Electronic Supplementary Information

Synthesis, characterization and photodynamic activity of Sn(IV) triarylcorroles with red-shifted Q bands

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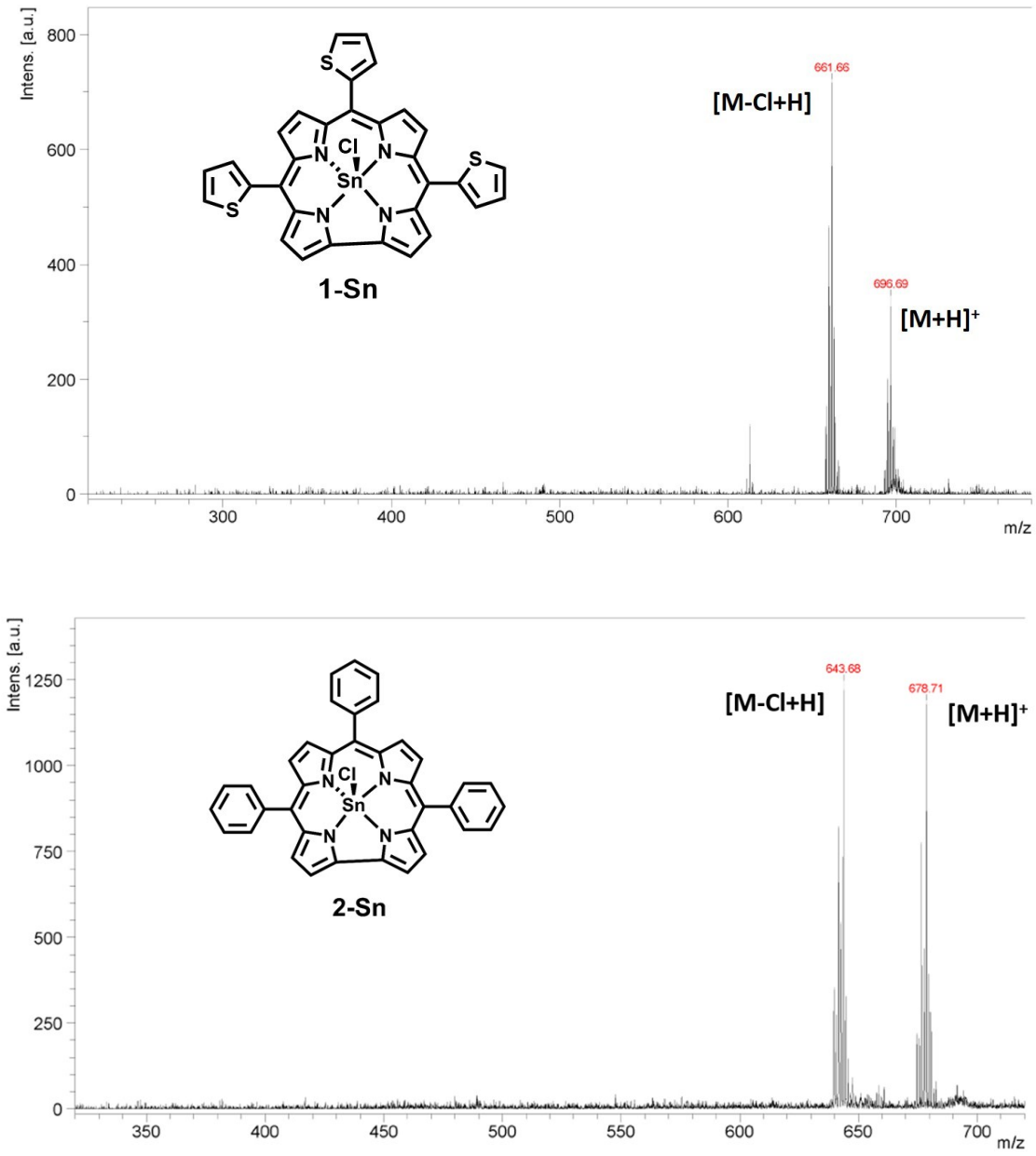

Figure S1. MALDI-TOF MS data for **1-Sn** and **2-Sn**.

