Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Excited-State Absorption in Tetrapyridyl Porphyrins: Comparing Real-Time and Quadratic-Response Time-Dependent Density Functional Theory

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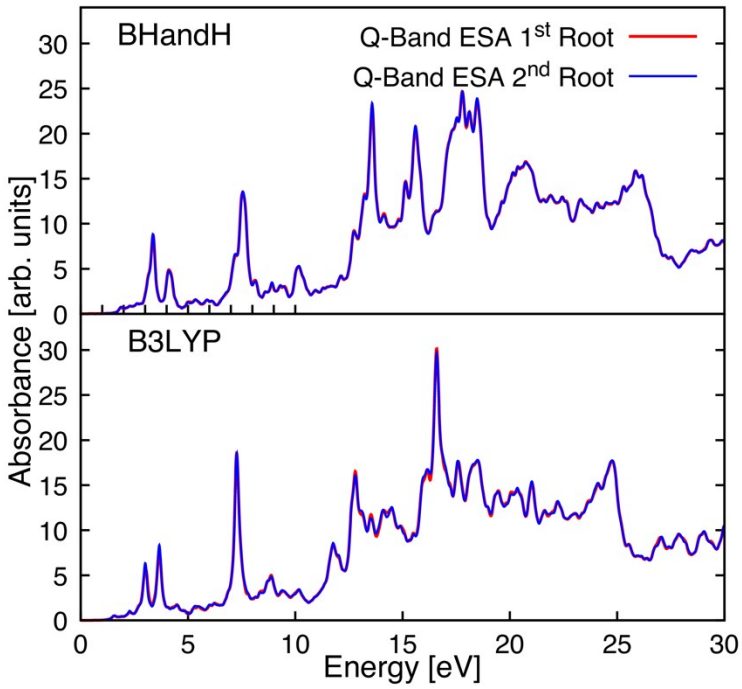

Figure S1. Calculated RT-TDDFT excited-state electronic absorption spectrum for freebase TPyP, for the first and second roots of LR-TDDFT at the BHandH/cc-pVDZ and B3LYP/cc-pVDZ levels of theory.

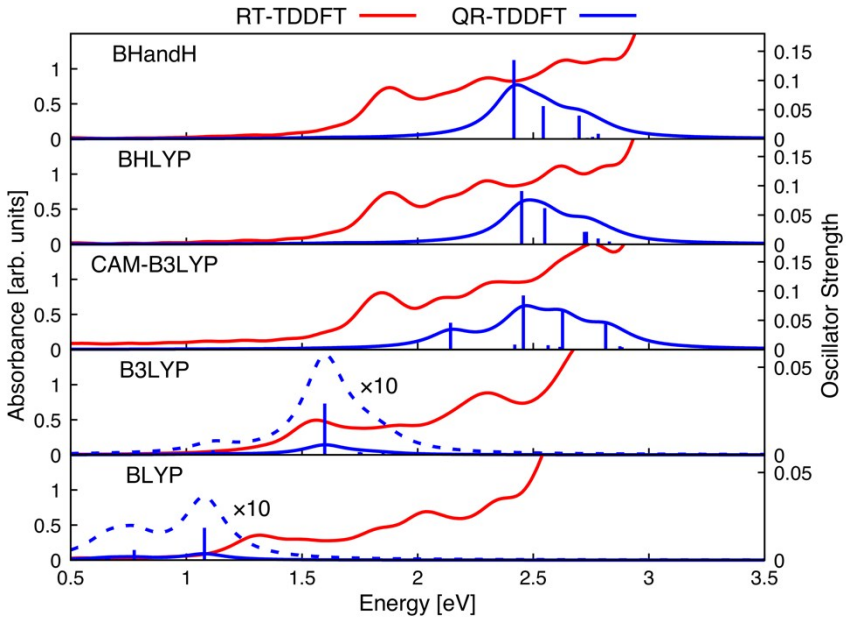

Figure S2. Excited-state absorbance spectra from the lowest energy Q band excitation of free base TPyP using RT-TDDFT with an excited-state density obtained from LR-TDDFT, and the analogous lowest energy portion of the excitation spectrum calculated with QR-TDDFT. All calculations utilized the 6-31G* basis. The simulated QR-TDDFT spectra were generated from the calculated discrete $S_1 \rightarrow S_n$ excitations using a Lorentzian broadening with a full-width-at-half-maximum of 0.22 eV.

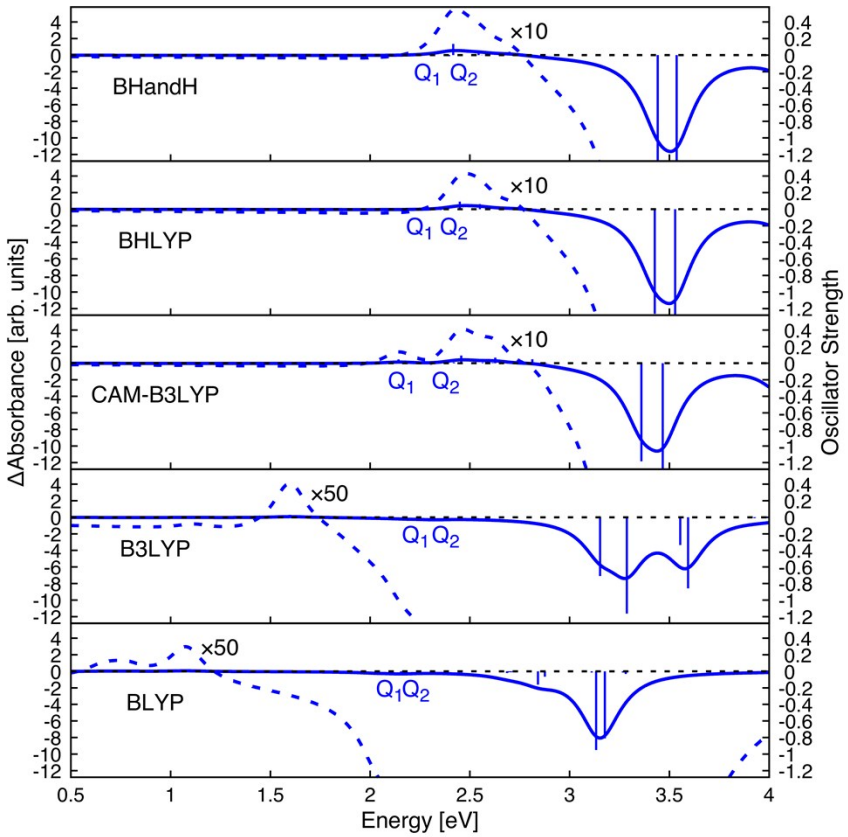

Figure S3. Differential molar absorptivity (excited-state – ground-state) for the lowest energy Q band excitations of free base TPyP calculated with LR-TDDFT (S_0 absorption) and QR-TDDFT (S_1 absorption) with 6-31G* basis set. Broadened spectra were produced from discrete spectra by using a Lorentzian broadening with a full-width-at-half-maximum of 0.22 eV.

Table S1. Summary of prominent QR-TDDFT excitations for free base TPyP at BHandH/cc-pVDZ level of theory. For a given excitation, $<S_A|\mu|S_B>$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation (f_{osc} > 0.01), and the major orbital contributions (coefficient^2 > 0.01) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	9	2.408	0.111	S_A:	**HOMO-1 → LUMO**	**(-0.66)**
					HOMO → LUMO+1	**(0.75)**
				S_B:	HOMO-15 → LUMO	(-0.10)
					HOMO-8 → LUMO	(-0.17)
					HOMO-2 → LUMO+1	(-0.16)
					HOMO → LUMO+2	**(-0.94)**
1	10	2.536	0.059	S_B:	HOMO-15 → LUMO+1	(0.11)
					HOMO-8 → LUMO+1	(0.11)
					HOMO-2 → LUMO	(-0.12)
					HOMO-1 → LUMO+2	**(0.93)**
					HOMO-1 → LUMO+6	(0.16)
					HOMO → LUMO+11	(0.14)
1	12	2.673	0.028	S_B:	HOMO-21 → LUMO+1	(0.12)
					HOMO-15 → LUMO	**(0.35)**
					HOMO-14 → LUMO	**(0.33)**
					HOMO-13 → LUMO	(0.13)
					HOMO-13 → LUMO+1	(-0.15)
					HOMO-11 → LUMO	(0.16)
					HOMO-8 → LUMO	**(-0.29)**
					HOMO-6 → LUMO	**(0.27)**
					HOMO-6 → LUMO+2	(0.10)
					HOMO-5 → LUMO+1	**(-0.38)**
					HOMO-4 → LUMO	**(-0.54)**
1	13	2.682	0.015	S_B:	HOMO-15 → LUMO	(0.17)
					HOMO-14 → LUMO	**(0.63)**
					HOMO-13 → LUMO	(0.15)
					HOMO-13 → LUMO+1	(0.10)
					HOMO-11 → LUMO	(0.15)
					HOMO-9 → LUMO	(0.11)
					HOMO-8 → LUMO	(0.18)
					HOMO-6 → LUMO	**(0.37)**
					HOMO-5 → LUMO+1	**(0.29)**
					HOMO-4 → LUMO	**(0.39)**

