Supporting Information

Influence of Diketopyropyrole spacer on the Ultrafast Nonlinear Optical Properties and Excited state dynamics of Dimeric Zinc Porphyrin Molecules

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TRPL decay parameters of the samples measured using TSCPC by exciting with 475 nm. All the experimentally obtained decay times are properly aligned with bi-exponential decay functions fitted by the deconvolution formulae using the IRF:[1]

$$Fit = A + B_1 \exp\left(\frac{-t}{\tau_1}\right) + B_2 \exp\left(\frac{-t}{\tau_2}\right) \quad \textbf{1}$$

The average decay lifetimes were obtained using the following equation:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

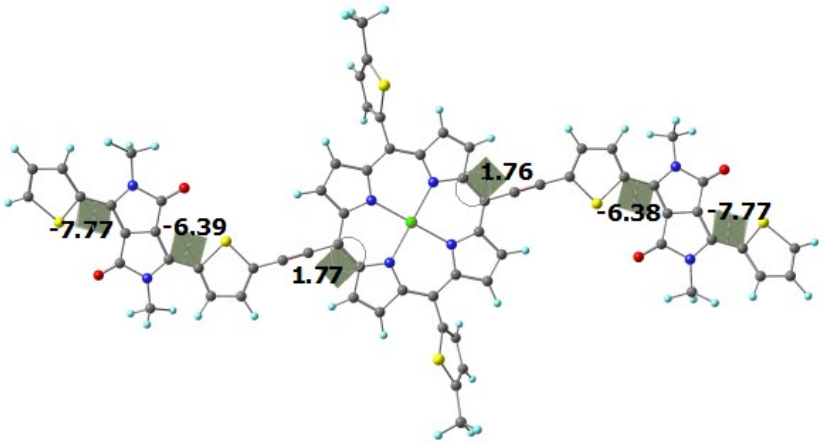
Here τ_{avg} is the average lifetime obtained. τ_1, τ_2 are the PL lifetime components, with A_1 and A_2 being their respective magnitudes.

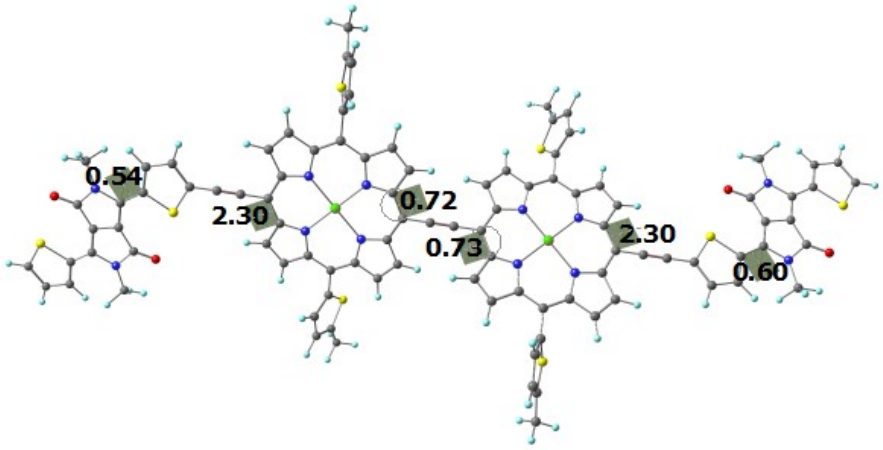
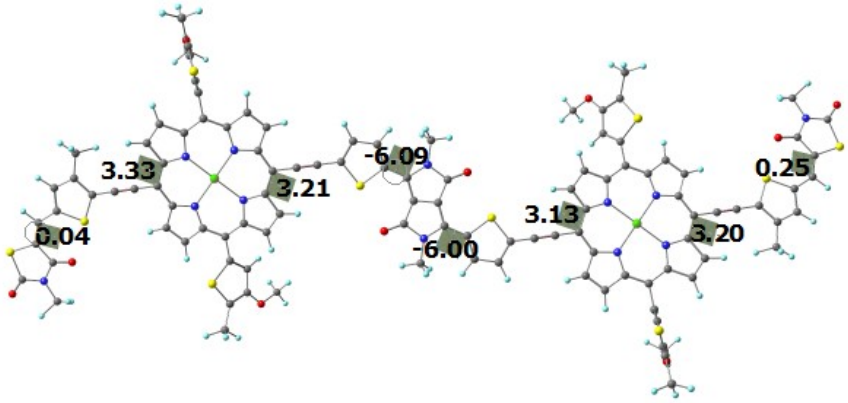
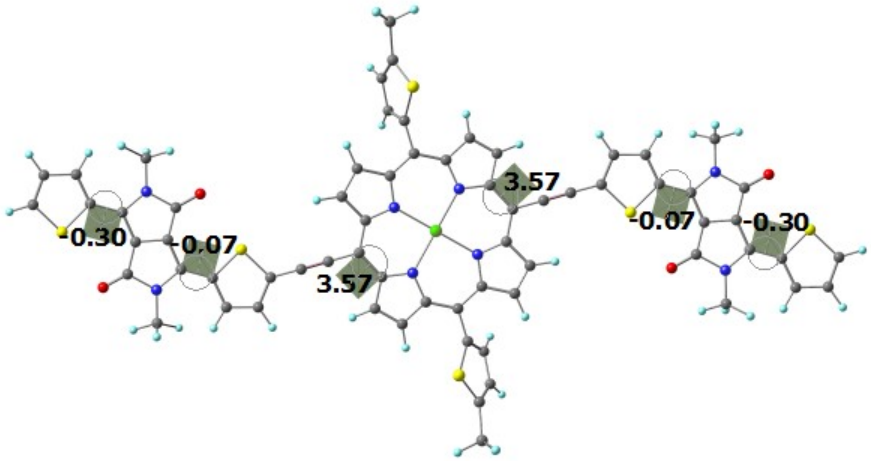
The decay time parameters along with their relative % are tabulated below.