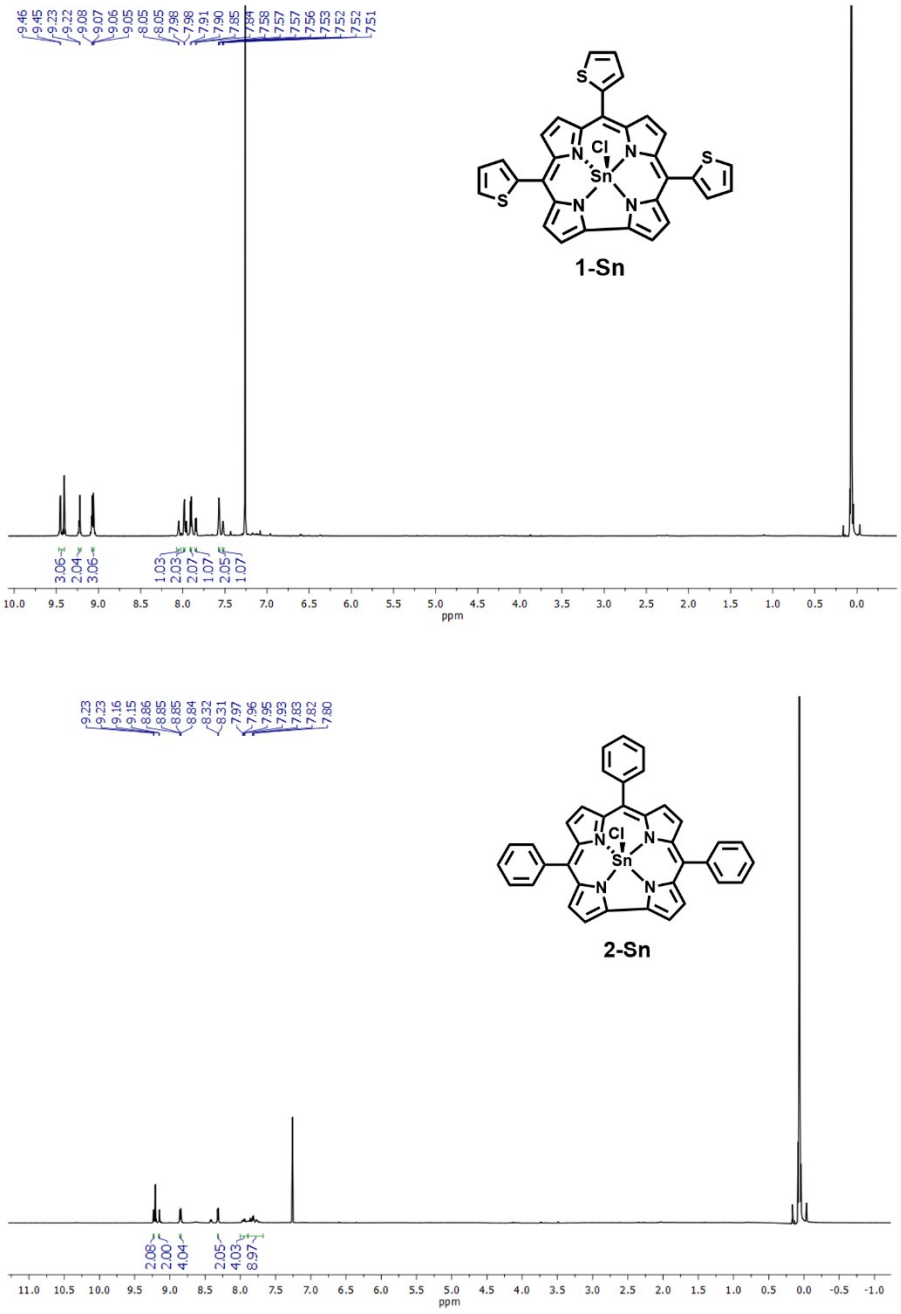

Figure S2. ^{1}H NMR (600 MHz) spectra of **1-Sn** and **2-Sn** in $CDCl_3$.