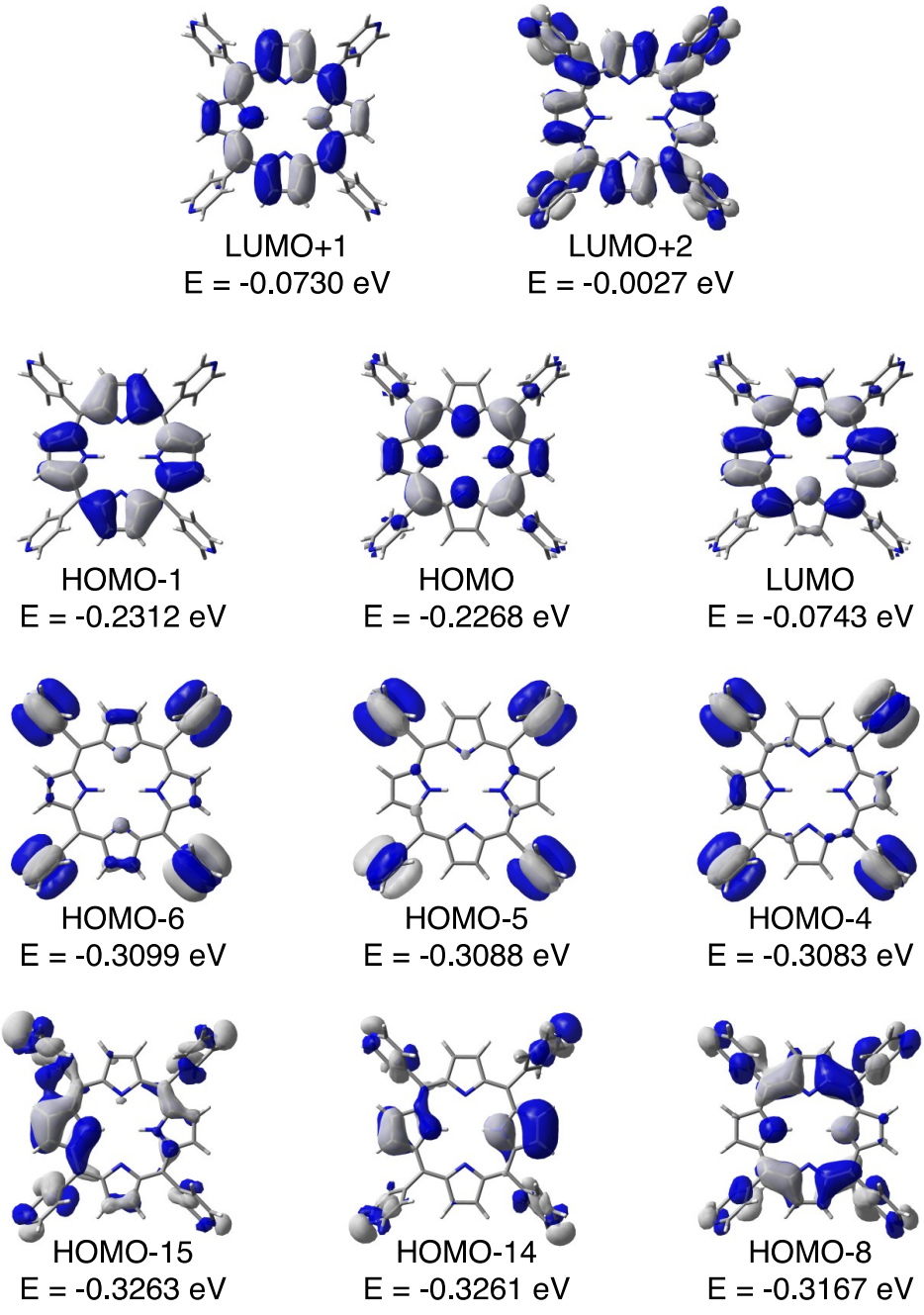

Figure S4. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S1, for free base TPyP at BHandH/cc-pVDZ level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

Table S2. Summary of prominent QR-TDDFT excitations for free base TPyP at BHLYP/cc-pVDZ level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.01$), and the major orbital contributions (coefficient$^2 > 0.01$) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	9	2.440	0.096	S_A:	**HOMO-1 → LUMO**	**(-0.67)**
					HOMO → LUMO+1	**(0.74)**
				S_B:	HOMO-10 → LUMO	(-0.10)
					HOMO-8 → LUMO	(-0.15)
					HOMO-2 → LUMO+1	(-0.16)
					HOMO → LUMO+2	**(-0.95)**
1	10	2.544	0.062	S_B:	HOMO-10 → LUMO+1	(-0.11)
					HOMO-8 → LUMO+1	(-0.10)
					HOMO-2 → LUMO	(0.13)
					HOMO-1 → LUMO+2	**(-0.93)**
					HOMO-1 → LUMO+6	(-0.17)
					HOMO → LUMO+11	(-0.14)
1	12	2.707	0.040	S_B:	HOMO-21 → LUMO+1	(-0.16)
					HOMO-15 → LUMO	(0.12)
					HOMO-11 → LUMO	(-0.16)
					HOMO-10 → LUMO	**(-0.24)**
					HOMO-9 → LUMO+1	**(-0.23)**
					HOMO-8 → LUMO	**(0.33)**
					HOMO-6 → LUMO+2	(-0.12)
					HOMO-5 → LUMO+1	**(0.45)**
					HOMO-4 → LUMO	**(0.65)**
1	14	2.761	0.011	S_B:	HOMO-21 → LUMO	(0.13)
					HOMO-20 → LUMO+1	(-0.10)
					HOMO-18 → LUMO+1	(-0.12)
					HOMO-16 → LUMO+2	(-0.11)
					HOMO-9 → LUMO	**(0.37)**
					HOMO-8 → LUMO+1	**(0.71)**
					HOMO-5 → LUMO	**(-0.43)**
					HOMO-4 → LUMO+1	**(0.24)**

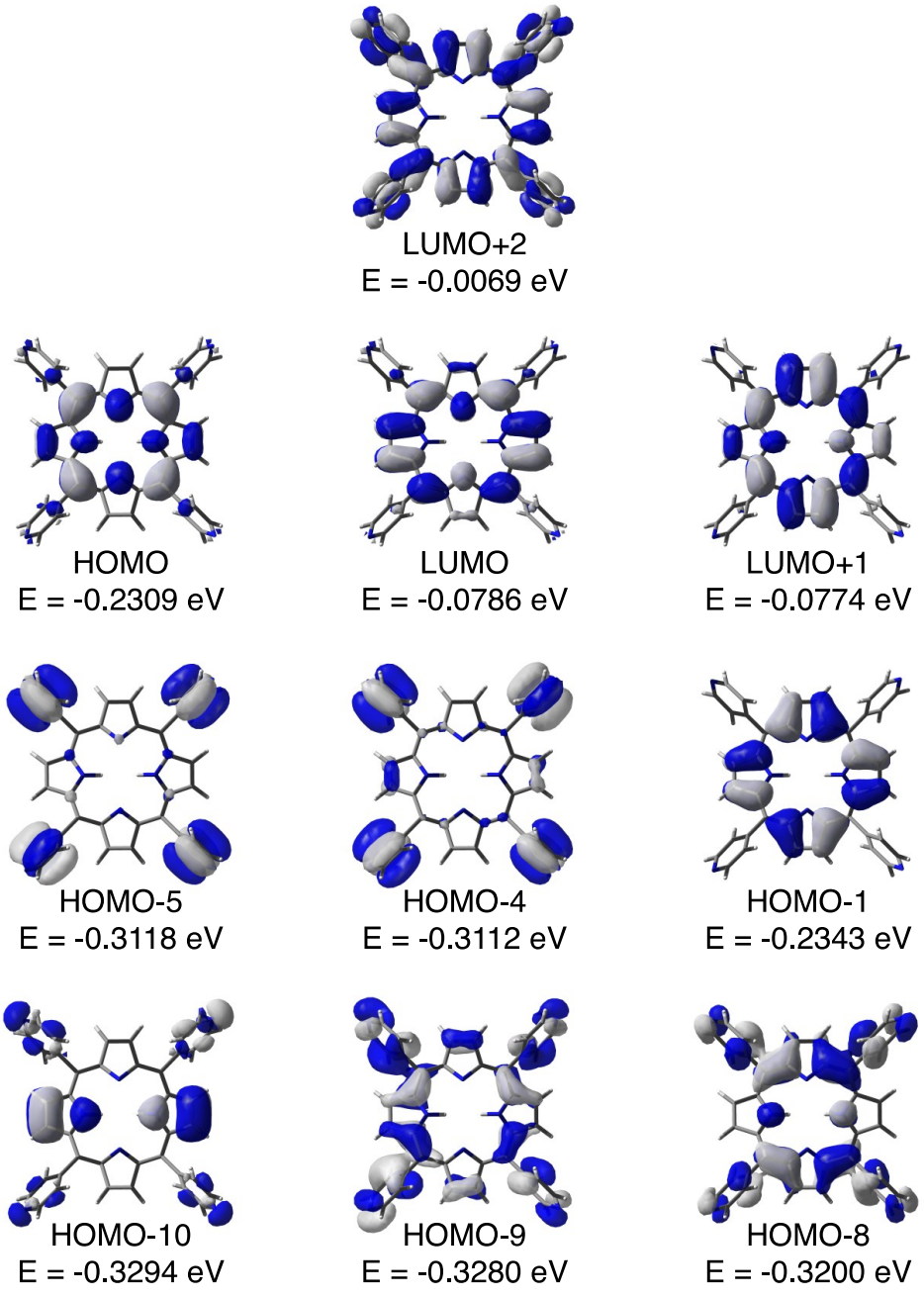

Figure S5. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S2, for free base TPyP at BHLYP/cc-pVDZ level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

Table S3. Summary of prominent QR-TDDFT excitations for free base TPyP at CAM-B3LYP/cc-pVDZ level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation (f_{osc} > 0.01), and the major orbital contributions (coefficient^2 > 0.01) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	7	2.140	0.030	S_A:	**HOMO-1 → LUMO**	**(-0.65)**
					HOMO → LUMO+1	**(0.76)**
				S_B:	**HOMO-2 → LUMO**	**(0.97)**
					HOMO-1 → LUMO+2	(-0.14)
1	9	2.427	0.033	S_B:	HOMO-19 → LUMO+1	(0.12)
					HOMO-18 → LUMO+1	**(-0.61)**
					HOMO-17 → LUMO+1	**(-0.29)**
					HOMO-17 → LUMO+2	(0.15)
					HOMO-16 → LUMO+1	**(0.34)**
					HOMO-14 → LUMO+1	(-0.19)
					HOMO-12 → LUMO	(-0.18)
					HOMO → LUMO+2	**(0.50)**
1	11	2.451	0.076	S_B:	**HOMO-18 → LUMO+1**	**(-0.41)**
					HOMO-17 → LUMO+1	**(-0.24)**
					HOMO-17 → LUMO+2	(0.11)
					HOMO-16 → LUMO+1	**(0.23)**
					HOMO-15 → LUMO	(-0.14)
					HOMO-14 → LUMO	(0.13)
					HOMO-14 → LUMO+1	(-0.11)
					HOMO-13 → LUMO	(-0.11)
					HOMO-12 → LUMO	**(0.29)**
					HOMO-2 → LUMO+1	(0.14)
					HOMO → LUMO+2	**(-0.70)**
1	13	2.616	0.032	S_B:	**HOMO-18 → LUMO**	**(0.37)**
					HOMO-17 → LUMO	**(0.53)**
					HOMO-16 → LUMO	(-0.17)
					HOMO-13 → LUMO	(0.14)
					HOMO-12 → LUMO	(-0.17)
					HOMO-12 → LUMO+1	(-0.12)
					HOMO-1 → LUMO+2	**(0.60)**
					HOMO-1 → LUMO+6	(-0.14)
					HOMO → LUMO+11	(0.10)

(Table S3. Continued)