Table S1. TRPL decay parameters of the samples measured using TSCPC by exciting with 475 nm. Respective decay time parameters along with their relative % are tabulated below.

Sample	**τ_1**	**Rel. %**	**τ_2**	**Rel. %**	**τ_{avg}**	**χ^2**
ZnP1	0.32	88%	5.16	12%	0.8787	1.58
ZnP2	0.729	93%	7.71	7%	1.2189	1.17
ZnP3	0.5	91%	4.72	9%	0.89	1.6

Table S2. Optimized Structures of all the molecules at B3LYP/6-31G (D, P) in combination with LANL2DZ along with dipole moment and dihedral angles

	Ground State Structures (S0)	Dipole (Debye)
ZnP1		0.24

ZnP2		0.83
ZnP3		4.30
Molecules	Excited State Structures (S1)	
ZnP1		0.52

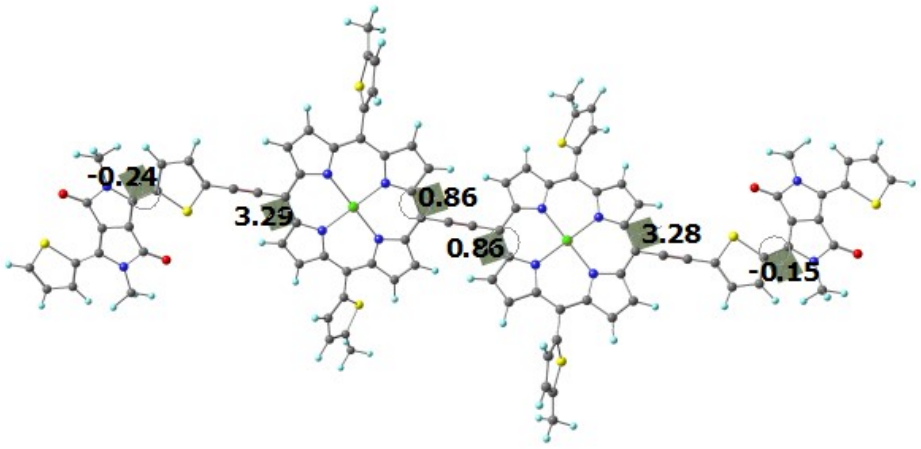
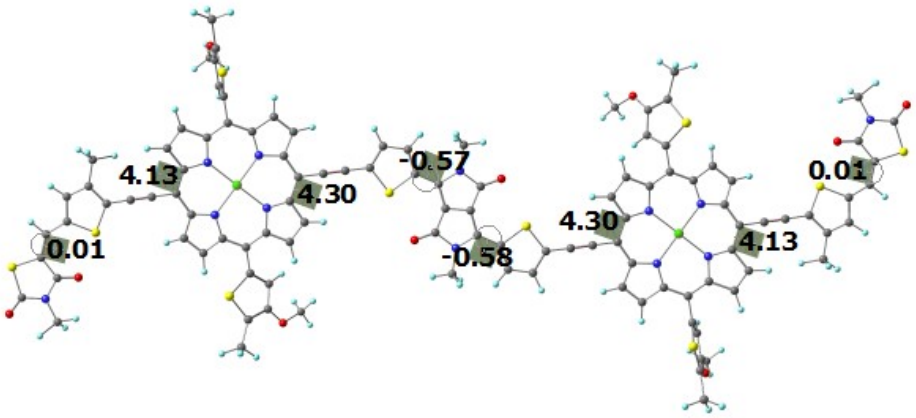
ZnP2		0.90
ZnP3		5.04