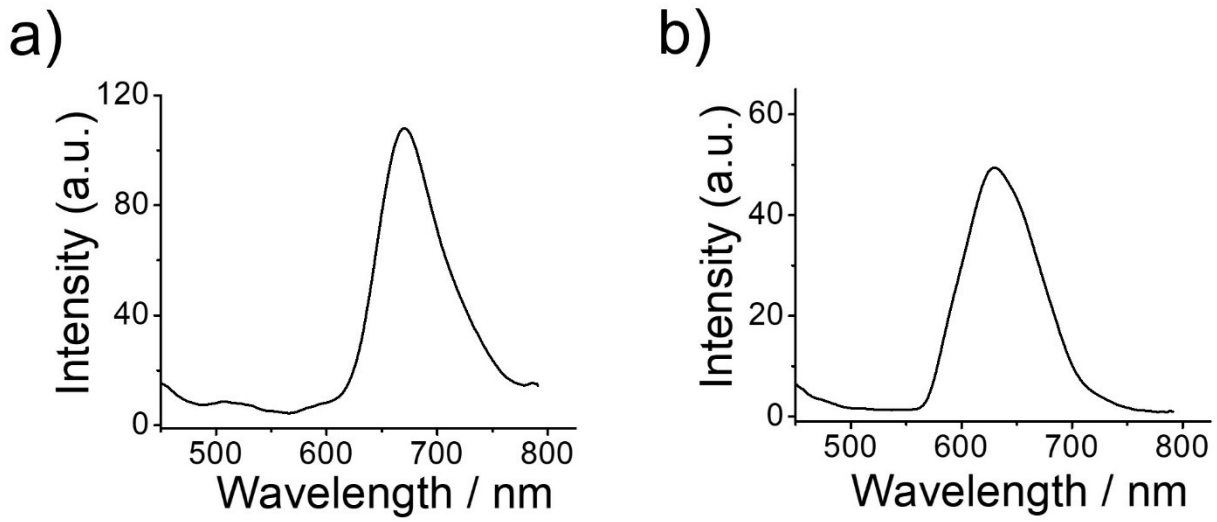

Figure S3. Emission spectra of (a) **2** and (b) **2-Sn** in DMF upon excitation at the B band maximum.