1	14	2.618	0.018	S_B:	**HOMO-18 → LUMO**	**(0.23)**
					HOMO-17 → LUMO	**(-0.74)**
					HOMO-16 → LUMO	**(-0.20)**
					HOMO-15 → LUMO	(-0.15)
					HOMO-14 → LUMO	(0.11)
					HOMO-12 → LUMO	(0.18)
					HOMO-12 → LUMO+1	(-0.10)
					HOMO-1 → LUMO+2	**(0.43)**
1	16	2.623	0.024	S_B:	**HOMO-15 → LUMO**	**(-0.65)**
					HOMO-15 → LUMO+2	(-0.11)
					HOMO-14 → LUMO	**(-0.52)**
					HOMO-14 → LUMO+2	(0.11)
					HOMO-13 → LUMO	(0.19)
					HOMO-10 → LUMO	**(-0.29)**
					HOMO-6 → LUMO	**(-0.20)**
					HOMO-3 → LUMO	**(-0.20)**
1	17	2.796	0.041	S_B:	HOMO-21 → LUMO+1	(0.18)
					HOMO-20 → LUMO	(-0.13)
					HOMO-15 → LUMO	**(-0.22)**
					HOMO-14 → LUMO	(0.12)
					HOMO-14 → LUMO+1	(0.11)
					HOMO-13 → LUMO	(-0.11)
					HOMO-13 → LUMO+1	(0.17)
					HOMO-12 → LUMO	**(-0.29)**
					HOMO-7 → LUMO+3	(0.14)
					HOMO-6 → LUMO+1	(0.12)
					HOMO-6 → LUMO+2	(-0.16)
					HOMO-6 → LUMO+6	(-0.10)
					HOMO-5 → LUMO+1	**(-0.38)**
					HOMO-5 → LUMO+3	(-0.14)
					HOMO-4 → LUMO	**(0.58)**
					HOMO-4 → LUMO+4	(-0.10)

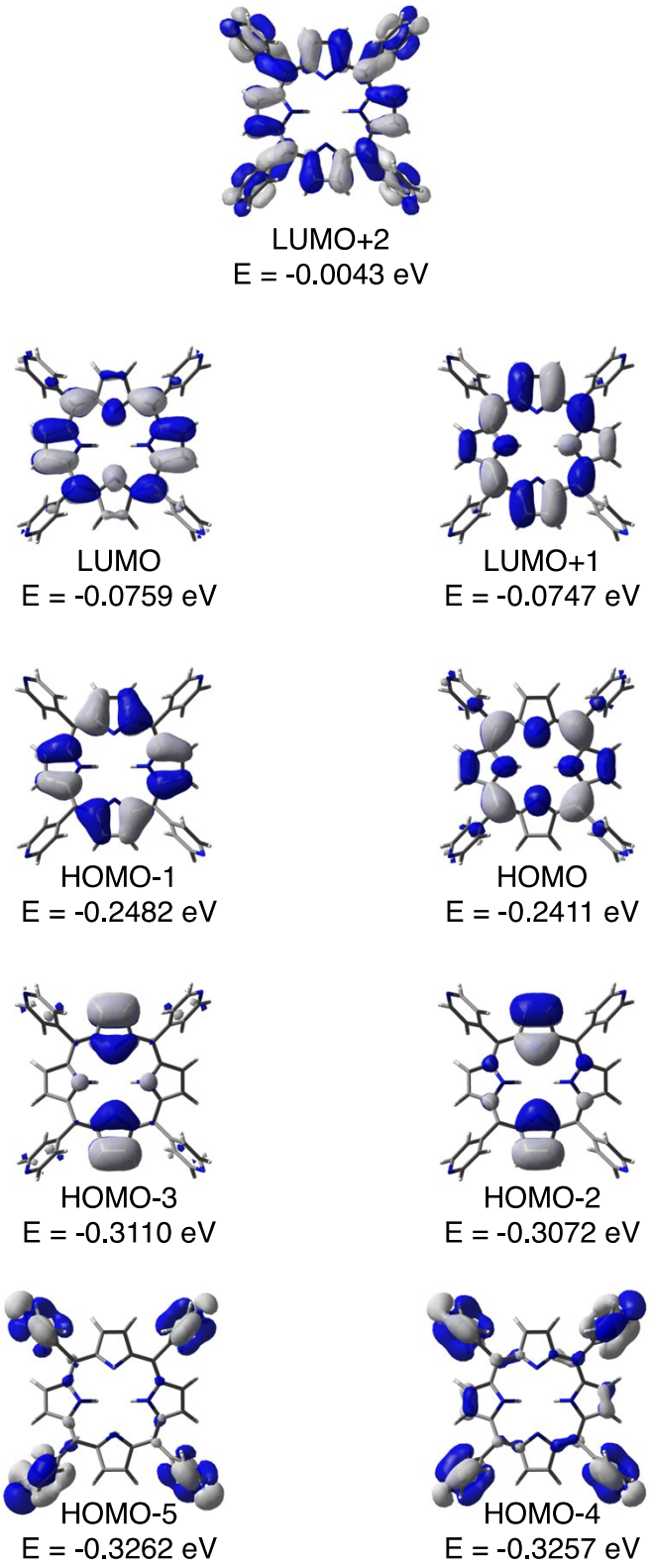

Figure S6. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S3, for free base TPyP at CAM-B3LYP/cc-pVDZ level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$. Additional orbitals shown in Figure S9.

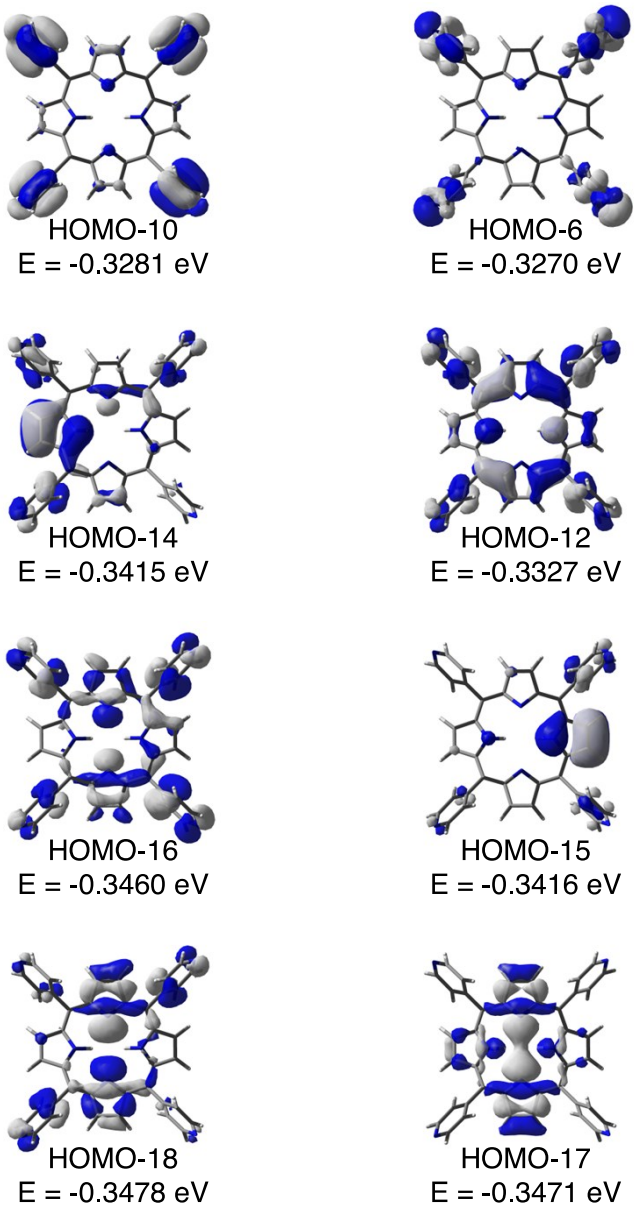

Figure S7. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S3, for free base TPyP at CAM-B3LYP/cc-pVDZ level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$. Additional orbitals shown in Figure S8.

Table S4. Summary of prominent QR-TDDFT excitations for free base TPyP at B3LYP/cc-pVDZ level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.01$), and the major orbital contributions (coefficient$^2 > 0.01$) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	9	1.597	0.030	S_A:	**HOMO-1 → LUMO**	**(0.60)**
					HOMO → LUMO+1	**(-0.80)**
				S_B:	HOMO-12 → LUMO	(0.10)
					HOMO-2 → LUMO+1	(-0.10)
					HOMO → LUMO+2	**(-0.97)**

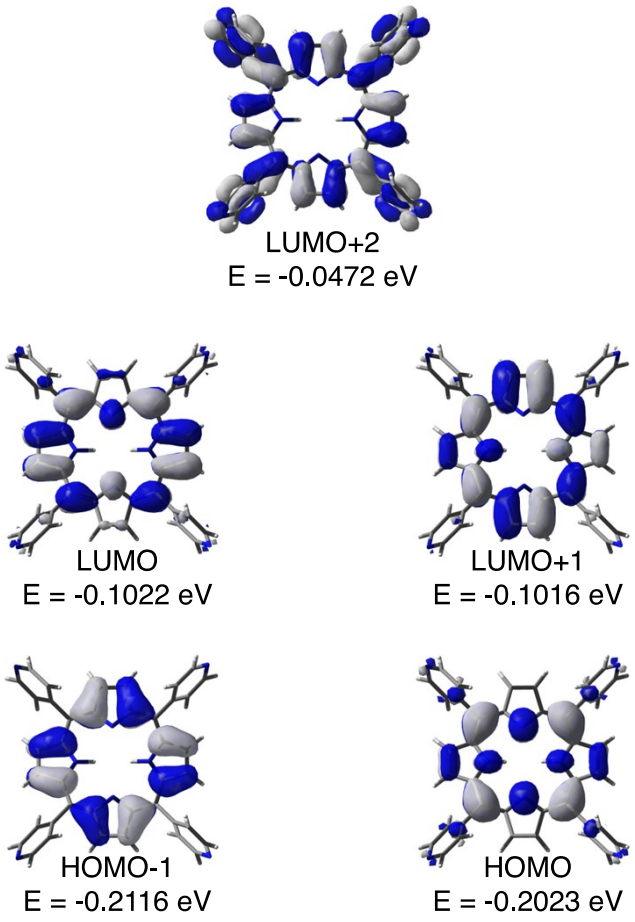

Figure S8. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S4, for free base TPyP at B3LYP/cc-PVDZ level of theory plotted with an isovalue of 0.02 $e^-/Å^3$.

Table S5. Summary of prominent QR-TDDFT excitations for free base TPyP at BLYP/cc-pVDZ level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation (f_{osc} > 0.01), and the major orbital contributions (coefficient^2 > 0.01) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	15	1.082	0.017	S_A:	**HOMO-1 → LUMO**	**(-0.56)**
					HOMO → LUMO+1	**(0.82)**
				S_B:	HOMO-16 → LUMO	(0.13)
					HOMO-13 → LUMO	(-0.18)
					HOMO-7 → LUMO	(0.11)
					HOMO-1 → LUMO+1	(-0.14)
					HOMO → LUMO+2	**(0.92)**
					HOMO → LUMO+6	(0.16)

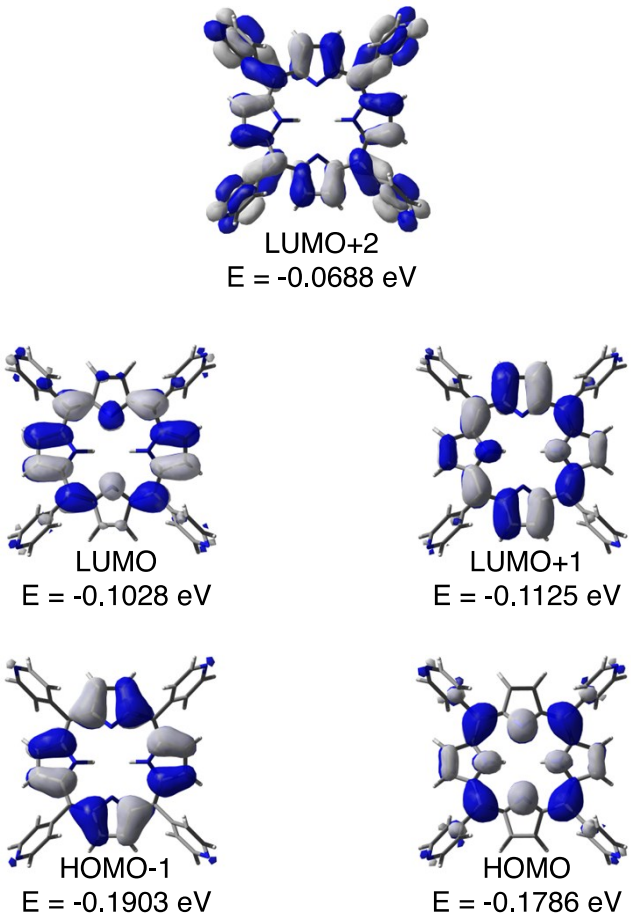

Figure S9. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S5, for free base TPyP at BLYP/cc-pVDZ level of theory plotted with an isovalue of 0.02 $e^-/Å^3$.

