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Aromaticity and photophysics of tetrasila- and tetragerma-annelated tetrathienylenes as new representatives of the hetero[8]circulenes family

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Computational details on photophysics calculations

The ISC and IC non-radiative rate constants were calculated using the method describing in Ref.[1] The general formula for the calculation of radiationless rate constants (k_{nr}) according to this method is:

$$k_{\mathrm{nr}} = \sum_n \left|V_{i0,fn}\right|^2 \Gamma_{fn} \left[\Delta_{if}^2 + \frac{\Gamma_{fn}^2}{4} \right]^{-1} \text{(1)},$$

where i is the initial electronic state, f is the final electronic state, n is a vibrational level of f, Γ_{fn} is the relaxation width of the vibronic level $|fn>$, $\Delta_{if} = |\, E_{i0}\text{-}E_{fn} \,|$ is the resonance defect energy between the initial and final vibronic states, and $V_{i0,fn}$ is the matrix element of the perturbation operator. Only the lowest vibronic state is considered for the initial state at room temperature. In the case of ISC, the perturbation operator is the spin-orbit coupling interaction, and for IC is the non-adiabatic coupling interaction one. Eq. (1) written in atomic units holds at ambient temperatures (T $\leq$ 300 K) when $k_{\mathrm{nr}} << \Gamma_{fn}$. Γ_{fn} is about 10^{14} s^{-1}, and is generally much larger than k_{nr} which typically has values around 10^{7}-10^{12} s^{-1}.[1] The Δ_{if} value is not larger than 100 cm^{-1} for polyatomic molecules.[1] The expression can be simplified to Eq. (2) when assuming that Γ_{fn} depends only weakly on the vibrational level n, and that $\Delta_{if} << \Gamma_{fn}$:[1]

$$k_{\mathrm{nr}} = 1.6 \cdot 10^{9} \sum_n \left|V_{i0,fn}\right|^2 \text{(2).}$$

where $\left|V_{i0,fn}\right|$ in cm^{-1}, k_{nr} in s^{-1}. The matrix element $\left|V_{i0,fn}\right|$ of ISC is

$$\left|V_{i0,fn}\right| = < i \,|\, \hat{H}_{SO} \,|\, f > \left(\prod_{k=1}^{3N-6} \sqrt{\frac{\exp(-y_k)\, y_k^{n_k}}{n_k!}} \right) \text{(3)}$$

and for IC is

$$\left|V_{i0,fn}\right| = -\sum_{v} \sum_{q=x,y,z} M_v^{-1} < i \,|\, \frac{\partial}{\partial R_{qv}} \,|\, f > \left[\sum_{j=1}^{3N-6} B_{vqj} < 0_j \,|\, \frac{\partial}{\partial Q_j} |n_j > \prod_{\substack{k \neq j \\ k=1}}^{3N-6} \sqrt{\frac{\exp(-y_k)\, y_k^{n_k}}{n_k!}} \right] \text{(4),}$$

where y_k is the Huang-Rhys factor of the *k-th* mode and ω_k is the frequency of the *k-th* mode, $<i|H_{SO}|f>$ and $<i|\frac{\partial}{\partial R_{qv}}|f>$ are the matrix elements of the spin-orbital coupling interaction operator H_{SO} and non-adiabatic coupling interaction operator ($\frac{\partial}{\partial R_{qv}}$) between the initial and final electronic states *i* and *f*, respectively. The E_{if} is the energy gap between the electronic states, $\{R_{qv}\}$ are the Cartesian coordinates, M_v is mass of *v*-th atom. The $|n_j>$ is the wave-function of *j*-th harmonic oscillator and n_j is number of excitation and Q_j is its normal coordinate. The B_{vqj} is the matrix relationship between $\{R_{qv}\}$ and $\{Q_j\}$.

The Huang-Rhys factors were calculated according to Eq (5):

$$y_j = \frac{1}{2}\omega_j \Delta Q_j^2 \quad (4),$$

where ΔQ_j^2 is the equilibrium position displacement of the *j-th* mode[1].

The radiative rate constant was calculated using modified Strickler–Berg equation[2]:

$$k_r = \frac{1}{1.5003} f \cdot E_{if}^2 \quad (5),$$

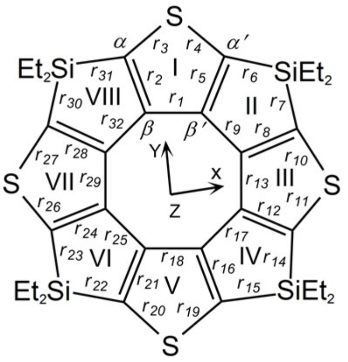
where *f* – ocillator strenghts and E_{if} (in cm^{-1}).

