Supporting Information

Ultrafast Intramolecular Energy Relaxation Dynamics of Benzoporphyrins: Influence of Fused Benzo-rings on Singlet Excited States

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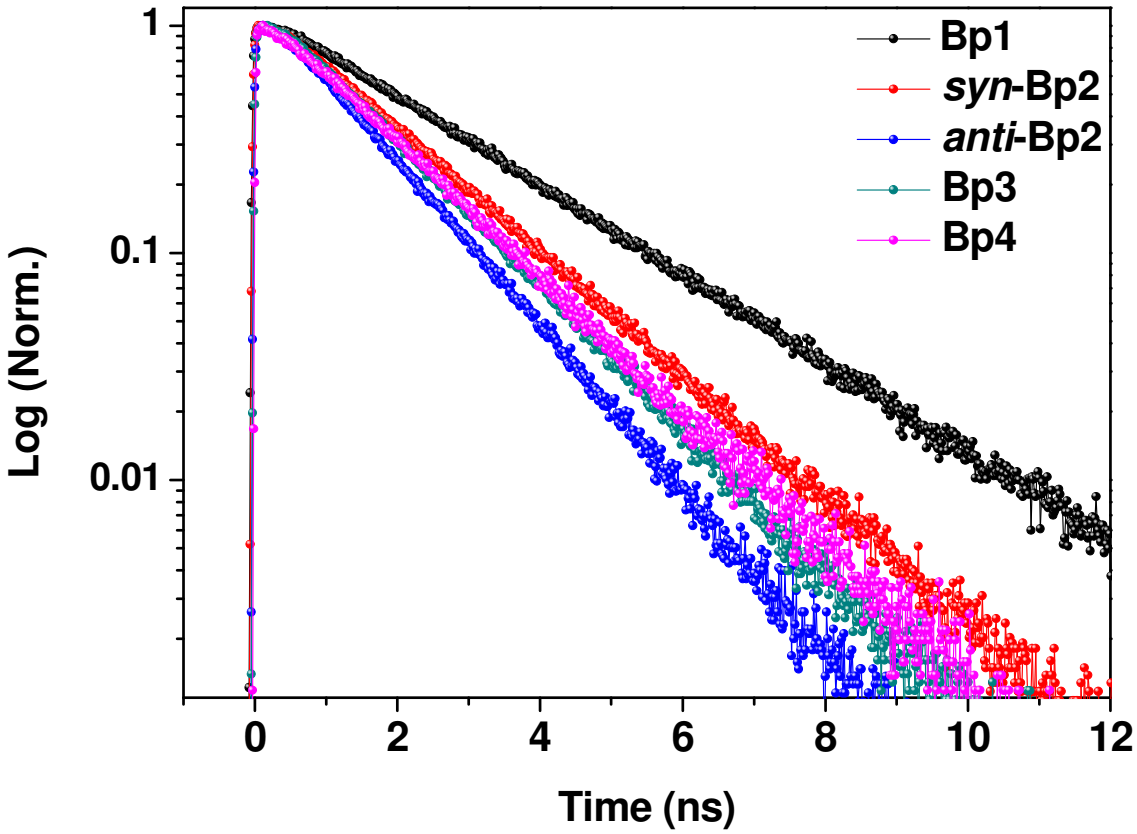

Figure S1. Fluorescence decay profiles of benzoporphyrins observed at the maximum of emission band after photoexcitation at B band.