Table S6. Summary of prominent QR-TDDFT excitations for free base TPyP at BHandH/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.01$), and the major orbital contributions (coefficient$^2 > 0.01$) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	9	2.416	0.135	S_A:	**HOMO-1 → LUMO**	**(-0.66)**
					HOMO → LUMO+1	**(0.75)**
				S_B:	HOMO-14 → LUMO	(0.10)
					HOMO-8 → LUMO	(0.16)
					HOMO-2 → LUMO+1	(0.15)
					HOMO → LUMO+2	**(-0.95)**
1	10	2.543	0.056	S_B:	HOMO-14 → LUMO+1	(-0.11)
					HOMO-8 → LUMO+1	(-0.10)
					HOMO-2 → LUMO	(0.13)
					HOMO-1 → LUMO+2	**(0.93)**
					HOMO-1 → LUMO+6	(-0.16)
					HOMO → LUMO+11	(-0.14)
1	13	2.698	0.040	S_B:	HOMO-21 → LUMO+1	(-0.16)
					HOMO-20 → LUMO	(0.11)
					HOMO-15 → LUMO+1	(-0.13)
					HOMO-14 → LUMO	**(-0.23)**
					HOMO-13 → LUMO	(-0.15)
					HOMO-13 → LUMO+1	(-0.10)
					HOMO-10 → LUMO+1	(-0.13)
					HOMO-9 → LUMO	(-0.14)
					HOMO-8 → LUMO	**(0.34)**
					HOMO-6 → LUMO	(-0.10)
					HOMO-6 → LUMO+2	(-0.12)
					HOMO-5 → LUMO+1	**(0.45)**
					HOMO-4 → LUMO	**(0.64)**

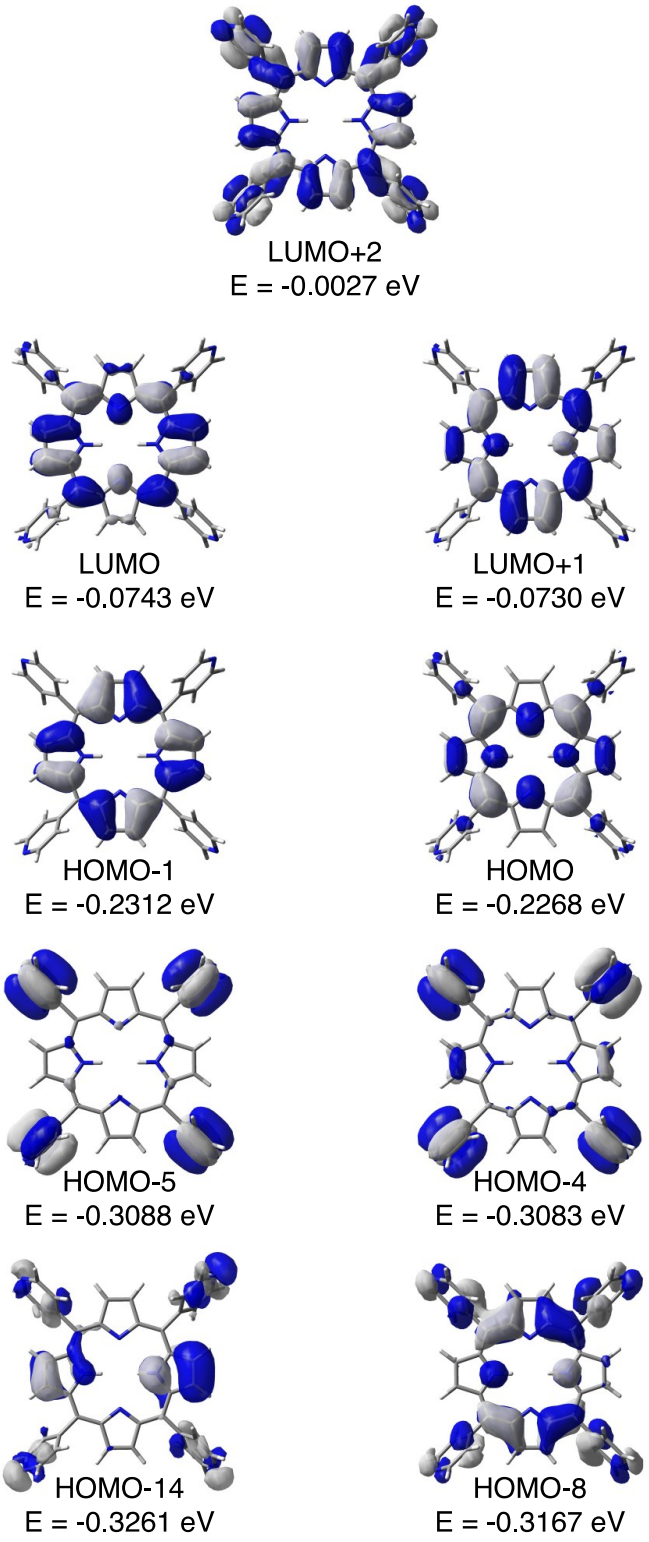

Figure S10. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S6, for free base TPyP at BHandH/6-31G* level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

Table S7. Summary of prominent QR-TDDFT excitations for free base TPyP at BHLYP/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.01$), and the major orbital contributions (coefficient$^2 > 0.01$) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	9	2.450	0.091	S_A:	**HOMO-1 → LUMO**	**(0.67)**
					HOMO → LUMO+1	**(-0.74)**
				S_B:	HOMO-10 → LUMO	(-0.11)
					HOMO-8 → LUMO	(-0.14)
					HOMO-2 → LUMO+1	(-0.15)
					HOMO → LUMO+2	**(0.95)**
1	10	2.550	0.062	S_B:	HOMO-10 → LUMO+1	(-0.12)
					HOMO-2 → LUMO	(0.13)
					HOMO-1 → LUMO+2	**(0.93)**
					HOMO-1 → LUMO+6	(-0.16)
					HOMO → LUMO+11	(-0.14)
1	12	2.721	0.021	S_B:	HOMO-21 → LUMO+1	(0.12)
					HOMO-15 → LUMO	(0.11)
					HOMO-11 → LUMO	**(-0.57)**
					HOMO-10 → LUMO	**(0.22)**
					HOMO-10 → LUMO+2	(-0.11)
					HOMO-9 → LUMO+1	(0.18)
					HOMO-8 → LUMO	**(-0.28)**
					HOMO-6 → LUMO	**(0.28)**
					HOMO-5 → LUMO+1	**(-0.31)**
					HOMO-4 → LUMO	**(-0.48)**
1	13	2.730	0.021	S_B:	HOMO-21 → LUMO+1	(-0.12)
					HOMO-14 → LUMO	(0.11)
					HOMO-12 → LUMO	(-0.10)
					HOMO-11 → LUMO	**(-0.62)**
					HOMO-10 → LUMO	(-0.17)
					HOMO-10 → LUMO+2	(-0.11)
					HOMO-9 → LUMO+1	(-0.17)
					HOMO-8 → LUMO	**(0.24)**
					HOMO-6 → LUMO	**(0.30)**
					HOMO-5 → LUMO+1	**(0.31)**
					HOMO-4 → LUMO	**(0.44)**

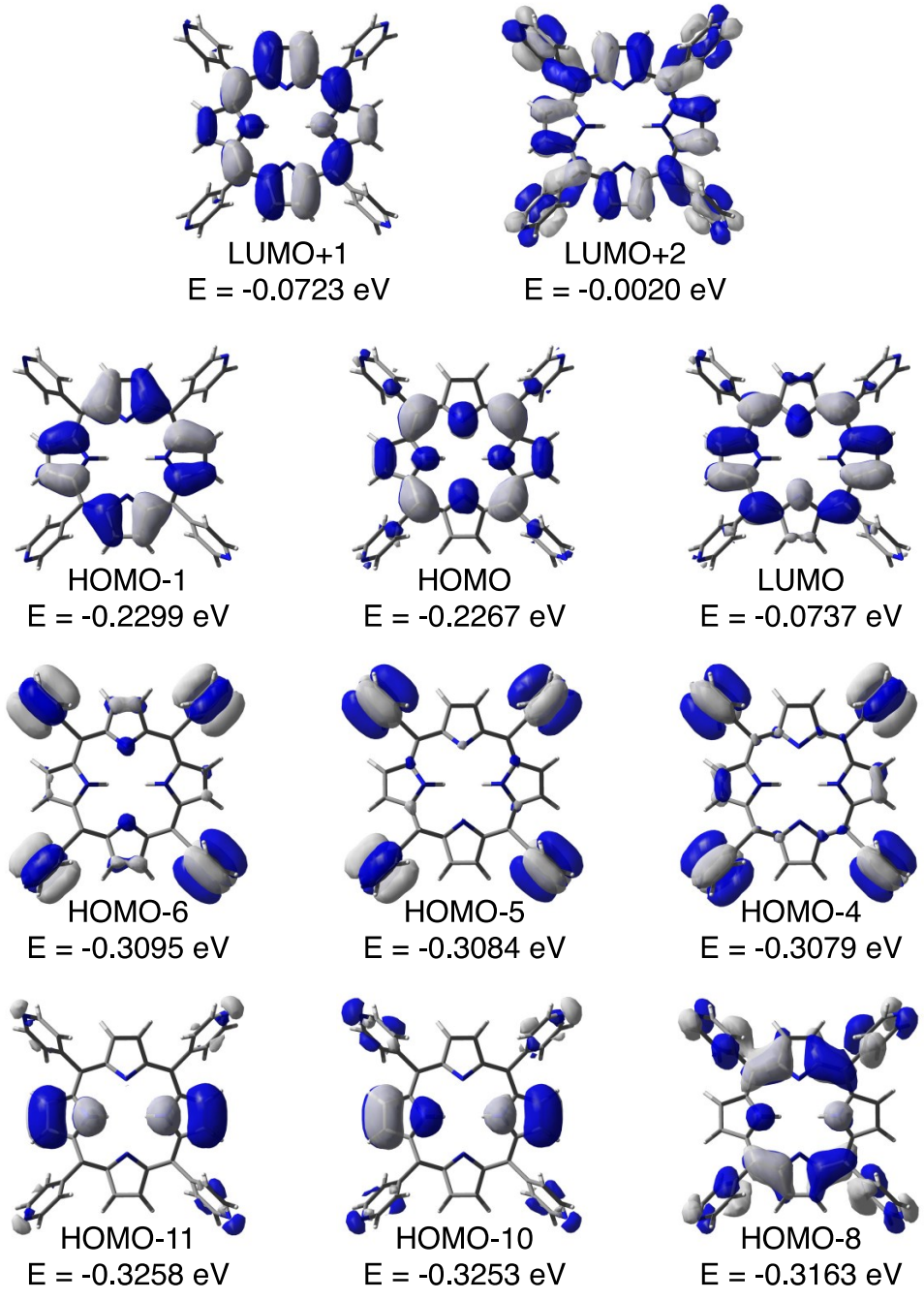

Figure S11. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S7, for free base TPyP at BHLYP/6-31G* level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