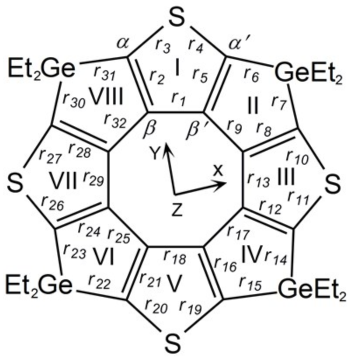
[1] R. R. Valiev, V. N. Cherepanov, G. V. Baryshnikov and D. Sundholm, *Phys. Chem. Chem. Phys.*, 2018, **20**, 6121.

[2] Strickler S. J. and Berg R. A. // J. Chem. Phys. – 1962. – V. 37. – No. 4 – P. 814–822.

Table S1. Calculated bond lengths (Å) in the ground and first excited singlet state of tetrasilatetrathia[8]circulene and tetragermatetrathia[8]circulene molecules

Bond	Si		Ge	
	S_0	S_1	S_0	S_1
r_1	1.437/**1.428**	1.429	1.442/**1.437**	1.434
r_2	1.400/**1.401**	1.443	1.397/**1.397**	1.396
r_3	1.718/**1.704**	1.710	1.712/**1.697**	1.749
r_4	1.718/**1.704**	1.754	1.712/**1.698**	1.704
r_5	1.400/**1.401**	1.398	1.397/**1.394**	1.445
r_6	1.871/**1.863**	1.884	1.921/**1.939**	1.921
r_7	1.871/**1.866**	1.853	1.921/**1.930**	1.920
r_8	1.400/**1.396**	1.408	1.397/**1.395**	1.444
r_9	1.493/**1.489**	1.485	1.495/**1.496**	1.446
r_{10}	1.718/**1.704**	1.733	1.712/**1.696**	1.704
r_{11}	1.718/**1.703**	1.732	1.712/**1.698**	1.750
r_{12}	1.400/**1.399**	1.410	1.397/**1.398**	1,397
r_{13}	1.437/**1.431**	1.423	1.442/**1.433**	1.434
r_{14}	1.871/**1.865**	1.864	1.922/**1.930**	1.930
r_{15}	1.872/**1.865**	1.862	1.922/**1.928**	1.907
r_{16}	1.400/**1.398**	1.410	1.396/**1.394**	1.405
r_{17}	1.493/**1.490**	1.480	1.495/**1.487**	1.486
r_{18}	1.437/**1.430**	1.422	1.442/**1.439**	1.429
r_{19}	1.718/**1.705**	1.732	1.712/**1.692**	1.726
r_{20}	1.718/**1.705**	1.735	1.712/**1.696**	1.726
r_{21}	1.400/**1.400**	1.409	1.397/**1.392**	1.405
r_{22}	1.871/**1.862**	1.852	1.921/**1.929**	1.915
r_{23}	1.871/**1.862**	1.884	1.921/**1.926**	1.916
r_{24}	1.400/**1.402**	1.399	1.397/**1.391**	1.405
r_{25}	1.493/**1.488**	1.484	1.494/**1.491**	1.483
r_{26}	1.718/**1.704**	1.754	1.712/**1.700**	1.725
r_{27}	1.718/**1.702**	1.711	1.712/**1.698**	1.724
r_{28}	1.400/**1.400**	1.443	1.397/**1.391**	1.404
r_{29}	1.437/**1.429**	1.429	1.442/**1.433**	1.430
r_{30}	1.871/**1.861**	1.870	1.921/**1.926**	1.907
r_{31}	1.871/**1.864**	1.872	1.921/**1.934**	1.930
r_{32}	1.493/**1.489**	1.447	1.494/**1.490**	1.486





Experimental data (in bold) from Refs.[22,23] obtained by X-ray analysis.
Parameter *r* denotes the bond in accordance with Figure presented from the right on Table.