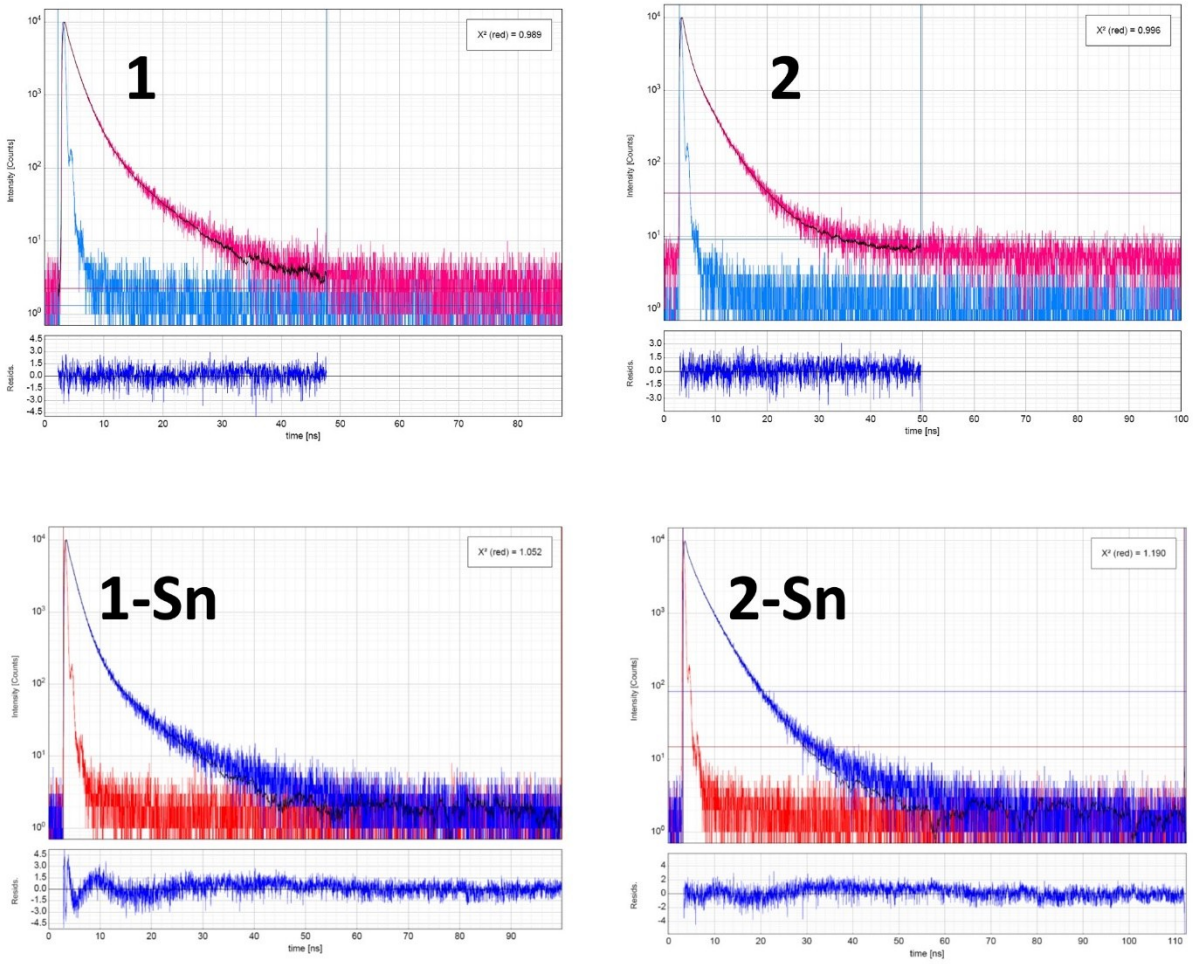

Figure S4. Fluorescence decay (magenta or royal blue) and IRF (light blue or red) curves for **1**, **2**, **1-Sn**, **2-Sn** in DMF.

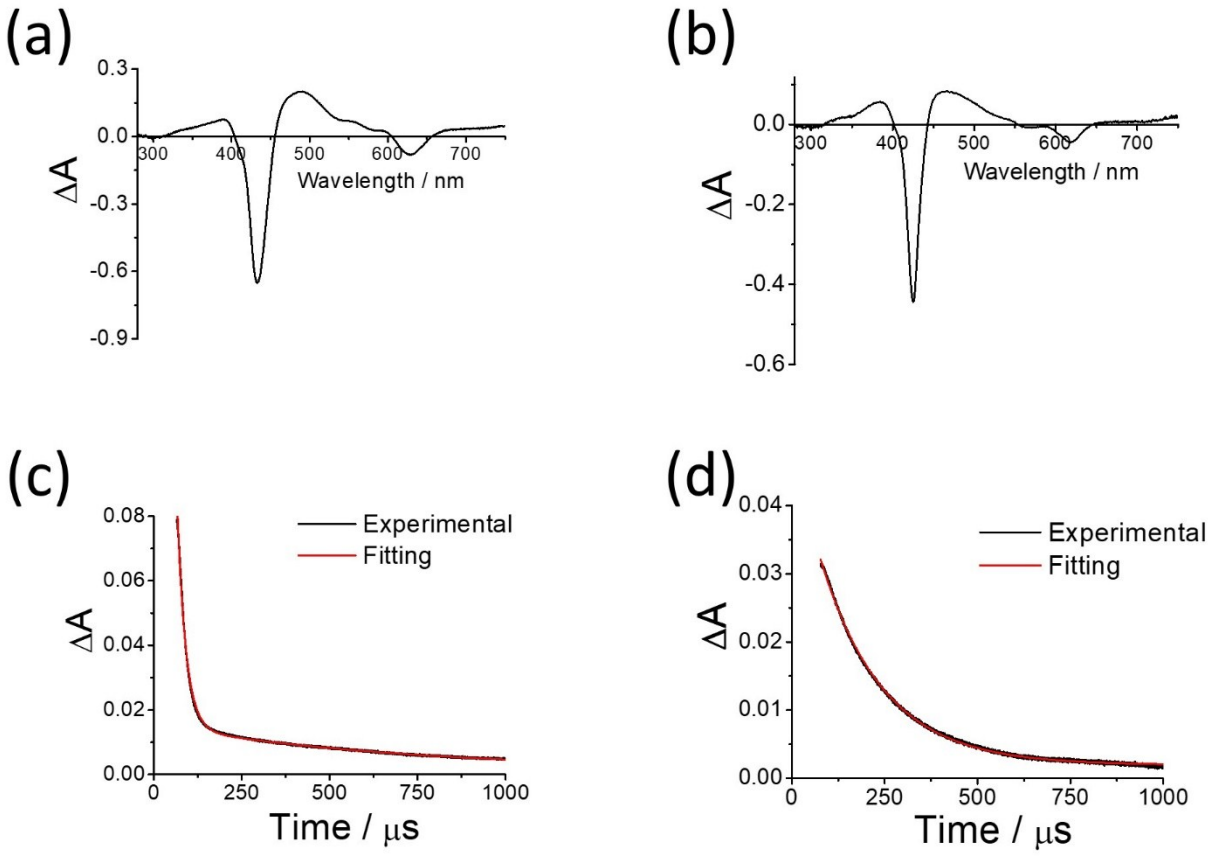

Figure S5. Transient absorption curve for (a) **1-Sn**, (b) **2-Sn** in DMF upon irradiation at 425 nm. The decay curves for (c) **1-Sn** and (d) **2-Sn** at 500 nm.