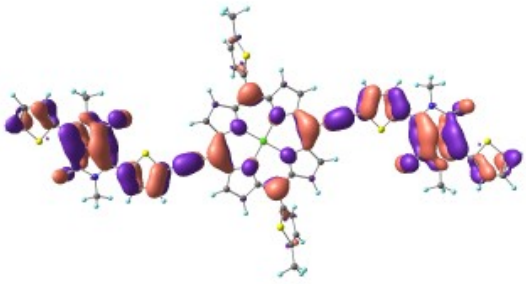
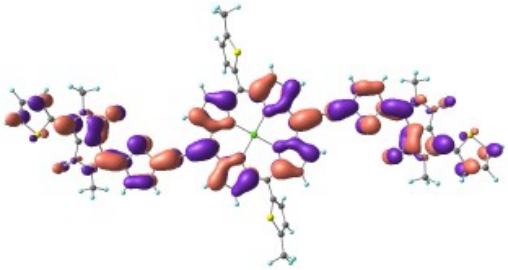
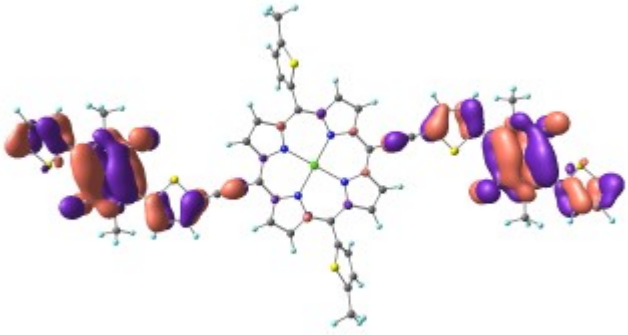
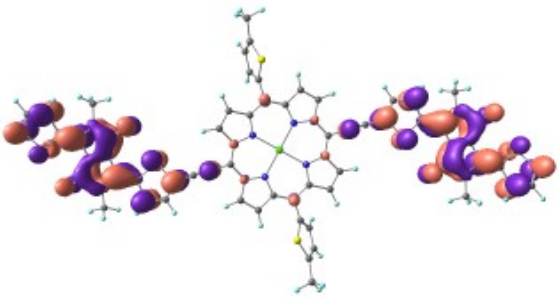
Table S3. Absorption at B3LYP/6-31G (D, P) in combination with LANL2DZ having %Ci > 10

