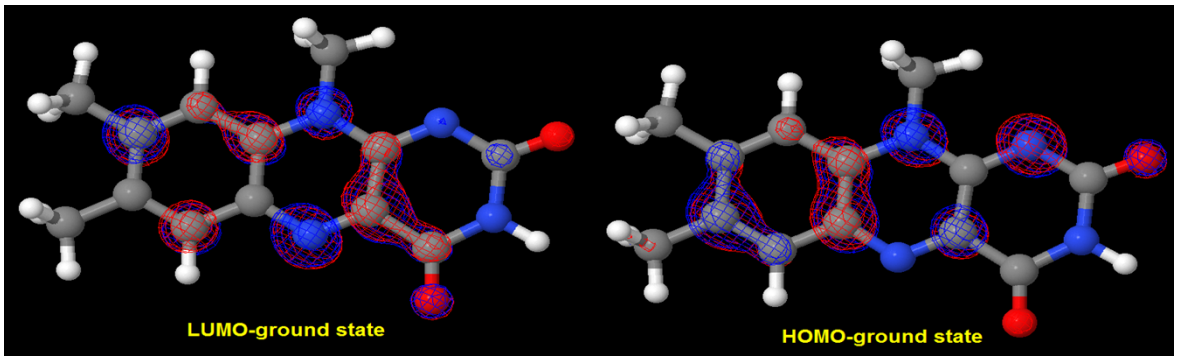


Figure S11 Atom numbering of hydrogen bonded systems in DAOB dimer for MOPAC calculation.

Iso forms hydrogen bondings (H-bond) with Ala49, Leu51 and Thr317 in Sub A, while it forms H-bonds with Ala49 and Leu51 in Sub B.



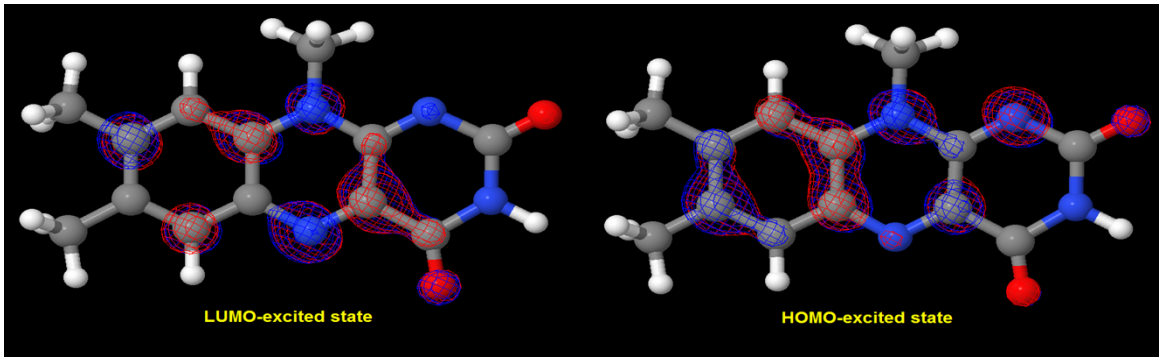


Figure S12 HOMO-LUMO orbitals of Iso alone.

MOs were calculated with semi-empirical MOPAC method. PM6 basis set was used. Other key words were same with those in the previous work,[35] except for EPS (static dielectric constant) key words which were all 2.6 (ε_0^{DA} was nearly equal to ε_0^{DB}, 2.6, see Table 3) in the present work.

Table S1 Decay parameters of the DAOB dimer[a]

Wavelength (λ_i) (nm)	τ_1 (ps)	α_1	τ_2 (ps)	α_2
480	0.30	0.815	1.9	0.185
485	0.42	0.71	4.23	0.29
490	0.506	0.600	4.46	0.400
510	0.942	0.22	4.47	0.78
530	1.486	0.337	4.95	0.663
550	1.46	0.36	5.00	0.64
580	0.94	0.26	4.52	0.74
600	0.877	0.25	4.40	0.75
630	0.84	0.486	6.46	0.514
640	0.713	0.47	7.34	0.53

[a] Data are taken from Mataga *et al*. (2000)[21].

Table S2. ET parameters in the DAOB monomer obtained with a similar model as with the DAOB dimer[a]

Protein	G_{Iso}^{0} (eV)	R_0^{Bz} (nm)	ε_0	ε_0^{DA}	χ^2
DAOB monomer	8.53	0.384	5.78	2.45	4.38×10^{-21}

[a] ET parameters were recalculated with the model where the static dielectric constant in the region between Iso and the donors with Rc values of less than 1 nm (Bz, Tyr224 and Tyr228)[33] was ε_0^{DA} (eqn (2) and Nueungaudom *et al*. (2014)[34]). In the previous work[33] the dielectric constant in this region between Iso and these donors was assumed to be equal to ε_0.