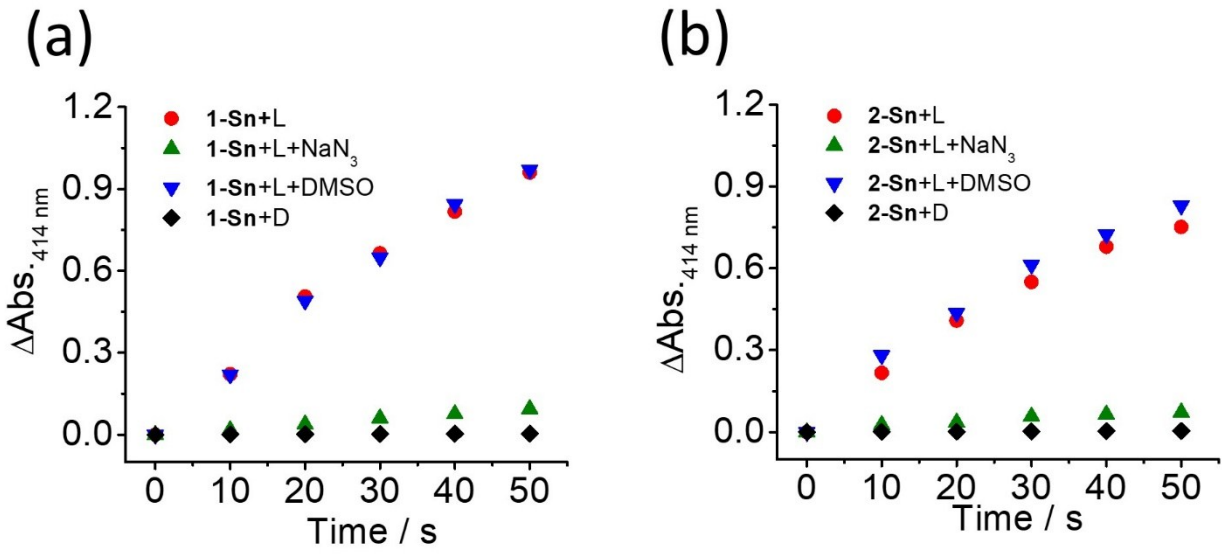

Figure S6. Plots of the change in absorbance for DPBF at 414 nm *vs*. irradiation time; (a) **1-Sn** and (b) **2-Sn** in the presence of different quenchers. L and D refers to light and dark, respectively.

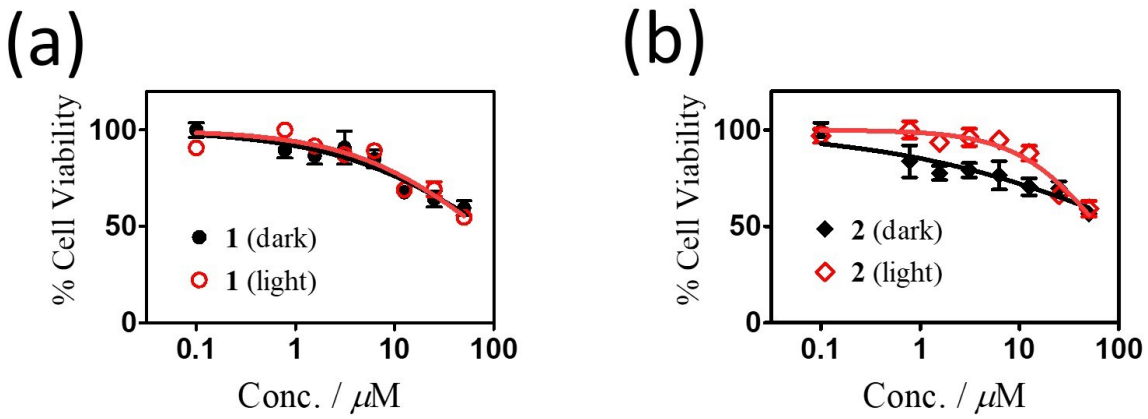

Figure S7. Cytotoxicity of (a) **1** and (b) **2** in MCF-7 cells after 24 h incubation in the dark followed by photo-irradiation (30 min) with a Thorlabs 625 nm LED as determined by MTT assay. The dark treated cells are denoted with solid black circles, while red circles are used for the photoexposed cells (30 min).