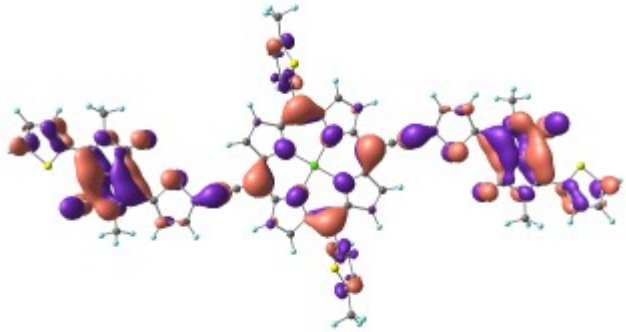
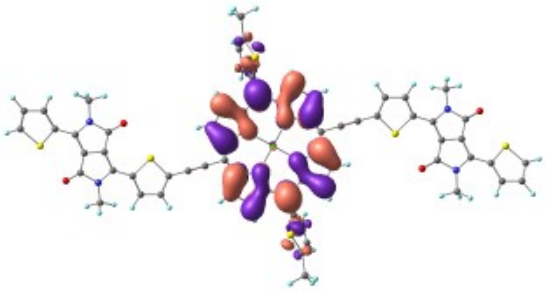
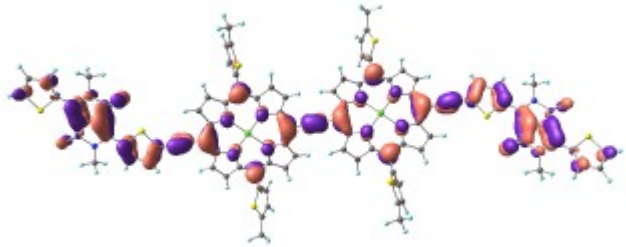
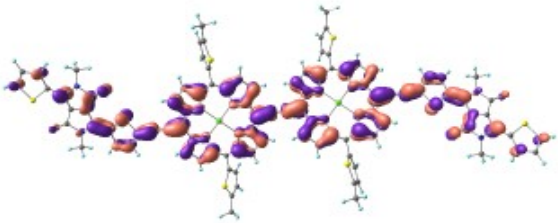
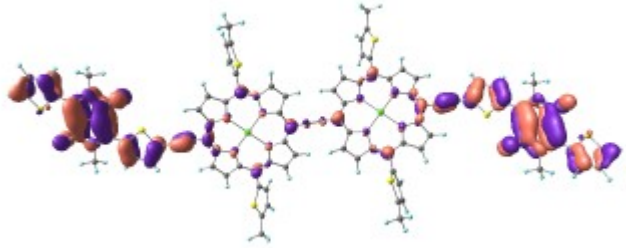
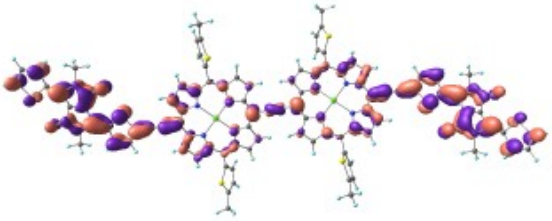
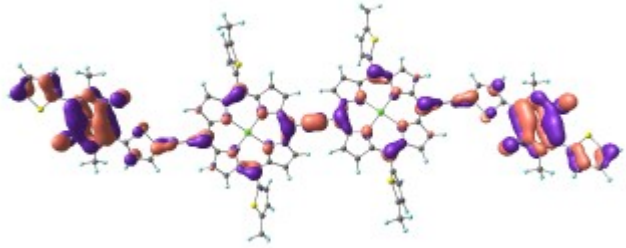
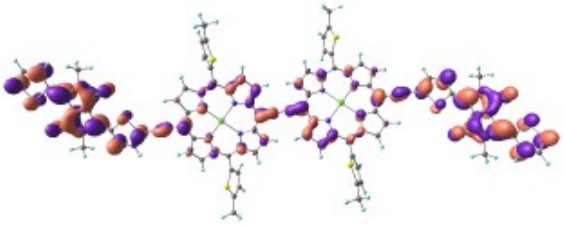
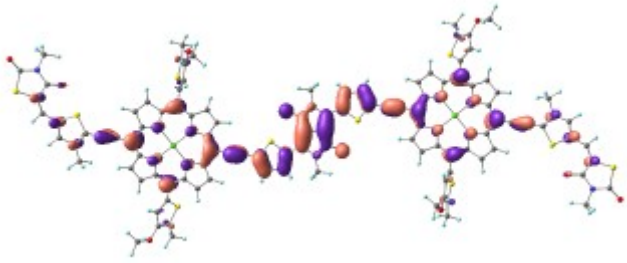
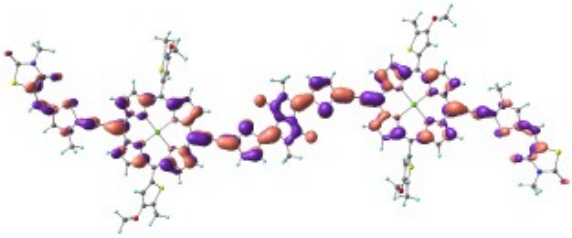
Molecules	States	Absorption nm (eV)	*f*	M.T.	%Ci	λ_{em} (*f*)*
ZnP1	S1	788 (1.57)	2.1599	H → L	98	922 (2.7504)
	S2	686 (1.81)	0.0001	H-1 → L	84	
				H → L+1	14	
	S3	649 (1.91)	0.0085	H-3 → L	32	
				H → L+2	63	
	S4	609 (2.03)	0.0001	H-1 → L	15	
				H → L+1	85	
	S5	605 (2.05)	0.0572	H-2 → L	81	
				H → L+3	11	
ZnP2	S1	834 (1.48)	2.8808	H → L	96	978 (3.5948)
	S2	723 (1.71)	0.0021	H → L+1	15	

	S3	685 (1.81)	0.0180	H-1 → L	15	
				H → L+1	81	
	S4	649 (1.91)	0.0185	H-4 → L	26	
				H → L+3	59	
	S5	648 (1.913)	0.0018	H-5 → L	13	
				H-3 → L	13	
				H → L+4	60	
ZnP3	S1	891 (1.39)	3.4395	H → L	96	1066 (4.0092)
	S2	755 (1.64)	0.0003	H-1 → L	30	
				H → L+1	67	
	S3	721 (1.72)	0.0082	H-1 → L	63	
				H → L+1	29	
	S4	666 (1.86)	0.2342	H-2 → L	41	
				H-1 → L+1	30	
				H → L+2	22	
	S5	656 (1.89)	0.1711	H-2 → L	34	
				H-1 → L+1	59	

* TDDFT derived emission energies (λ_{em} nm) obtained at TD-B3LYP/6-31G (d, p) in combination with LANL2DZ in THF solvent.