Table S3 Charge density of Iso with and without H-bonds[a]

Molecule	Atom No.	Iso without H-bond		Ground		Excited	
		Ground	Excited	Sub A	Sub B	Sub A	Sub B
Iso	1	-0.613	-0.467	-0.616	-0.614	-0.440	-0.471
	2	0.747	0.713	0.750	0.750	0.716	0.717
	3	-0.519	-0.498	-0.514	-0.510	-0.480	-0.484
	4	-0.621	-0.616	-0.620	-0.624	-0.615	-0.616
	5	0.325	0.324	0.343	0.340	0.342	0.338
	6	0.659	0.651	0.662	0.661	0.653	0.653
	7	-0.501	-0.489	-0.535	-0.525	-0.511	-0.523
	8	-0.194	-0.122	-0.211	-0.212	-0.106	-0.131
	9	-0.101	-0.298	-0.093	-0.090	-0.277	-0.285
	10	-0.074	0.246	-0.075	-0.082	0.219	0.237
	11	-0.085	-0.319	-0.079	-0.075	-0.278	-0.302
	12	-0.028	0.247	-0.029	-0.035	0.230	0.244
	13	-0.477	-0.538	-0.477	-0.476	-0.537	-0.539
	14	0.174	0.197	0.173	0.172	0.197	0.196
	15	0.174	0.196	0.176	0.172	0.197	0.191
	16	0.172	0.190	0.172	0.175	0.190	0.200
	17	0.211	-0.060	0.216	0.217	-0.077	-0.065
	18	-0.526	-0.475	-0.527	-0.528	-0.476	-0.476
	19	0.189	0.174	0.189	0.179	0.175	0.171
	20	0.189	0.175	0.190	0.189	0.175	0.175
	21	0.179	0.171	0.179	0.190	0.171	0.175
	22	-0.348	-0.209	-0.352	-0.353	-0.209	-0.211
	23	0.193	-0.021	0.198	0.201	-0.026	-0.023
	24	0.194	0.181	0.195	0.194	0.183	0.182
	25	0.188	0.212	0.187	0.188	0.210	0.214
	26	0.384	0.323	0.387	0.387	0.317	0.329
	27	-0.137	-0.129	-0.138	-0.144	-0.179	-0.139
	28	-0.325	-0.335	-0.324	-0.324	-0.340	-0.343
	29	0.212	0.209	0.210	0.177	0.209	0.183
	30	0.179	0.188	0.178	0.212	0.183	0.217
	31	0.178	0.179	0.180	0.178	0.182	0.183
Ala49	32			-0.553	-0.553	-0.553	-0.557
	33			0.237	0.236	0.239	0.250
	34			-0.063	-0.062	-0.057	-0.058
	35			0.165	0.165	0.163	0.161
	36			-0.485	-0.480	-0.493	-0.489
	37			0.165	0.164	0.163	0.161
	38			0.172	0.169	0.171	0.170

	39	0.165	0.172	0.174	0.170
	40	0.349	0.353	0.344	0.347
	41	-0.503	-0.505	-0.505	-0.510
	42	0.128	0.120	0.131	0.133
	43	0.221	0.219	0.222	0.219
Leu51	44	-0.534	-0.535	-0.541	-0.536
	45	0.230	0.238	0.242	0.236
	46	-0.107	-0.095	-0.100	-0.102
	47	0.176	0.164	0.168	0.175
	48	-0.327	-0.325	-0.322	-0.330
	49	0.173	0.173	0.168	0.173
	50	0.149	0.154	0.154	0.151
	51	0.030	0.031	0.025	0.031
	52	0.108	0.107	0.110	0.106
	53	-0.508	-0.508	-0.508	-0.508
	54	0.155	0.160	0.156	0.160
	55	0.151	0.155	0.149	0.154
	56	0.161	0.151	0.160	0.153
	57	-0.509	-0.509	-0.507	-0.509
	58	0.153	0.154	0.154	0.154
	59	0.156	0.155	0.156	0.156
	60	0.159	0.158	0.157	0.158
	61	0.365	0.362	0.364	0.362
	62	-0.523	-0.520	-0.522	-0.526
	63	0.125	0.221	0.222	0.226
	64	0.225	0.118	0.121	0.121
Thr317	65	-0.525		-0.530	
	66	0.228		0.230	
	67	-0.227		-0.227	
	68	0.198		0.199	
	69	0.251		0.255	
	70	0.110		0.111	
	71	-0.538		-0.539	
	72	0.182		0.181	
	73	0.174		0.176	
	74	0.173		0.175	
	75	-0.590		-0.599	
	76	0.349		0.350	
	77	0.365		0.367	
	78	-0.492		-0.492	
	79	0.228		0.231	
	80	0.112		0.112	

a Charge densities were obtained with a semi-empirical MO of MOPAC (PM6). Other key words were same with those in the previous work,[35] except for EPS (static dielectric constant) key words which were all 2.6 (ε_0^{DA} was nearly equal to ε_0^{DB}, 2.6, see Table 3) in the present work. Ground and Excited denote the ground and excited states of Iso. Atom numbering of Iso and H-bond amino acids are indicated in Figure S11.