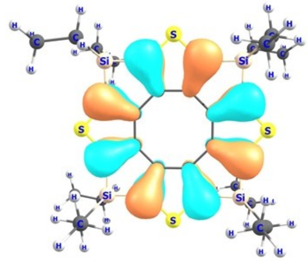
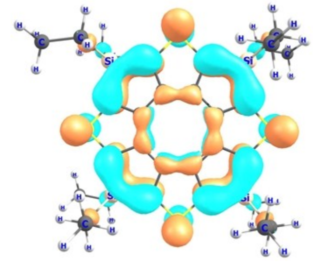
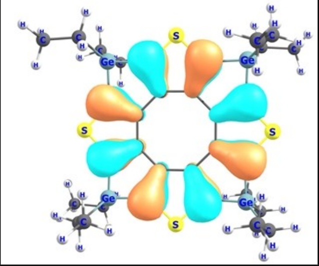
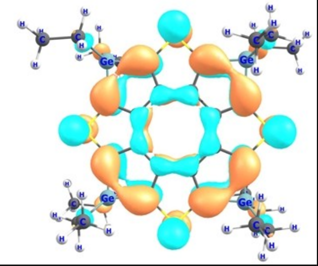
			
HOMO (4S4SiEt$_2$)	LUMO (4S4SiEt$_2$)	HOMO	LUMO

Figure S1. The shape of frontier molecular orbitals of the 4S4SiEt$_2$ and 4S4GeEt$_2$ molecules

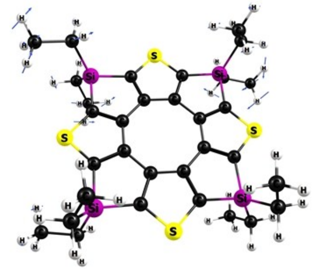
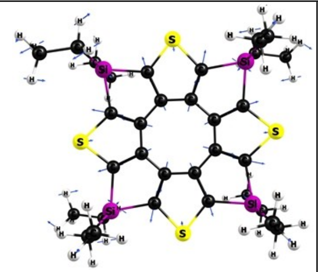
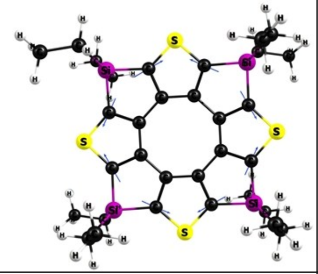
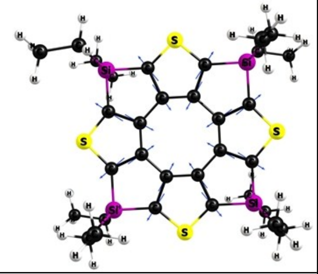
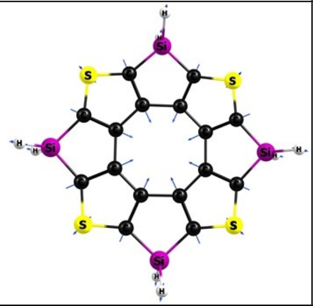
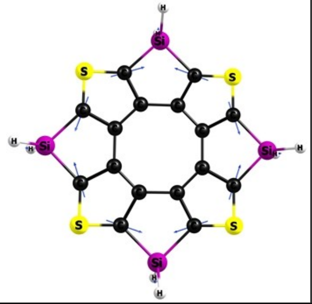
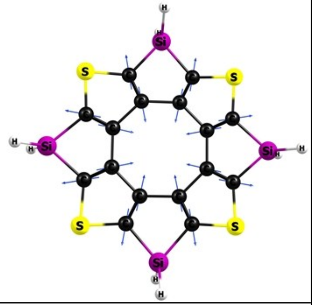
			
84 (74)	794 (763)	1139 (1117)	1329 (1320)
–			
	784 (754)	1152 (1138)	1326 (1317)

Figure S2. The shape of promotive modes in the absorption vibronic spectra of 4S4SiEt$_2$ (4S4GeEt$_2$) molecules (top) and their H-substituted 4S4SiH$_2$ (4S4GeH$_2$) models (bottom). Numbers are in cm^{-1}. The scaled displacement vectors are absolutely the same for the pairs of 4S4SiEt$_2$ (4S4GeEt$_2$) and 4S4SiH$_2$ (4S4GeH$_2$) molecules, that is why only Si-containing systems are presented.

