



Supporting Information

for

On the photoluminescence in triarylmethyl-centered mono-, di-, and multiradicals

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Information about performed DFT calculations and photoluminescence quantum yield measurements

DFT calculations

The theoretical calculations of PTM-PTM and *m*-PTH were performed with ORCA 5.0.3.^[1] The molecular geometry optimizations were carried out with the UB3LYP functional at the def2-SVP level of theory in vacuum using dispersion correction with the Becke-Johnson damping scheme (D3BJ).^[2]

The singlet-triplet energy gap (ΔE_{ST}) was calculated with the Yamaguchi spin decontamination correction according to the following equation:^[3]

$$\Delta E_{ST} = 2J = -\frac{2(E_T - E_{BS})}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}}$$

Here, J corresponds to the intramolecular exchange interaction within the diradicals, E_T and E_{BS} represent the total energy of the calculated triplet and broken-symmetry state and $\langle S^2 \rangle_T$ and $\langle S^2 \rangle_{BS}$ correspond to the respective expectation value of the total spin squared operator. The diradical character y_0 was calculated from the occupation number of the highest occupied natural orbital (n_{HONO}) and of the lowest unoccupied natural orbital (n_{LUNO}) according to Yamaguchi:^[4]

$$y_0 = 1 - \frac{2T_0}{1 + T_0^2}$$
$$T_0 = \frac{n_{HONO} - n_{LUNO}}{2}$$

Table S1: Calculated electronic properties of PTM-PTM and *m*-PTH at the UB3LYP/def2-SVP level of theory.

	PTM-PTM	<i>m</i> -PTH
E_T [kcal mol ⁻¹]	-8993695.883	-7695210.997
E_{BS} [kcal mol ⁻¹]	-8993695.891	-7695210.244
ΔE_{ST} [kcal mol ⁻¹]	<0.1	1.6
$\langle S^2 \rangle_T$	2.0418	2.0509
$\langle S^2 \rangle_{BS}$	1.0423	1.0226
y_0	0.998	0.777

Photoluminescence Quantum Yield

Photoluminescence quantum yields ϕ are determined with a Hamamatsu Quantaurus-QY (C11347) for cyclohexane solutions (10^{-5} M) at room temperature (293 K).

References

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