Table S8. Summary of prominent QR-TDDFT excitations for free base TPyP at CAM-B3LYP/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.01$), and the major orbital contributions (coefficient$^2 > 0.01$) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	7	2.142	0.046	S_A:	**HOMO-1 → LUMO**	**(0.65)**
					HOMO → LUMO+1	**(-0.76)**
				S_B:	**HOMO-2 → LUMO**	**(0.97)**
					HOMO-1 → LUMO+2	(-0.14)
1	11	2.457	0.092	S_B:	HOMO-18 → LUMO+1	(-0.17)
					HOMO-17 → LUMO+1	(-0.17)
					HOMO-16 → LUMO+1	(-0.17)
					HOMO-14 → LUMO	(0.14)
					HOMO-13 → LUMO	**(0.22)**
					HOMO-12 → LUMO	**(0.36)**
					HOMO-2 → LUMO+1	(0.15)
					HOMO → LUMO+2	**(-0.80)**
1	15	2.627	0.066	S_B:	HOMO-18 → LUMO	(0.17)
					HOMO-16 → LUMO	**(0.20)**
					HOMO-13 → LUMO+1	(0.10)
					HOMO-12 → LUMO+1	(0.19)
					HOMO-2 → LUMO	(-0.16)
					HOMO-1 → LUMO+2	**(-0.85)**
					HOMO-1 → LUMO+6	(0.19)
					HOMO → LUMO+11	(0.15)
1	17	2.813	0.047	S_B:	HOMO-21 → LUMO+1	(-0.19)
					HOMO-20 → LUMO	(-0.14)
					HOMO-15 → LUMO+1	**(0.23)**
					HOMO-14 → LUMO	**(0.21)**
					HOMO-13 → LUMO	**(0.23)**
					HOMO-12 → LUMO	**(-0.33)**
					HOMO-7 → LUMO+3	(0.12)
					HOMO-6 → LUMO+2	(-0.15)
					HOMO-5 → LUMO+1	**(-0.40)**
					HOMO-4 → LUMO	**(-0.60)**

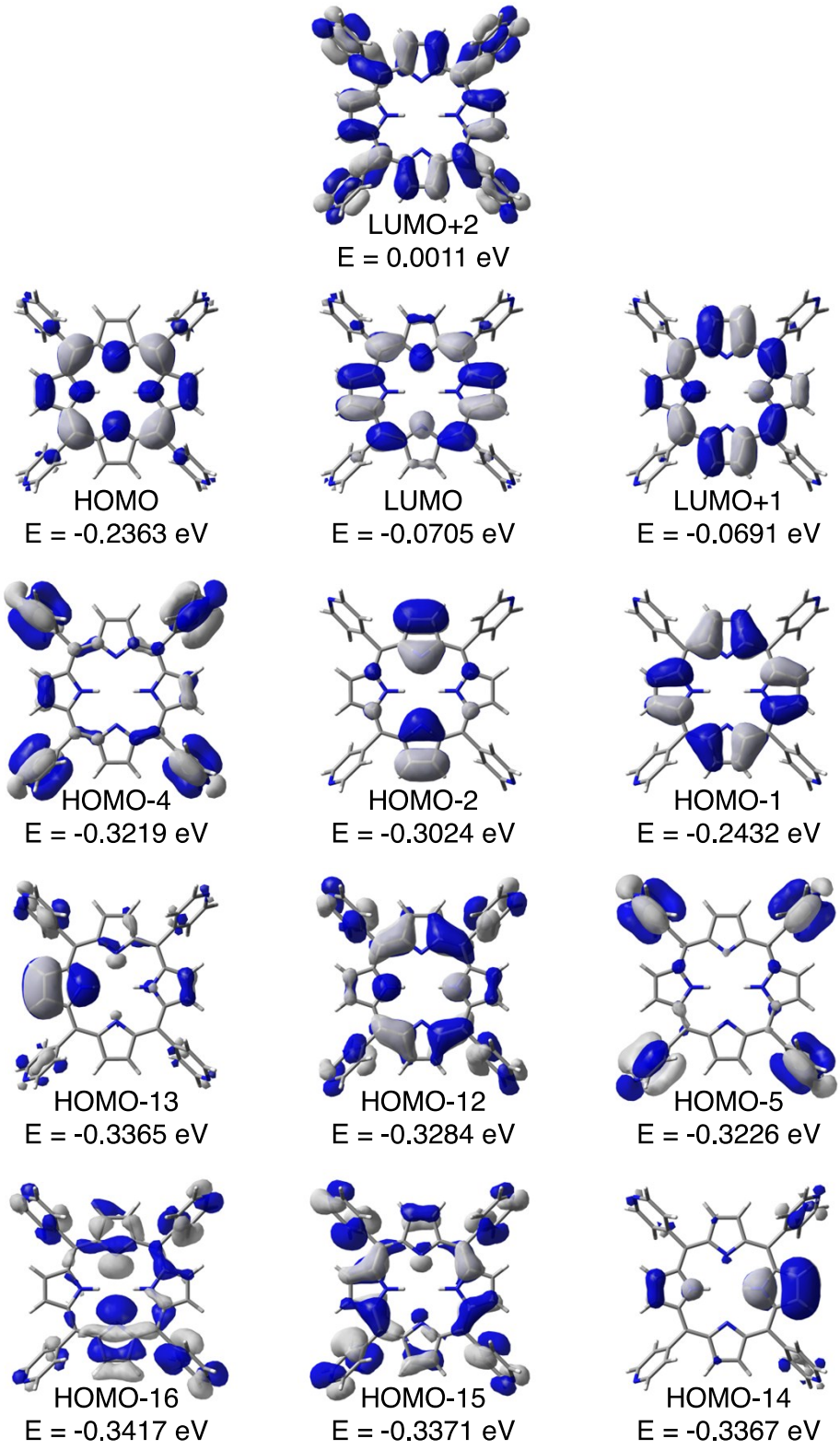

Figure S12. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S8, for free base TPyP at CAM-B3LYP/6-31G* level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

Table S9. Summary of prominent QR-TDDFT excitations for free base TPyP at B3LYP/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.01$), and the major orbital contributions (coefficient$^2 > 0.01$) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	9	1.598	0.029	S_A:	**HOMO-1 → LUMO**	**(-0.61)**
					HOMO → LUMO+1	**(0.79)**
				S_B:	HOMO-12 → LUMO	(-0.10)
					HOMO-2 → LUMO+1	(-0.10)
					HOMO → LUMO+2	**(0.97)**

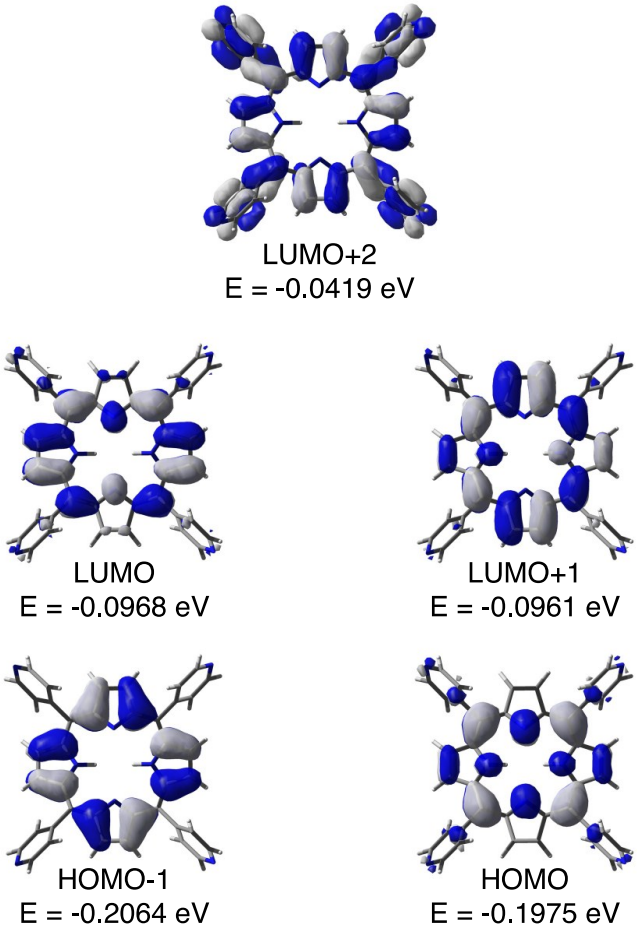

Figure S13. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S9, for free base TPyP at B3LYP/6-31G* level of theory plotted with an isovalue of 0.02 $e^-/Å^3$.

