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Spectroscopic and nonlinear optical properties of the four positional isomers of 4α-(4-tert-butylphenoxy)phthalocyanine

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1.0 Calculated electronic absorption spectra

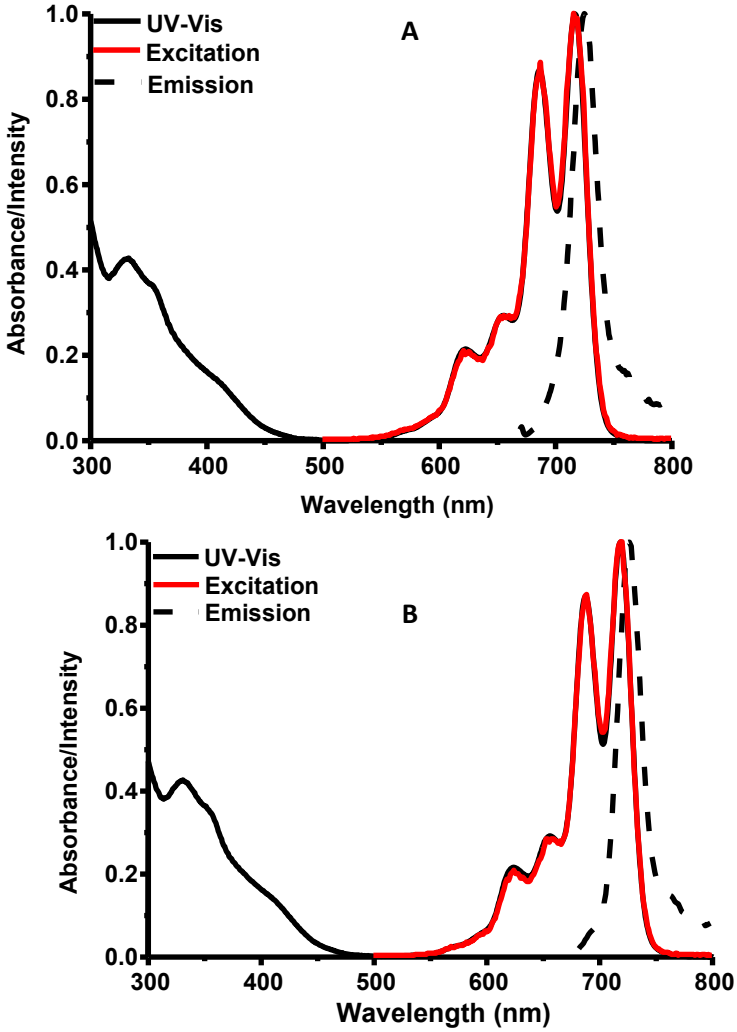
Table S1. TD-DFT spectra of the B3LYP optimized geometries of the four positional isomers of the $H_2(OH)_4Pc$ model compound calculated with the B3LYP functional and 6-31G(d) basis sets.

				C_{2v}			
Band[a]	**#[b]**		**Calc[c]**			**Exp[d]**	**Wavefunction=[e]**
--	**1**	---	---	---	---	---	Ground state
Q	**2**	15.8	632	(0.41)	13.9	714	**93% a → -a; 4% s → -s;** 3% H–6 ($2a_{2u}$) → -s; …
Q	**3**	16.0	626	(0.47)	14.6	683	**96% a → -s;** 3% H–6 ($2a_{2u}$) → -a; **2% s → -a;** …
B1	**9**	25.8	388	(0.14)	25.0	~400	**46% s → -s;** 24% H–3 ($1e_g$) → -a; …
B1	**15**	27.5	364	(0.01)			**74% s → -a;** …
B2	**17**	29.0	345	(0.26)	28.6	~350	38% H–8 ($2a_{1u}$) → -a; 38% H–6 ($2a_{2u}$) → -s; …
B2	**18**	29.2	342	(0.15)			38% H–8 ($2a_{1u}$) → -s; 36% H–6 ($2a_{2u}$) → -s; …
				C_{4h}			
Band[a]	**#[b]**		**Calc[c]**			**Exp[d]**	**Wavefunction=[e]**
--	**1**	---	---	---	---	---	Ground state
Q	**2**	15.8	632	(0.42)	13.9	719	**61% a → -a; 33% a → -s; 3% s → -s;** …
Q	**3**	16.0	624	(0.47)	14.6	689	**63% a → -s; 32% a → -a;** …
B1	**9**	25.9	386	(0.20)	25.0	~400	**70% s → -s;** 24% H–2 ($1b_{1u}$) → -a; …
B1	**15**	27.5	364	(0.01)			**77% s → -a;** …
B2	**17**	29.0	344	(0.27)	28.6	~350	53% H–7 ($2a_{1u}$) → -a; 41% H–6 ($2a_{2u}$) → -s; …
B2	**18**	29.3	342	(0.11)			56% H–7 ($2a_{1u}$) → -s; 39% H–6 ($2a_{2u}$) → -s;