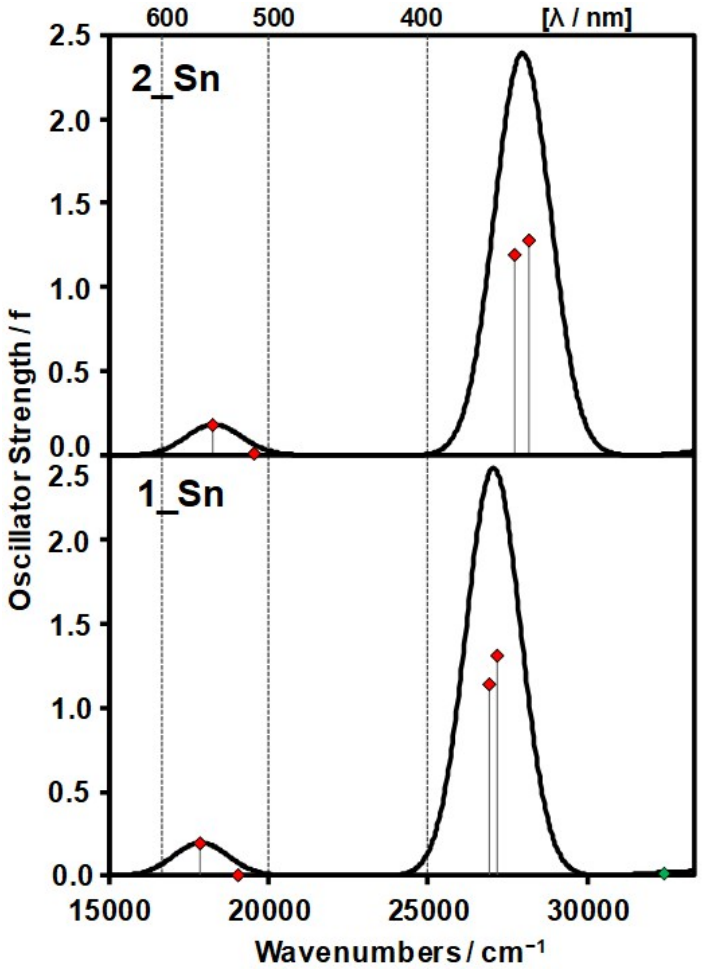

Figure S8. The calculated TD-DFT spectra of **1-Sn** and **2-Sn** at the CAM-B3LYP/SDD level of theory. The Q and B bands are highlighted with red diamonds. The simulated spectra were generated with the Chemcraft program with a fixed bandwidth of 2000 cm^{-1}.

Table S1. Calculated and observed electronic excitation wavelengths of the B3LYP/6-31G(d) optimized geometries of **1-Sn** and **2-Sn** at the CAM-B3LYP/SDD level of theory, and their calculated oscillator strengths and wavefunctions.

	# [a]	λ_{exp} [b]	λ_{calc} [c]	ν_{calc} [d]	*f* [e]	Wavefunction = [f]
			1-Sn			
Q	1	627	560	17.9	0.19	**74% s → a**; **25% a → s**; …
	2	---	525	19.1	0.00	**59% a → a**; **39% s → s**; …
B	3	434	372	26.9	1.14	**58% s → s**; **37% a → a**; …
	4		368	27.2	1.31	**68% a → s**; **24% s → a**; …
			2-Sn			
Q	1	617	548	18.3	0.18	**75% s → a**; **24% a → s**; …
	2	---	512	19.5	0.01	**59% a → a**; **40% s → s**; …
B	3	426	360	27.7	1.19	**60% s → s**; **38% a → a**; …
	4		355	28.2	1.28	**73% a → s**; **25% s → a**; …

[a] Excited state number assigned in increasing energy in the TD-DFT calculations. Only states located below 33,333 cm^{-1} resulting from allowed electronic transitions with an oscillator strength greater than 0.5 are consistently included. [b] Experimental wavelengths in nm, recorded in Table 1. [c] Calculated wavelengths in nm. [d] Calculated band energy (10^3 cm^{-1}). [e] Calculated oscillator strengths. [f] Wavefunctions describing the MOs involved in the transition based on eigenvectors predicted by TD-DFT. Only one-electron transition contributions of more than 5% are included. **a**, **s**, **-a** and **-s** refer to the MO nomenclature of Michl's perimeter model.

Full Reference

32. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.