Table S4. Frontier Molecular Orbitals of all molecules at B3LYP/6-31G (D, P) in combination with LANL2DZ

Molecules	FMOs	
ZnP1	HOMO 	LUMO 
	HOMO-1 	LUMO+1 

	HOMO-2 	LUMO+2 
ZnP2	HOMO 	LUMO 
	HOMO-1 	LUMO+1 
	HOMO-2 	LUMO+2 
ZnP3	HOMO 	LUMO 

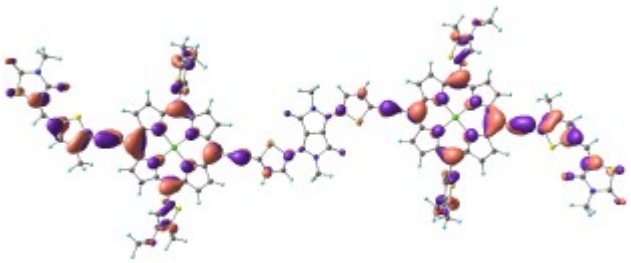
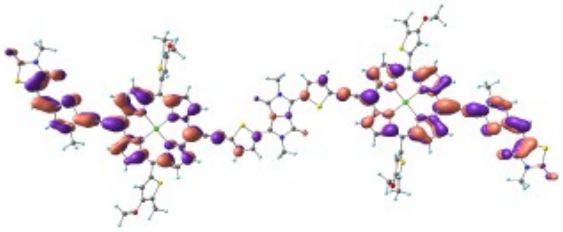
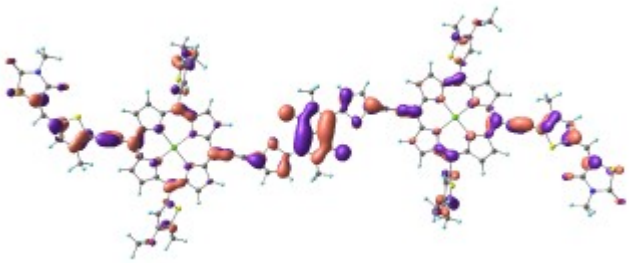
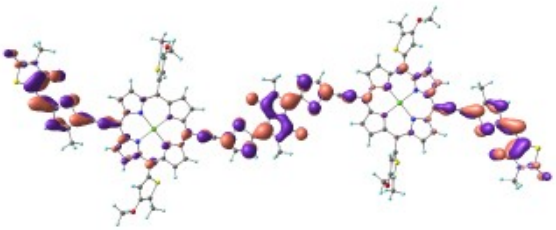
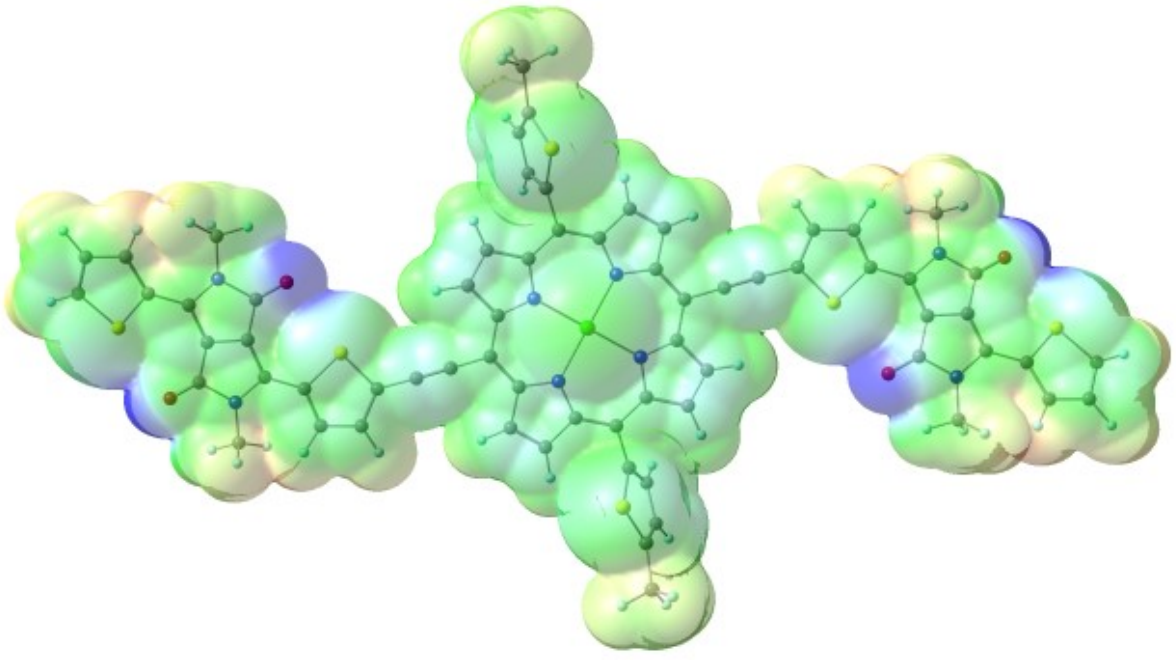
	HOMO-1 	LUMO+1 
	HOMO-2 	LUMO+2 