C_s							
Band[a]	**#**[b]	**Calc**[c]			**Exp**[d]		**Wavefunction=**[e]
--	**1**	---	---	---	---	---	Ground state
Q	**2**	15.8	632	(0.41)	13.9	718	**92% a → -a; 4% s → -s;** 3% H–6 ($2a_{2u}$) → -s; …
Q	**3**	16.0	626	(0.48)	14.5	688	**95% a → -s;** 3% H–6 ($2a_{2u}$) → -a; **2% s → -a;** …
B1	**9**	25.9	386	(0.19)	25.0	~400	**68% s → -s;** …
B1	**15**	27.4	364	(0.02)			**73% s → -a;** …
B2	**17**	29.0	345	(0.24)	28.6	~350	53% H–8 ($2a_{1u}$) → -a; 40% H–6 ($2a_{2u}$) → -s; …
B2	**18**	29.2	342	(0.10)			56% H–8 ($2a_{1u}$) → -s; 38% H–6 ($2a_{2u}$) → -s; …
D_{2h}							
Band[a]	**#**[b]	**Calc**[c]			**Exp**[d]		**Wavefunction=**[e]
--	**1**	---	---	---	---	---	Ground state
Q	**2**	15.8	634	(0.40)	14.0	715	**79% a → -a; 15% a → -s; 4% s → -s;** 2% H–6 ($2a_{2u}$) → -s; …
Q	**3**	16.0	626	(0.49)	14.5	687	**81% a → -s; 15% a → -a; 2% s → -a;** 2% H–6 ($2a_{2u}$) → -a; …
B1	**9**	25.8	388	(0.23)	25.0	~400	**64% s → -s;** 13% H–2 ($1b_{1u}$) → -a; …
B1	**15**	27.3	366	(0.01)			**78% s → -a;** …
B2	**17**	29.0	345	(0.24)	28.6	~350	54% H–7 ($2a_{1u}$) → -a; 37% H–6 ($2a_{2u}$) → -s; …
B2	**19**	29.2	343	(0.10)			56% H–7 ($2a_{1u}$) → -s; 37% H–6 ($2a_{2u}$) → -s; …

a − Band assignment described in the text. b − The number of the state assigned in terms of ascending energy within the TD-DFT calculation. c − Calculated band energies ($10^3.cm^{-1}$), wavelengths (nm) and oscillator strengths in parentheses (f). d − Observed energies ($10^3.cm^{-1}$) and wavelengths (nm) in Figures 8-10. e − The wave functions based on the eigenvectors predicted by TD-DFT. One-electron transitions associated with Michl's perimeter model are highlighted in bold. H in H–n refers to the HOMO. When this nomenclature is used the symmetry label for the corresponding MO in the π-systems of D_{2h} MPc complexes is provided in parentheses where applicable.