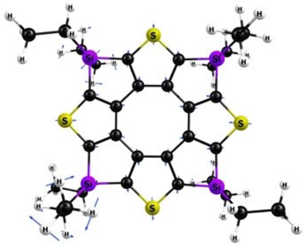
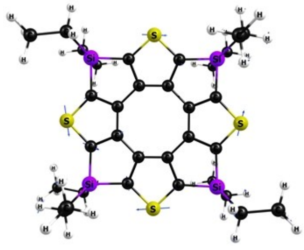
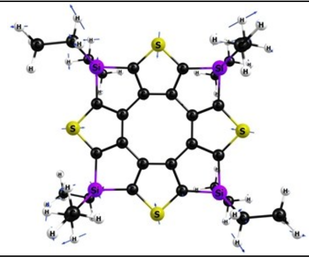
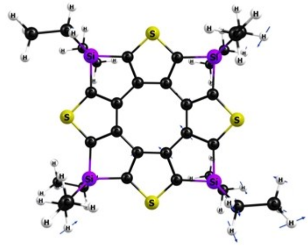
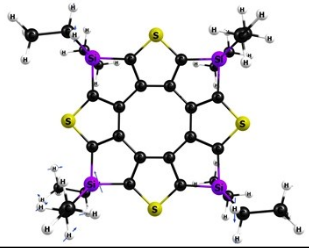
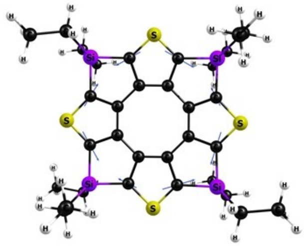
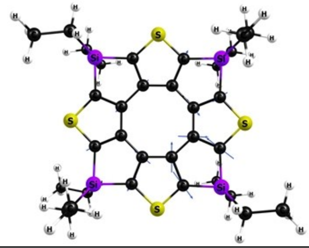
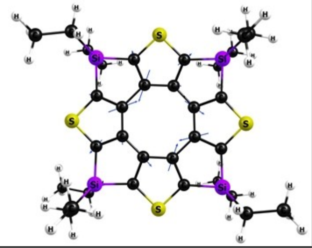
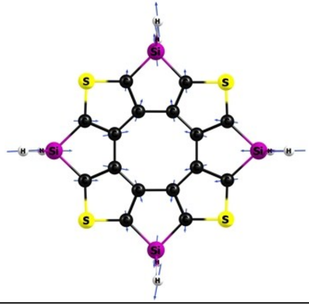
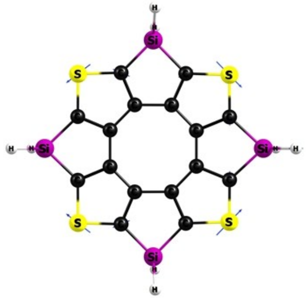
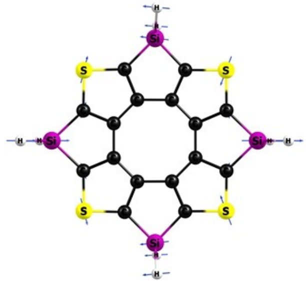
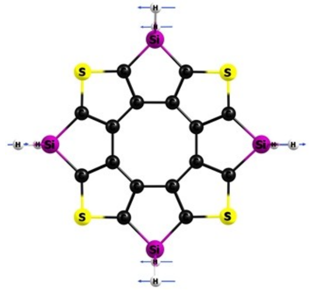
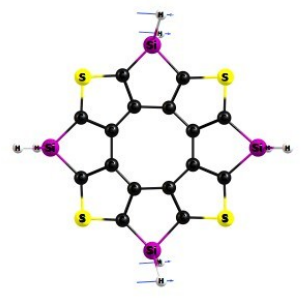
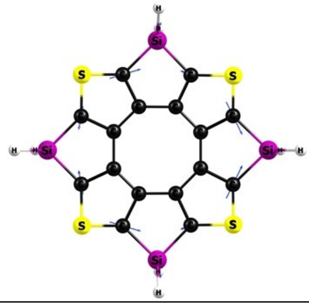
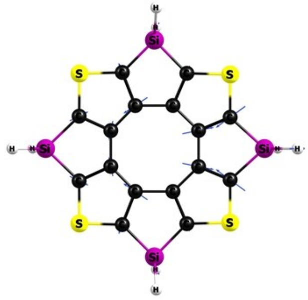
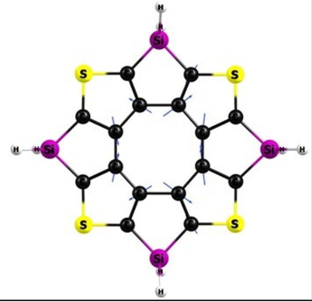
			
241 (223)	314 (321)	369 (343)	362 (397)
			
649 (648)	1125 (1119)	1197 (1166)	1314 (1312)
			
250 (180)	323 (297)	373 (321)	397 (341)
			
666 (628)	1137 (1127)	1193 (1185)	1312 (1331)

Figure S3. The shape of promotive modes in the fluorescence vibronic spectra of 4S4SiEt$_2$ (4S4GeEt$_2$) molecules (top) and their H-substituted 4S4SiH$_2$ (4S4GeH$_2$) models (bottom). Numbers are in cm^{-1}. The scaled displacement vectors are absolutely the same for the pairs of 4S4SiEt$_2$ (4S4GeEt$_2$) and 4S4SiH$_2$ (4S4GeH$_2$) molecules, that is why only Si-containing systems are presented.