Table S10. Summary of prominent QR-TDDFT excitations for free base TPyP at BLYP/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation (f_{osc} > 0.01), and the major orbital contributions (coefficient^2 > 0.01) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
1	15	1.078	0.018	S_A:	**HOMO-1 → LUMO**	**(-0.57)**
					HOMO → LUMO+1	**(0.82)**
				S_B:	HOMO-16 → LUMO	(-0.14)
					HOMO-13 → LUMO+1	(0.18)
					HOMO → LUMO+2	**(0.94)**
					HOMO → LUMO+6	(0.16)

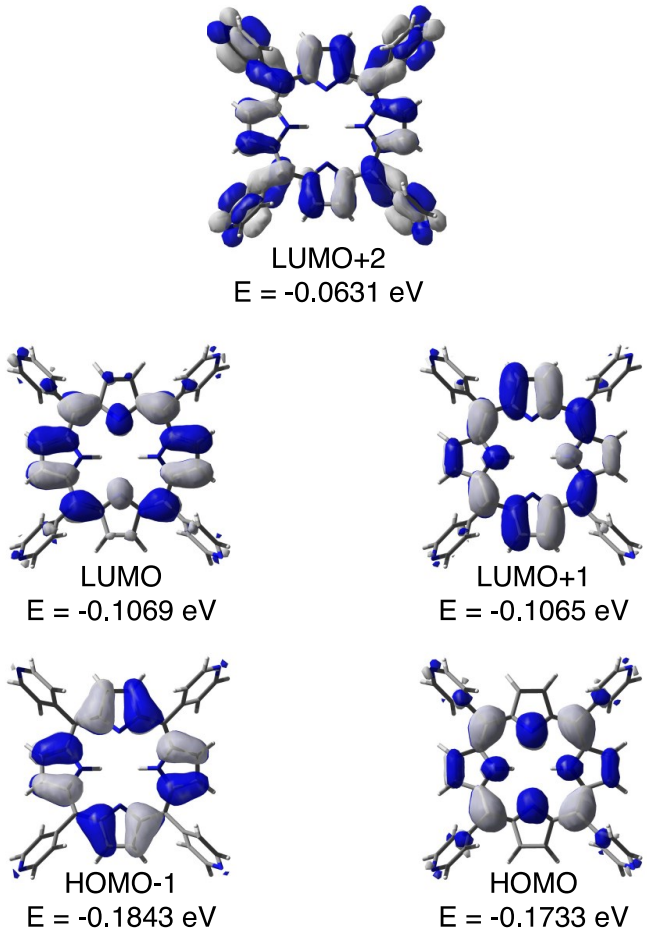

Figure S14. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S5, for free base TPyP at BLYP/6-31G* level of theory plotted with an isovalue of 0.02 $e^-/Å^3$.

Table S11. Summary of prominent QR-TDDFT excitations for Ni(II) TPyP at BHandH/6-31G* level of theory. For a given excitation, $<S_A|\mu|S_B>$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation (f_{osc} > 0.01), and the major orbital contributions (coefficient^2 > 0.01) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
5	15	2.239	0.089	S_A:	**HOMO-1 → LUMO**	**(-0.66)**
					HOMO-1 → LUMO+1	(-0.13)
					HOMO → LUMO	(-0.13)
					HOMO → LUMO+1	**(0.73)**
				S_B:	HOMO-3 → LUMO+1	(0.15)
					HOMO-2 → LUMO	(-0.15)
					HOMO-1 → LUMO+2	**(0.20)**
					HOMO-1 → LUMO+13	(-0.10)
					HOMO → LUMO+2	**(0.93)**
5	16	2.310	0.073	S_B:	**HOMO-1 → LUMO+2**	**(-0.95)**
					HOMO → LUMO+2	(0.17)
5	19	2.572	0.019	S_B:	HOMO-12 → LUMO+3	(-0.11)
					HOMO-11 → LUMO	(0.18)
					HOMO-11 → LUMO+1	**(-0.22)**
					HOMO-10 → LUMO	**(-0.22)**
					HOMO-10 → LUMO+1	(-0.18)
					HOMO-6 → LUMO	(0.18)
					HOMO-6 → LUMO+1	**(-0.36)**
					HOMO-5 → LUMO	**(-0.36)**
					HOMO-5 → LUMO+1	(-0.18)
					HOMO-4 → LUMO+2	(0.11)
					HOMO-1 → LUMO+3	(0.10)
					HOMO → LUMO+3	**(0.60)**
5	20	2.606	0.041	S_B:	HOMO-11 → LUMO	(0.18)
					HOMO-11 → LUMO+1	(-0.12)
					HOMO-10 → LUMO	(-0.12)
					HOMO-10 → LUMO+1	(-0.18)
					HOMO-6 → LUMO	**(0.21)**
					HOMO-6 → LUMO+1	**(-0.23)**
					HOMO-5 → LUMO	**(-0.23)**
					HOMO-5 → LUMO+1	**(-0.21)**
					HOMO-1 → LUMO+3	**(-0.57)**
					HOMO → LUMO+3	**(-0.55)**

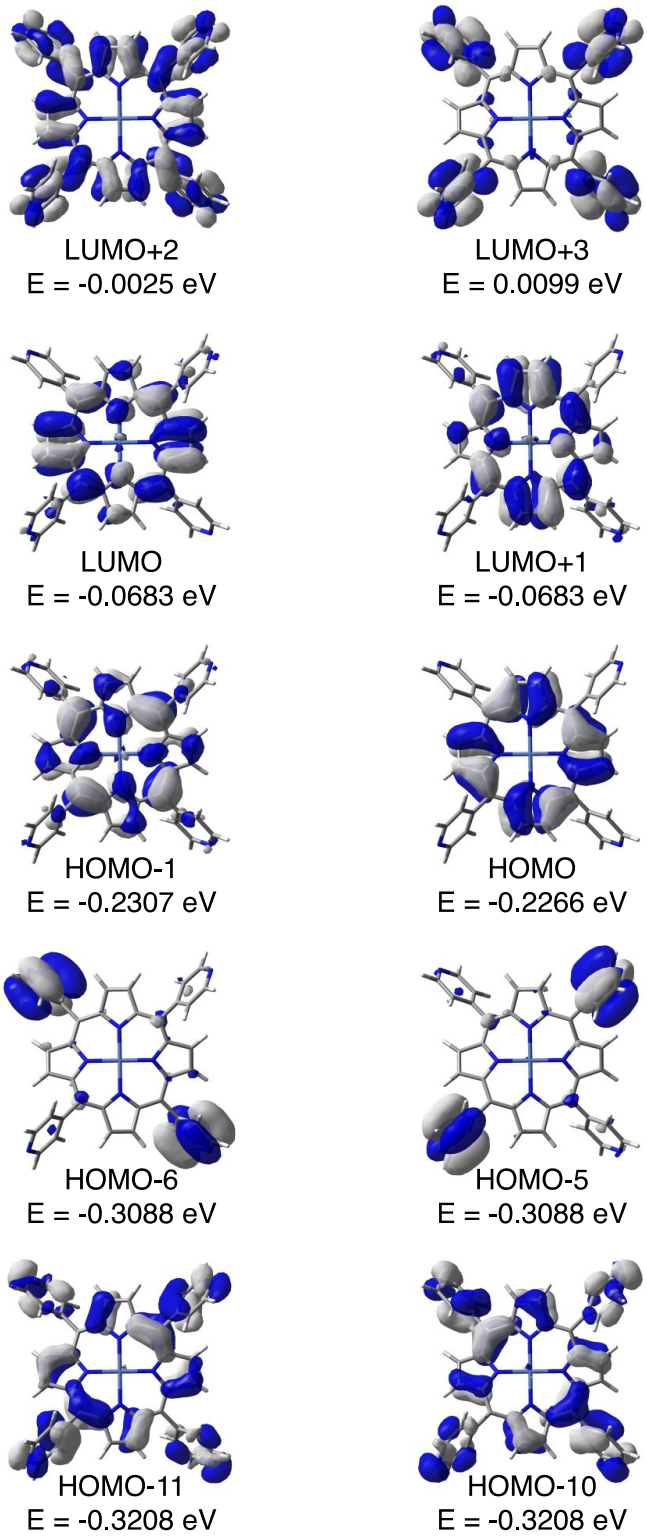

Figure S15. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S11, for Ni(II) at BHandH/6-31G* level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

Table S12. Summary of prominent QR-TDDFT excitations for Ni(II) TPyP at BHLYP/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.01$), and the major orbital contributions (coefficient$^2 > 0.01$) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient		
5	15	2.262	0.090	S_A:	**HOMO-1 → LUMO**	**(-0.66)**
					HOMO → LUMO+1	**(-0.74)**
				S_B:	HOMO-3 → LUMO+1	(0.19)
					HOMO-2 → LUMO	(-0.19)
					HOMO-1 → LUMO+2	(0.17)
					HOMO-1 → LUMO+13	(-0.11)
					HOMO → LUMO+2	**(0.92)**
					HOMO → LUMO+6	(0.11)
5	16	2.345	0.067	S_B:	**HOMO-1 → LUMO+2**	**(-0.96)**
					HOMO → LUMO+2	(0.15)
5	19	2.614	0.032	S_B:	HOMO-20 → LUMO+1	(-0.11)
					HOMO-19 → LUMO	(-0.11)
					HOMO-11 → LUMO	**(-0.28)**
					HOMO-11 → LUMO+1	**(-0.20)**
					HOMO-10 → LUMO	**(-0.20)**
					HOMO-10 → LUMO+1	**(0.28)**
					HOMO-6 → LUMO	**(-0.22)**
					HOMO-6 → LUMO+1	**(-0.40)**
					HOMO-5 → LUMO	**(-0.40)**
					HOMO-5 → LUMO+1	**(0.22)**
					HOMO-4 → LUMO+2	(-0.12)
					HOMO → LUMO+3	**(-0.49)**
5	20	2.649	0.041	S_B:	**HOMO-11 → LUMO**	**(-0.21)**
					HOMO-10 → LUMO+1	**(0.21)**
					HOMO-6 → LUMO	(-0.19)
					HOMO-6 → LUMO+1	(-0.15)
					HOMO-5 → LUMO	(-0.16)
					HOMO-5 → LUMO+1	(0.19)
					HOMO-1 → LUMO+3	**(0.47)**
					HOMO → LUMO+3	**(0.71)**

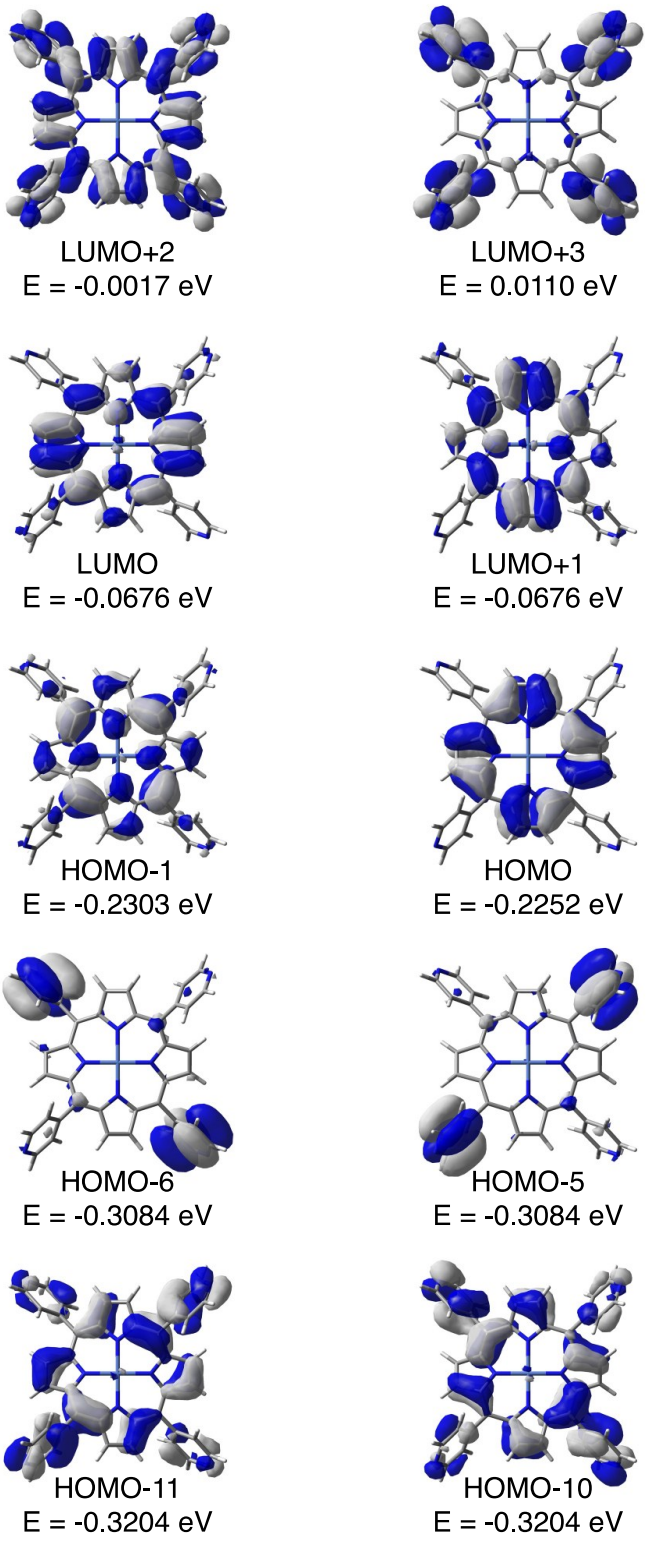

Figure S16. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S12, for Ni(II) at BHLYP/6-31G* level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