2.0 Uv/vis, excitation and Emission spectra



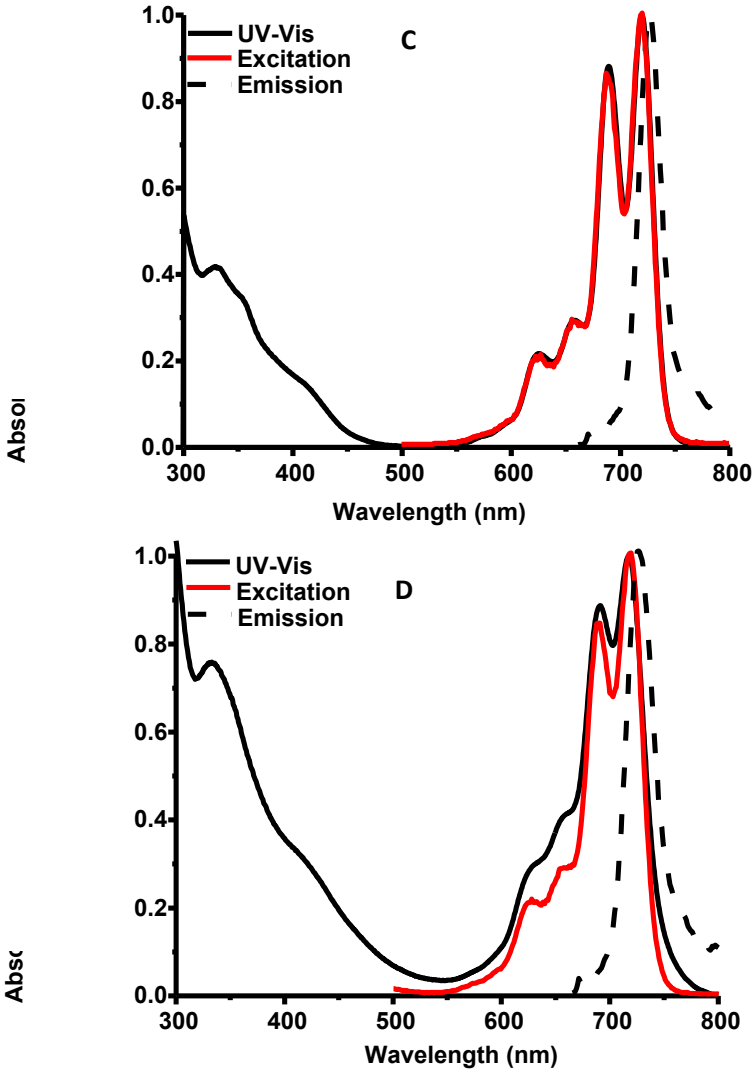


Figure 1: UV-visible absorption, excitation and fluorescence emission spectra of isomers C_s (A), C_{4h} (B), D_{2h} (C) and C_{2v} (D)($\lambda_{ex} = 670\ nm$) in DCM.

3.0 Time correlated single photon counting (TCSPC)

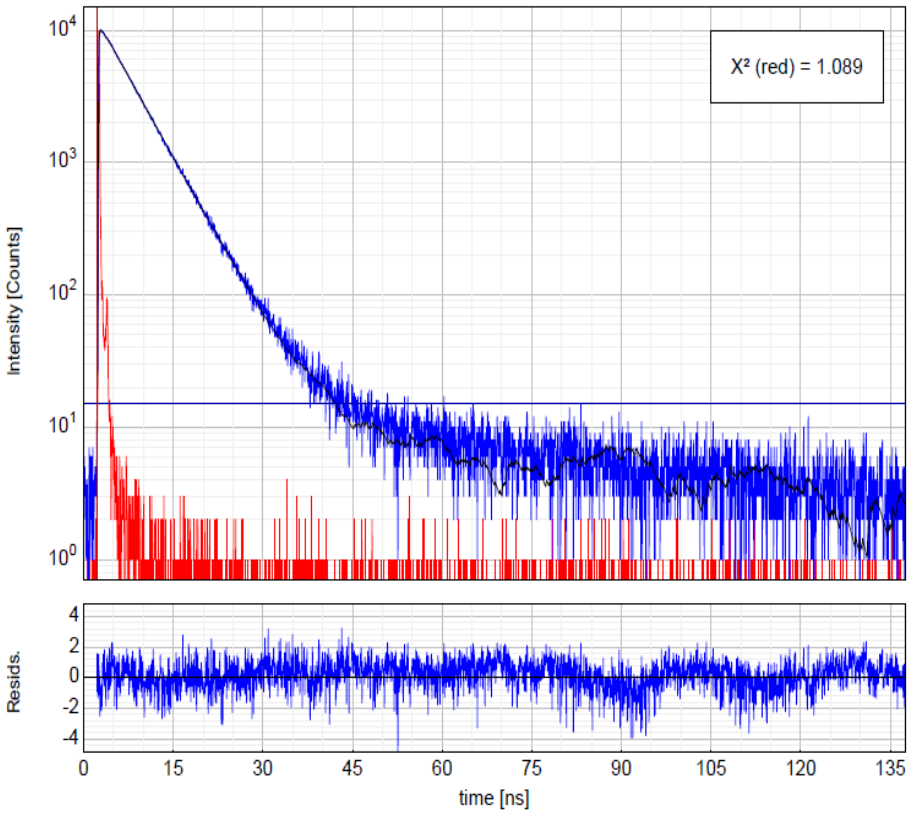


Figure 2: Fluorescence decay curve for the C_s isomer in DCM with residuals (λ_{ex} = 670 nm).