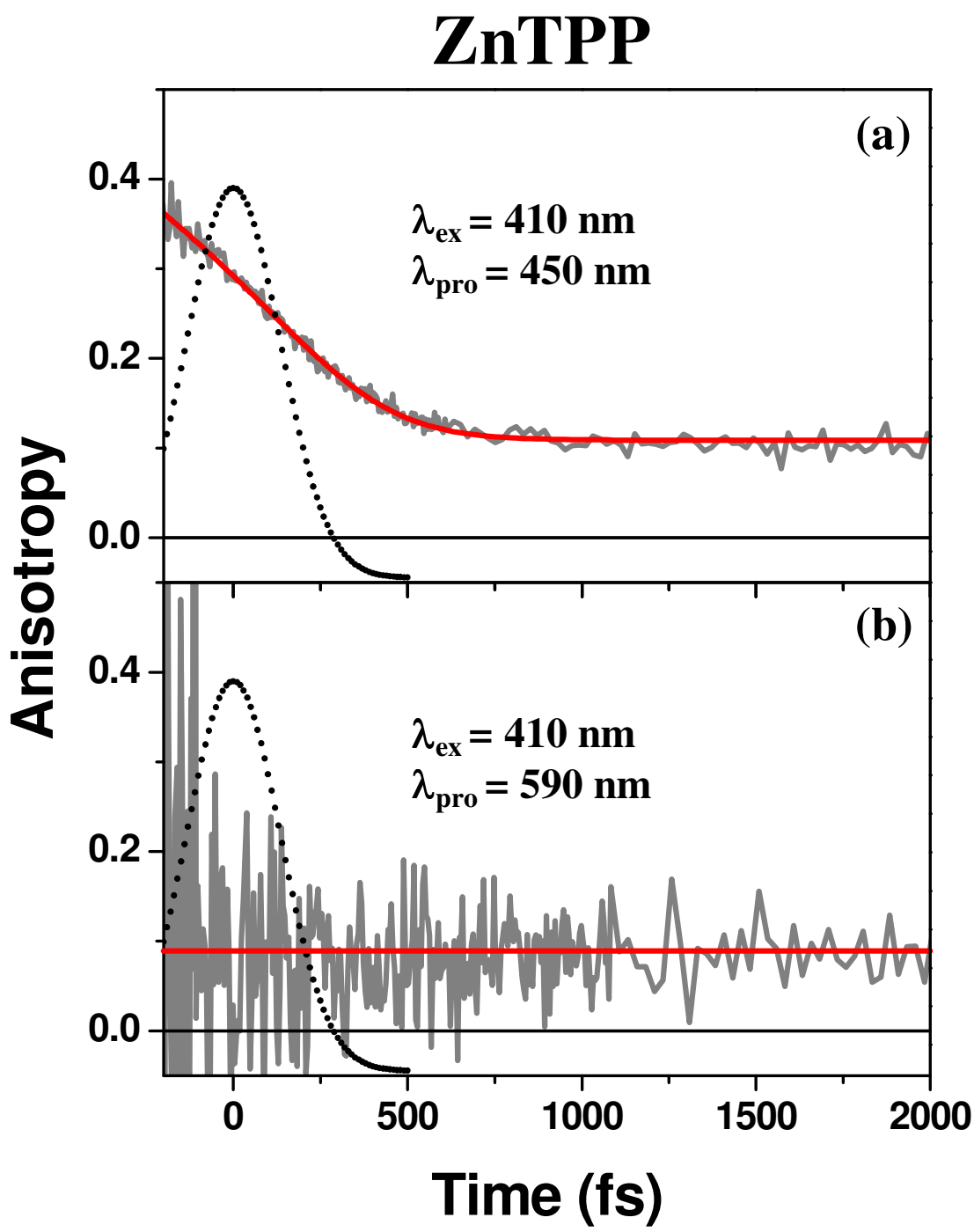

Figure S2. Anisotropy decay profiles of B (a) and Q state fluorescence (b) of **ZnTPP** in toluene obtained by femtosecond fluorescence up-conversion technique.