Table S13. Summary of prominent QR-TDDFT excitations for Ni(II) TPyP at B3LYP/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation (f_{osc} > 0.01), and the major orbital contributions (coefficient^2 > 0.01) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient
4	19	1.486	0.041	S_A: **HOMO-1 → LUMO+1 (0.67)** **HOMO → LUMO (0.72)** S_B: **HOMO → LUMO+3 (0.97)**
4	20	1.564	0.038	**HOMO-1 → LUMO+3 (0.97)**

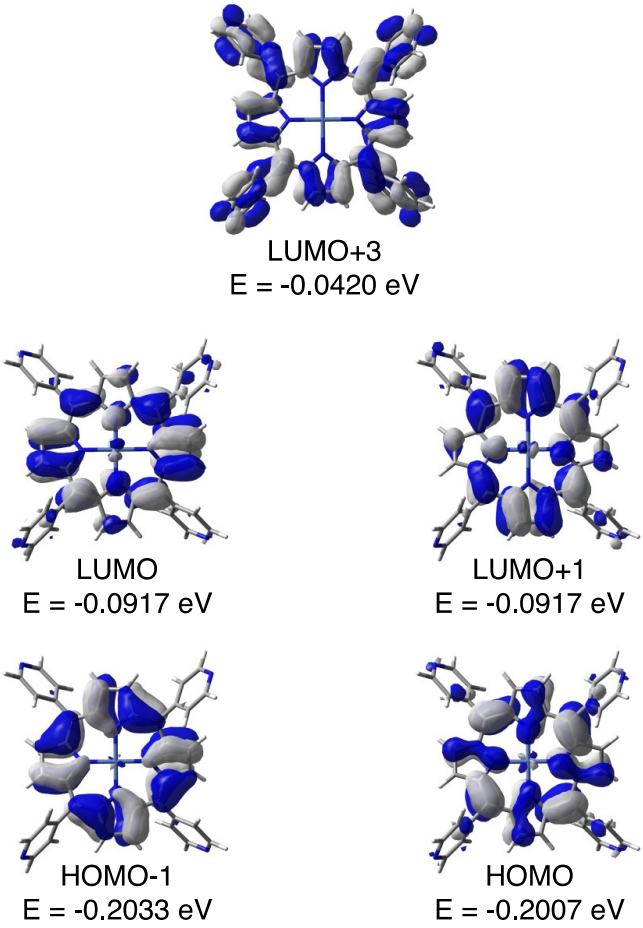

Figure S17. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S13, for Ni(II) TPyP at B3LYP/6-31G* level of theory plotted with an isovalue of 0.02 $e^-/Å^3$.

Table S14. Summary of prominent QR-TDDFT excitations for Ni(II) TPyP at BLYP/6-31G* level of theory. For a given excitation, $\langle S_A|\mu|S_B\rangle$ the value of A was chosen to correspond to the lowest energy Q Band excitation. The values of A, B, the excited-state absorption energy (in eV), the total oscillator strength of the excitation ($f_{osc} > 0.001$), and the major orbital contributions (coefficient^2 > 0.01) to S_A and S_B from LR-TDDFT in terms of ground state orbitals are given with scaled coefficient in parenthesis (S_A described once per functional).

A	B	Excitation Energy (eV)	f_{osc}	LR-TDDFT Characteristic of $S_{A,B}$ and scaled contribution coefficient	
7	16	0.604	0.002	S_A: **HOMO-4 → LUMO+1**	**(0.62)**
				HOMO-3 → LUMO	**(-0.75)**
				HOMO-3 → LUMO+1	(0.13)
				HOMO → LUMO+2	(0.12)
				S_B: **HOMO-7 → LUMO**	**(-0.45)**
				HOMO-7 → LUMO+1	**(-0.54)**
				HOMO-6 → LUMO	**(-0.55)**
				HOMO-6 → LUMO+1	**(0.45)**
7	17	0.605	0.001	S_B: **HOMO-7 → LUMO**	**(0.44)**
				HOMO-7 → LUMO+1	**(0.56)**
				HOMO-6 → LUMO	**(-0.55)**
				HOMO-6 → LUMO+1	**(0.43)**
7	20	0.612	0.001	S_B: **HOMO-7 → LUMO**	**(0.57)**
				HOMO-7 → LUMO+1	**(-0.45)**
				HOMO-6 → LUMO	**(0.42)**
				HOMO-6 → LUMO+1	**(0.55)**

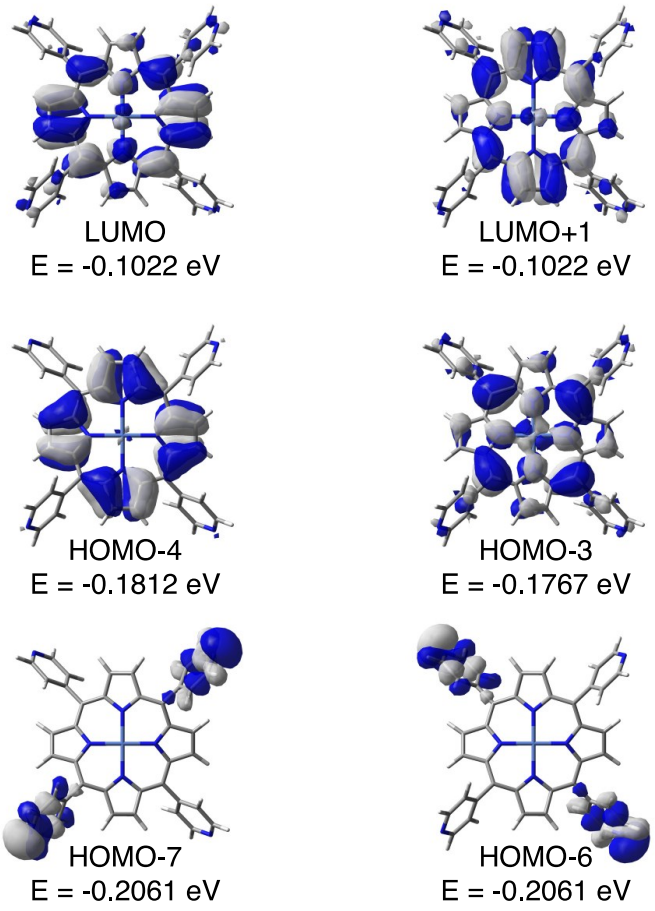

Figure S18. Orbitals with largest contribution to QR-TDDFT excitations, shown bolded in Table S14, for Ni(II) TPyP at BLYP/6-31G* level of theory plotted with an isovalue of 0.02 $e^{-}/Å^{3}$.

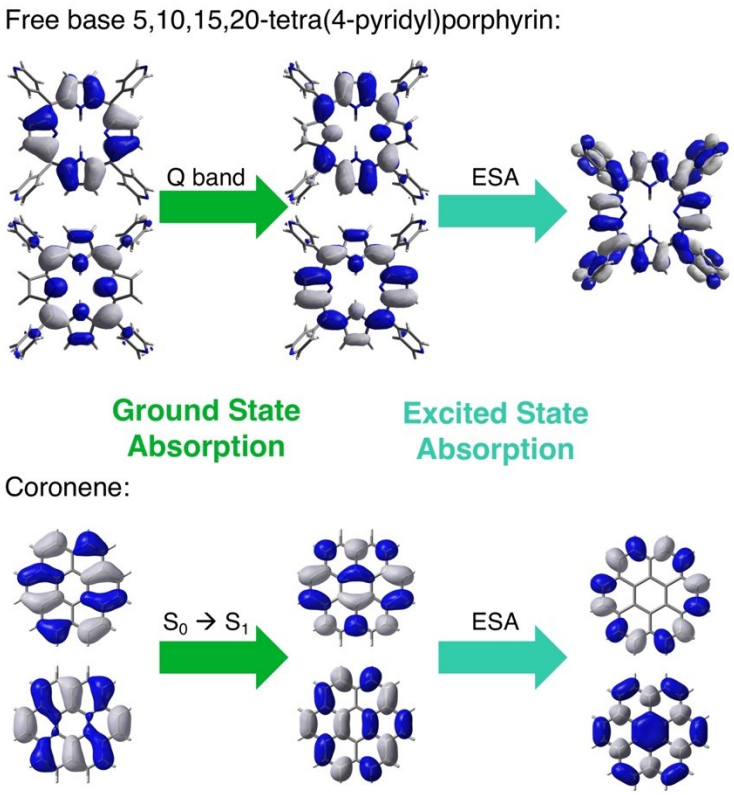

Figure S19. Comparison of free base TPyP and coronene ground and excited state absorption, based on LR- and QR-TDDFT. Frontier orbitals (HOMO-1 and HOMO) that contribute to the first significant ground state absorption excitations (on left). This state has significant electron density in LUMO and LUMO+1 (center), and the first significant excitation from this LR-TDDFT state adds electron density to higher lying LUMOs (right).