Table S5. Calculated Molecular Electrostatic Potential (ESP)

Molecules	ESP Spheres
ZnP1	

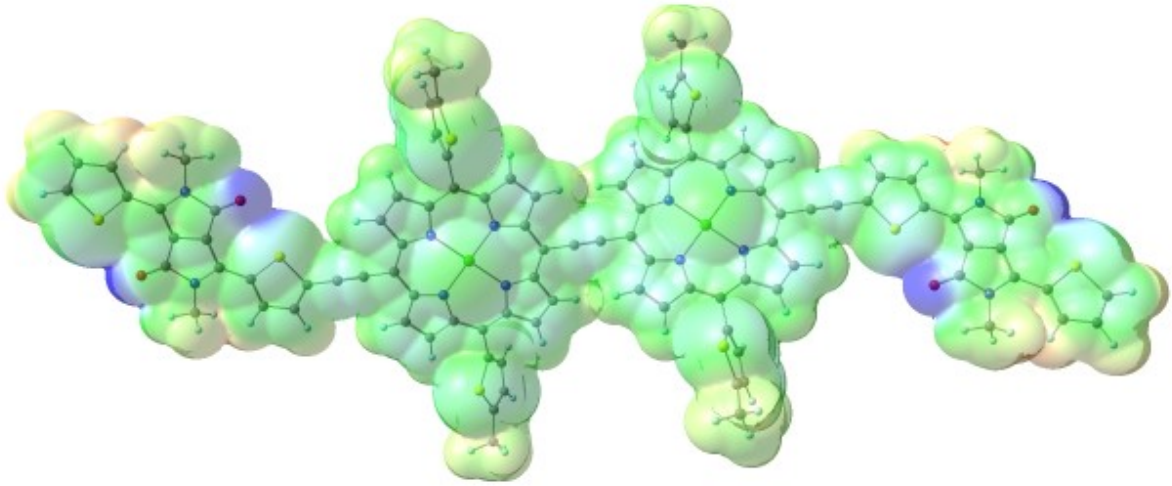
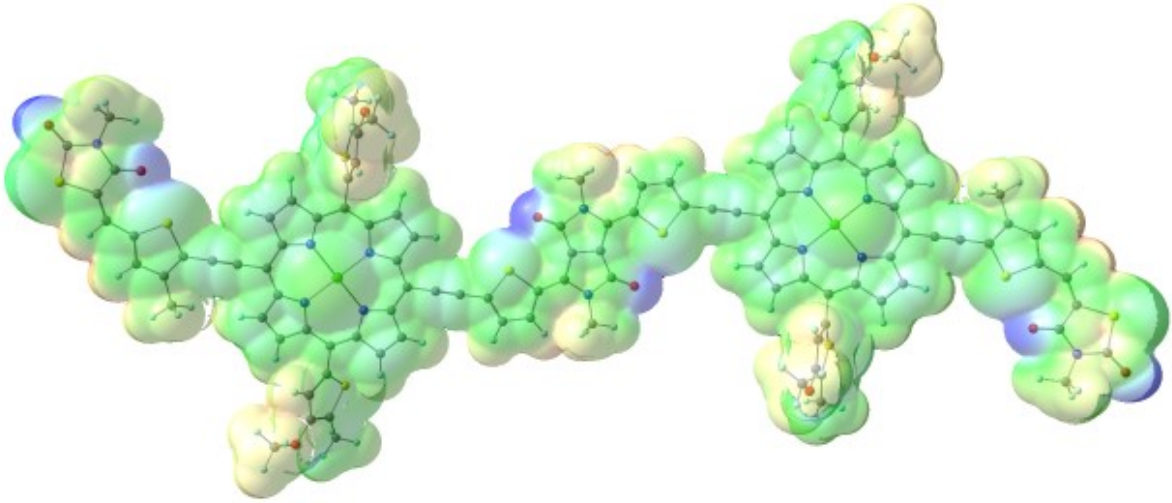
ZnP2	
ZnP3	

Table S6. Saturation intensities of the sample at various peak intensities

Sample	**I_s (GW/cm^2)**				
	I_1= 45 GW/cm^2	I_2= 90 GW/cm^2	I_3= 145 GW/cm^2	I_4= 190 GW/cm^2	I_5= 225 GW/cm^2
ZnP1	8.5	53.3	112.4	163.8	205.4
ZnP2	6.4	52.6	105.1	158.2	198.2
ZnP3	16.4	82.1	116.5	180.1	217.2