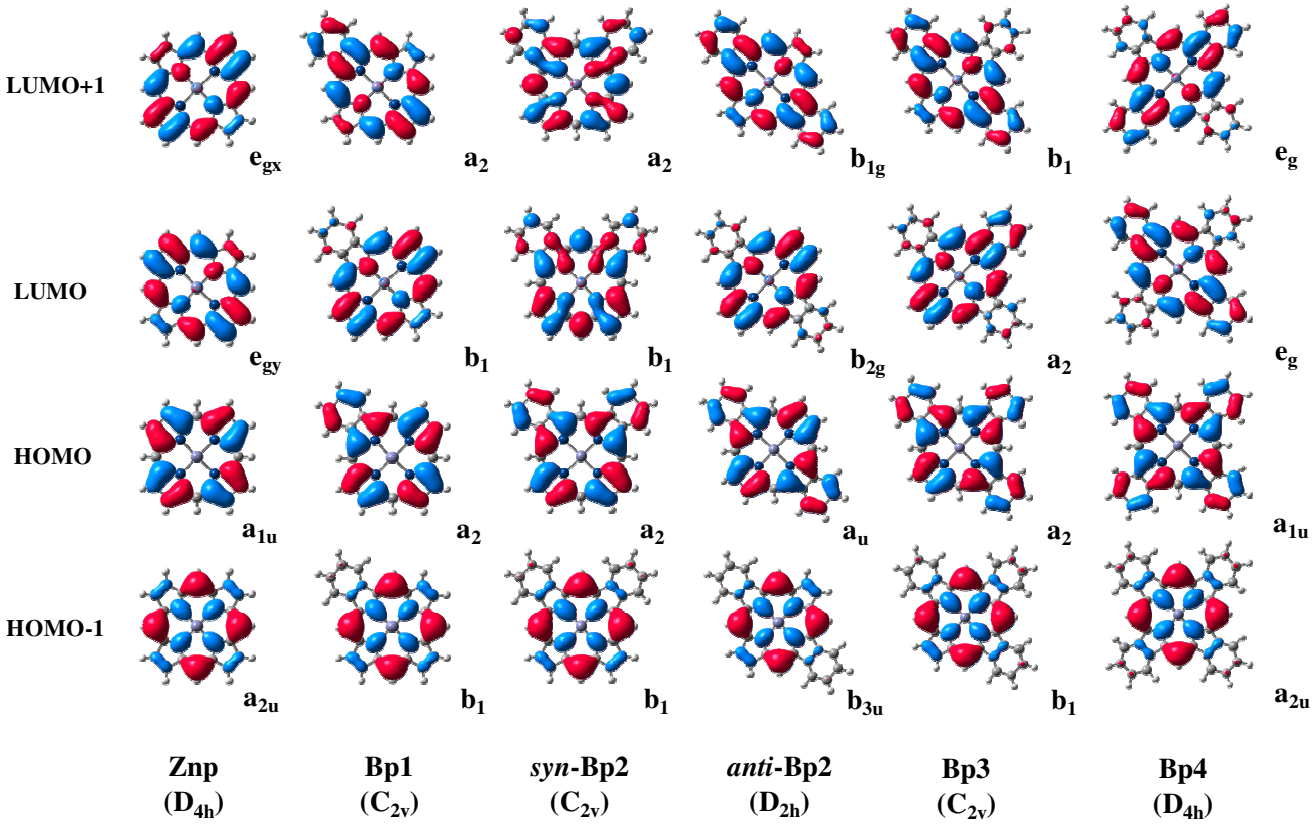

Figure S3. Four frontier MOs of **ZnP** and benzoporphyrins. The LUMO and LUMO+1 of **ZnP** and **Bp4** are degenerate because of D_{4h} sysmmetry.

Table S1. Calculated transition energies, oscillator strength and configuration interaction of B and Q band in **ZnP** and benzoporphyrins.

Samples	Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Polarization[a]	Configuration interaction[b]	
ZnP	19730	506	0.0025	x	H-1->L (39) H-1->L+1 (-12) H->L (13) H->L+1 (39)	Q
	19730	506	0.0025	y	H-1->L (-12) H-1->L+1 (-39) H->L (39) H->L+1 (-13)	Q
	28652	349	0.9028	x	H-1->L (-21) H->L+1 (22) H-1->L+1 (7) H->L (8)	B
	28652	349	0.9028	y	H-1->L+1 (21), H->L (22) H-1->L (7) H->L+1 (-8)	B
Bp1	19163	521	0.0266	y	H-1->L+1 (41) H->L (61)	Q
	19485	513	0.0118	x	H-1->L (-49) H->L+1 (53)	Q
	27667	361	1.2452	x	H-1->L (30) H->L+1 (29) H-7->LUMO (3%)	B
	27799	359	0.6673	y	H-1->L+1 (38) H->L (-18) H-3->LUMO (-7%)	B
***syn*-Bp2**	18865	530	0.0577	x	H-1->L+1 (38), H->L (63)	Q
	18960	527	0.0517	y	H-1->L (-39), H->L+1 (62)	Q
	27094	369	0.9974	x	H-1->L+1 (42), H->L (-18)	B
	27161	368	0.9816	y	H-1->L (42), H->L+1 (19)	B
***anti*-Bp2**	18327	545	0.0645	y	H-1->L+1 (32), H->L (67%)	Q
	19165	521	0.0309	x	H-1->L (-46), H->L+1 (56)	Q
	26849	372	1.621	x	H-1->L (33), H->L+1 (28)	B
	27820	359	0.6359	y	H-1->L+1 (51), H->L (-12)	B
Bp3	18060	553	0.1096	y	H-1->L+1 (30), H->L (69)	Q
	18537	539	0.0992	x	H-1->L (-36), H->L+1 (65)	Q
	26435	378	1.2651	x	H-1->L (45), H->L+1 (17)	B
	27155	368	0.8793	y	H-1->L+1 (53), H->L (-11)	B
Bp4	17620	567	0.1747	x	H-1->L+1 (-28), H->L (70)	Q
	17620	567	0.1746	y	H-1->L (28), H->L+1 (70)	Q
	26526	376	1.1194	x	H-1->L (55), H->L+1 (-10)	B
	26526	376	1.1195	y	H-1->L+1 (55), H->L (10)	B

[a] For **ZnP**, ***syn*-Bp2** and **Bp4** the x and y axes lie along the meso-meso direction.
[b] Percentage contribution of the configuration is given in parenthese. H and L mean HOMO and LUMO, respectively.