Cartesian Coordinates:

Free base TPyP, singlet:

C	-1.05779688	-2.88045185	-0.01810363
C	-0.63309557	-4.27771411	-0.04104718
H	-1.28468539	-5.13924811	-0.05847986
C	0.72011501	-4.26375023	-0.03791834
H	1.38975846	-5.11154500	-0.03897351
C	1.11571512	-2.85804923	-0.02844752
C	2.46228540	-2.43772991	-0.00074556
C	2.90262754	-1.10449949	0.02892947
C	4.26140239	-0.64450086	0.03643799
H	5.12776483	-1.28867307	0.03421926
C	4.24854454	0.72429430	0.04356047
H	5.10273551	1.38430425	0.05769286
C	2.88141161	1.15880007	0.02317557
C	2.41452855	2.48337939	0.00447503
C	1.05918260	2.87604403	-0.01479605
C	0.63634657	4.26993031	-0.11874459
H	1.28936268	5.12728370	-0.19458221
C	-0.71688135	4.25695752	-0.12654966
H	-1.38503479	5.10158695	-0.21198753
C	-1.11430228	2.85501736	-0.02728259
C	-2.46218606	2.43580367	-0.01757303

C	-2.90232641	1.10151236	-0.00782825
C	-4.25790137	0.64029345	0.08047234
H	-5.12208976	1.28340283	0.15145574
C	-4.24397518	-0.72852033	0.08150253
H	-5.09475971	-1.38934558	0.15242001
C	-2.87938081	-1.16194986	-0.00575302
C	-2.41291551	-2.48699744	-0.00534860
N	0.02040284	-2.04122800	-0.01890326
N	2.10985523	0.01980061	0.02385776
N	-0.01991519	2.03887937	0.02685375
N	-2.11018228	-0.02236259	-0.05458028
C	-3.45981044	-3.55742299	0.02375148
C	-3.63577436	-4.37924817	1.14538916
H	-3.01118913	-4.25123009	2.02423573
C	-4.62870275	-5.35891233	1.12230705
H	-4.77909267	-6.00239014	1.98780045
N	-5.44341504	-5.57366930	0.08154069
C	-5.27254082	-4.78651274	-0.98780086
H	-5.93756251	-4.97267967	-1.82978837
C	-4.31135831	-3.77823069	-1.06721652
H	-4.21871030	-3.17877362	-1.96790360
C	3.52992193	-3.48874291	-0.00665957
C	3.78102449	-4.26912310	-1.14321524
H	3.20192670	-4.12263420	-2.04996571
C	4.78886139	-5.23276715	-1.09780478
H	4.99717390	-5.84474791	-1.97408613
N	5.54996461	-5.46864873	-0.02169063
C	5.30704244	-4.72093376	1.06191661
H	5.92900454	-4.92416580	1.93237578
C	4.32423127	-3.73221925	1.12178807
H	4.17175832	-3.16507153	2.03520116
C	3.45821785	3.55740368	-0.00141675
C	3.63936701	4.40398131	1.10068553
H	3.02302674	4.29146532	1.98745758
C	4.62635840	5.38850201	1.04781987
H	4.78084116	6.05110266	1.89804550
N	5.42995873	5.58597291	-0.00487367
C	4.29701978	3.76111946	-1.10556016
H	4.19819167	3.14374370	-1.99337709
C	5.25309714	4.77616274	-1.05622687
H	5.90838770	4.94909795	-1.90859022
C	-3.52755832	3.48705013	-0.01066107
C	-4.40356352	3.65172098	-1.09253315
H	-4.31694979	3.02049552	-1.97180174
C	-5.38011449	4.64638443	-1.03332139
H	-6.06352794	4.78909437	-1.86903494
N	-5.54434325	5.47173315	0.00795356
C	-4.70618125	5.31125073	1.03985227
H	-4.85112535	5.98536530	1.88266037
C	-3.69616960	4.34996236	1.08113648
H	-3.05305243	4.26668597	1.95190696
H	-1.09559444	-0.01275449	-0.08391408
H	1.09477134	0.01033230	0.02683923

Ni(II) TPyP, singlet:

Ni	0.00000003	-0.00000001	-0.00008230
N	1.20428947	1.48960538	0.00438580
N	-1.48962349	1.20431440	-0.00450457
C	2.52764722	1.49656687	0.40461531
C	3.04612077	2.84009169	0.40572796
C	2.06385891	3.63988539	-0.08424008
C	0.91407131	2.80158749	-0.30400812
C	-0.35368540	3.29877350	-0.61395205
C	-0.47384486	4.71852476	-1.05934736
C	0.04831434	5.12278740	-2.29568272
C	-0.07010468	6.45822712	-2.68132675
C	-1.14661804	7.01429496	-0.75089065
C	-1.08238406	5.70572430	-0.27165207
C	-1.49658560	2.52769844	-0.40462710

C	-2.84008385	3.04625333	-0.40545526
C	-3.63990260	2.06388995	0.08426504
C	-2.80161298	0.91406307	0.30385214
C	3.29874617	0.35368192	0.61390283
C	4.71849933	0.47387726	1.05930467
C	5.12273308	-0.04825189	2.29566737
C	6.45818726	0.07005793	2.68128572
C	7.01424131	1.14680727	0.75098335
C	5.70568409	1.08255233	0.27170143
N	-1.20428946	-1.48960540	0.00438582
C	-2.52764721	-1.49656688	0.40461532
C	-3.04612077	-2.84009170	0.40572796
C	-2.06385891	-3.63988540	-0.08424007
C	-0.91407131	-2.80158748	-0.30400812
C	0.35368539	-3.29877351	-0.61395205
C	0.47384488	-4.71852475	-1.05934738
C	-0.04831435	-5.12278739	-2.29568272
C	0.07010478	-6.45822709	-2.68132677
C	1.14661806	-7.01429494	-0.75089068
C	1.08238407	-5.70572427	-0.27165209
C	1.49658558	-2.52769847	-0.40462709
N	1.48962346	-1.20431443	-0.00450454
C	2.80161295	-0.91406309	0.30385217
C	3.63990259	-2.06388996	0.08426507
C	2.84008385	-3.04625332	-0.40545529
C	-3.29874617	-0.35368194	0.61390284
C	-4.71849933	-0.47387727	1.05930469
C	-5.12273310	0.04825197	2.29566735
C	-6.45818723	-0.07005801	2.68128576
C	-7.01424131	-1.14680727	0.75098337
C	-5.70568409	-1.08255232	0.27170144
N	0.65583502	-7.40257285	-1.93461338
N	-7.40252440	-0.65591153	1.93465286
N	7.40252436	0.65591161	1.93465289
N	-0.65583514	7.40257277	-1.93461343
H	1.61281147	-7.79234417	-0.14828304
H	1.48691425	-5.45991674	0.70537622
H	-0.53258073	-4.40328455	-2.94902041
H	-0.32573472	-6.78512734	-3.64164082
H	7.79228866	1.61306187	0.14841716
H	6.78505793	-0.32573973	3.64162827
H	4.40324050	-0.53260911	2.94894406
H	5.45990337	1.48717019	-0.70529973
H	-1.48691425	5.45991674	0.70537623
H	-1.61281148	7.79234418	-0.14828304
H	0.53258072	4.40328455	-2.94902040
H	0.32573472	6.78512734	-3.64164084
H	-6.78505794	0.32573973	3.64162826
H	-4.40324049	0.53260911	2.94894406
H	-5.45990333	-1.48717015	-0.70529972
H	-7.79228863	-1.61306187	0.14841715
H	-2.08866500	-4.70885503	-0.23814379
H	-4.04031104	-3.12330498	0.71789440
H	-4.70887383	2.08869532	0.23814828
H	-3.12328079	4.04052630	-0.71737134
H	2.08866501	4.70885502	-0.23814379
H	4.04031105	3.12330499	0.71789440
H	3.12328081	-4.04052630	-0.71737134
H	4.70887382	-2.08869532	0.23814829

Cu(II) TPyP, doublet:

Cu	0.00069319	-0.00052692	-0.00129015
C	-0.71537949	-2.95959270	-0.00420031
C	-0.12017890	-4.27273352	-0.03801687
H	-0.66665353	-5.20415010	-0.05487035
C	1.22557152	-4.09521838	-0.04355476
H	1.99516773	-4.85277609	-0.05534423
C	1.45955858	-2.67257316	-0.02732139
C	2.73300094	-2.09671206	-0.00983896

C	2.95962350	-0.71753292	0.01564970
C	4.27334621	-0.12314115	0.03451807
H	5.20452052	-0.67020891	0.03924684
C	4.09630621	1.22271832	0.04371914
H	4.85427910	1.99154556	0.06690916
C	2.67374749	1.45759682	0.01366267
C	2.09749181	2.73128310	0.00347564
C	0.71762797	2.95728868	-0.00962399
C	0.12394167	4.26910998	-0.08946909
H	0.67124491	5.19816731	-0.14791737
C	-1.22170548	4.09250204	-0.09880563
H	-1.98901986	4.84937120	-0.16582170
C	-1.45762651	2.67208434	-0.02094902
C	-2.73280405	2.09675372	-0.00921482
C	-2.95821031	0.71625102	0.01084441
C	-4.26896266	0.12153920	0.09253247
H	-5.19868458	0.66763395	0.15362421
C	-4.09136957	-1.22398842	0.09792277
H	-4.84719624	-1.99242009	0.16375894
C	-2.67070280	-1.45882861	0.02012903
C	-2.09495372	-2.73293198	0.01489556
N	0.26277824	-1.98678571	-0.00430803
N	1.98755342	0.26111154	0.00353185
N	-0.26144916	1.98608513	0.02071251
N	-1.98571500	-0.26202669	-0.02074343
C	-3.00684047	-3.91978944	0.03442419
C	-3.11486344	-4.74097824	1.16461254
H	-2.53628695	-4.52637380	2.05810156
C	-3.98185089	-5.83367467	1.13126886
H	-4.07954922	-6.47845925	2.00334839
N	-4.73295731	-6.15974617	0.07189176
C	-4.62644001	-5.37274456	-1.00603297
H	-5.23953058	-5.64951616	-1.86244033
C	-3.79176930	-4.25687215	-1.07627281
H	-3.74714176	-3.66080926	-1.98285388
C	3.92100004	-3.00862911	-0.01761747
C	4.29873585	-3.70608629	-1.17237703
H	3.73433562	-3.59272771	-2.09318529
C	5.41356665	-4.54391828	-1.12652739
H	5.72143622	-5.09066113	-2.01655811
N	6.16295877	-4.73149437	-0.03295692
C	5.79830863	-4.06286867	1.06824982
H	6.41337825	-4.22548276	1.95203915
C	4.70210170	-3.20162828	1.12918369
H	4.45510923	-2.69177499	2.05565618
C	3.00702089	3.92019106	0.00101418
C	3.12361169	4.75146800	1.12289387
H	2.55513871	4.54212823	2.02413421
C	3.98536420	5.84763616	1.07100051
H	4.08965731	6.50034408	1.93643747
N	4.72308043	6.16808668	0.00061547
C	3.77730252	4.25188317	-1.12149309
H	3.72452700	3.64881300	-2.02297640
C	4.60767696	5.37185035	-1.06967758
H	5.20934737	5.64450720	-1.93540592
C	-3.92011471	3.00724086	-0.01820359
C	-4.77843854	3.07980617	-1.12380341
H	-4.59177067	2.47484597	-2.00586360
C	-5.87053141	3.94698795	-1.08203535
H	-6.54284061	4.01785595	-1.93579540
N	-6.16394290	4.72963843	-0.03605348
C	-5.34279711	4.65662742	1.01889942
H	-5.59366879	5.29447935	1.86518510
C	-4.22316946	3.82592531	1.07822392
H	-3.59925556	3.80908692	1.96668159