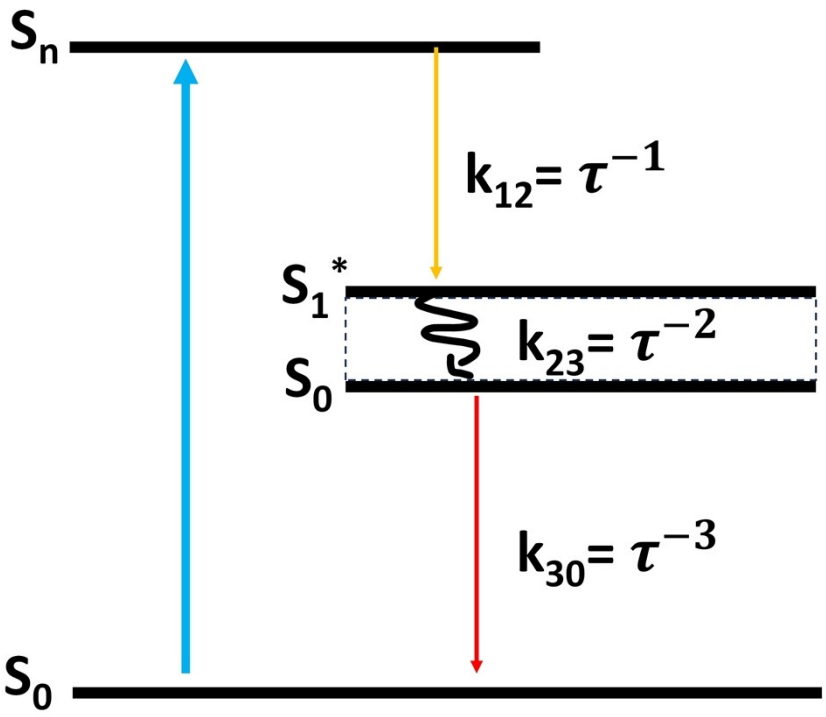


Fig. S1 Schematic of three level photophysical model used in global analysis of TAS data.

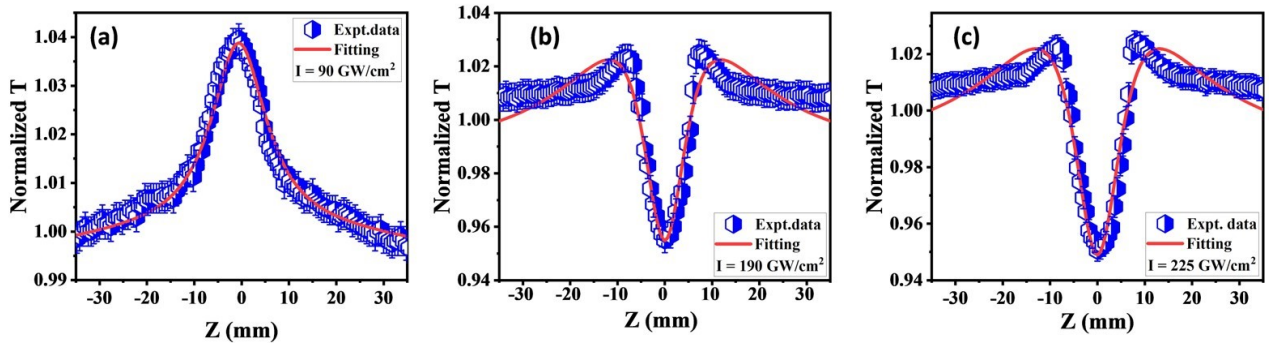


Fig. S2: Open aperture (OA) Z-scan figures of ZnP1 at : (a) 90 GW/cm^2; (b) 190 GW/cm^2; (c) 225 GW/cm^2. Scattered points represent experimental data whereas red solid line denotes their respective fits.

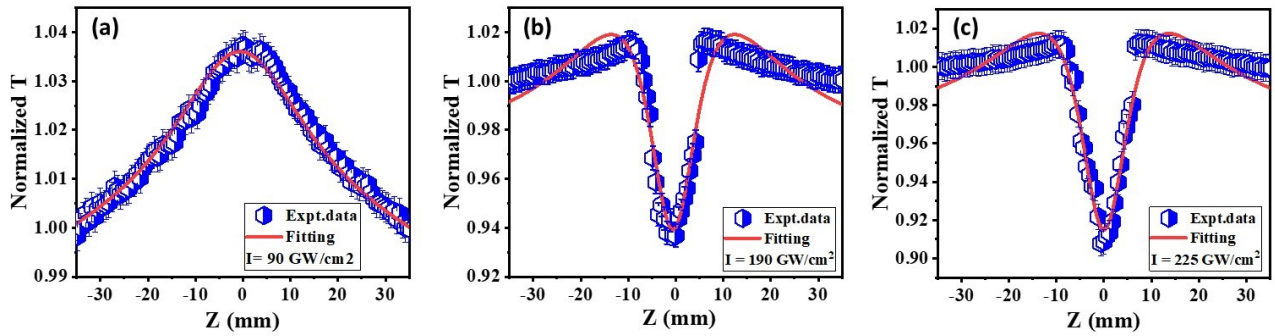


Fig S3: Open aperture (OA) Z-scan figures of ZnP2 at : (a) 90 GW/cm^2; (b) 190 GW/cm^2; (c) 225 GW/cm^2. Scattered points represent experimental data whereas red solid line denotes their respective fits.

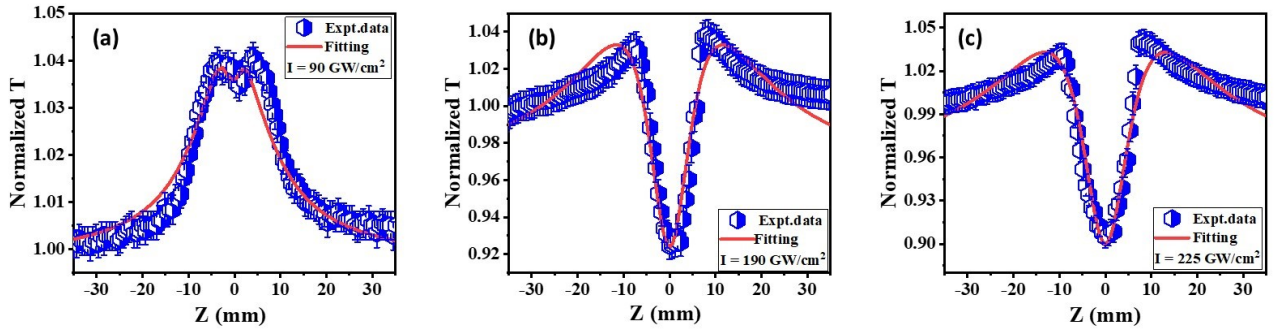


Fig. S4: Open aperture (OA) Z-scan figures of ZnP3 at : (a) 90 GW/cm^2; (b) 190 GW/cm^2; (c) 225 GW/cm^2. Scattered points represent experimental data whereas red solid line denotes their respective fits.

Thermogravimetric Analysis (TGA)

ZnP2 is thermally stable with less than 5% weight loss at 408^0C under a nitrogen atmosphere. Further to confirm any laser induced degradation we have cross measured the UV-Visible absorption of all the molecules before Z-scan measurements and after measurements. The TGA of ZnP3, showed less than 5% weight loss at 304^0C under a nitrogen atmosphere, indicating that the porphyrin is thermally stable for the OSCs.

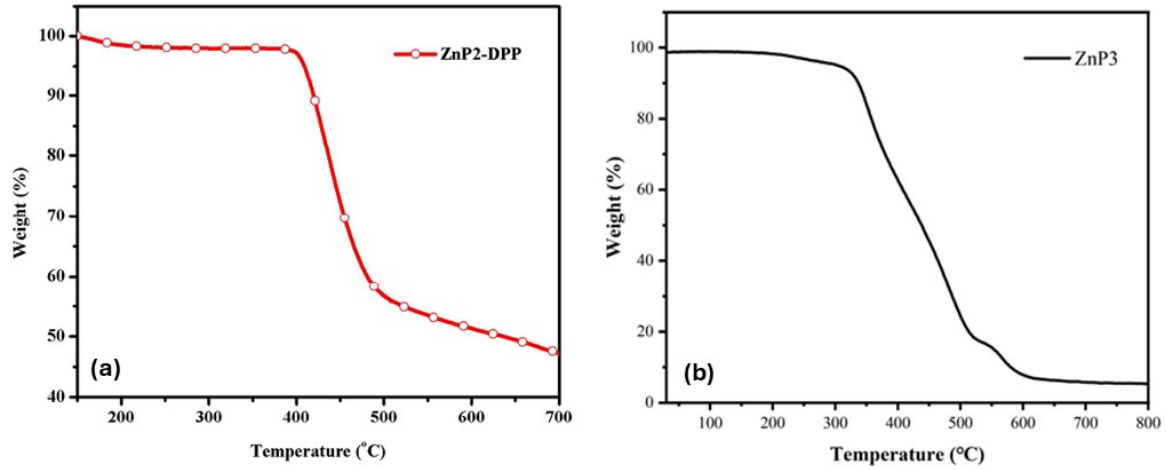


Fig **S5** : TGA thermogram of ZnP2-DPP (ZnP2) and HDDPP-EHTOM (ZnP3)-under inert atmosphere

References:

1. Ahmed, M.S., et al., *Metalated porphyrin-napthalimide based donor-acceptor systems with long-lived triplet states and effective three-photon absorption.* Journal of Photochemistry and Photobiology A: Chemistry, 2023. **435**: p. 114324.