

ELECTRONIC SUPPLEMENTARY INFORMATION

Why the presence of silicon atoms improves the emission properties of biphenyl derivatives? – verification of various hypotheses by experiment and theory

Karolina Rachuta,^[a] Malgorzata Bayda-Smykaj,^{*[a,b]} Jacek Koput,^[a] Gordon L. Hug,^[c] Mariusz Majchrzak,^[a] and Bronislaw Marciniak^[a,b]

^[a] Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland

^[b] Center for Advanced Technology, Adam Mickiewicz University, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland

^[c] Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

E-mail: mbayda@amu.edu.pl

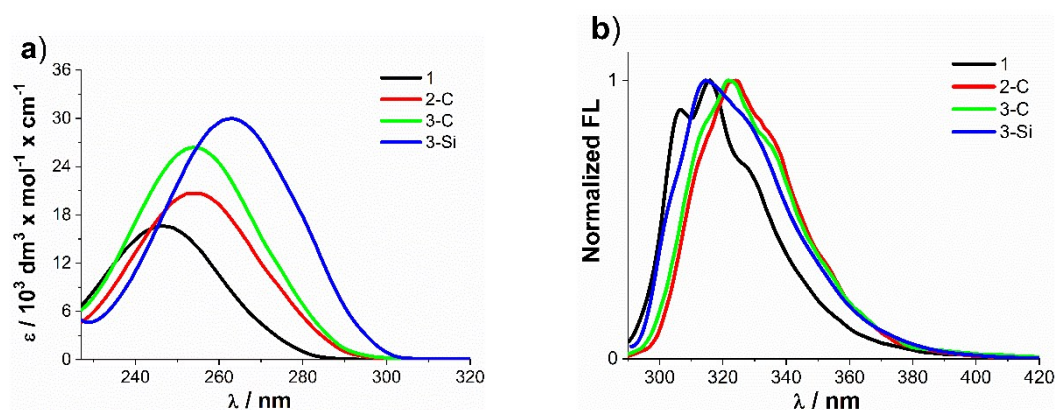
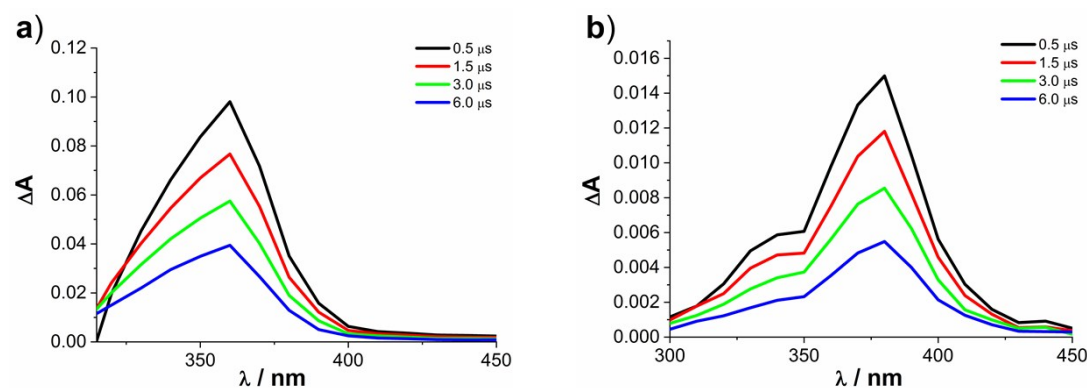


Figure S1. Absorption (a) and normalized fluorescence spectra (b) of 1, 2-C, 3-C and 3-Si in *n*-hexane, $\lambda_{exc}=280$ nm.

Table S1. Absorption and emission properties of compounds 1, 2-C, 3-C and 3-Si in *n*-hexane.

Compd.	$\lambda_{Abs, max} / nm$ ($\epsilon / M^{-1} \times cm^{-1}$)	$\lambda_f, max / nm$	$\tau_S^{[a]} / ns$	Φ_f	$k_f^{[b]} / 10^9 \times s^{-1}$	$k_{nr}^{[c]} / 10^9 \times s^{-1}$	$k_f (S-B)^{[d]} / 10^9 \times s^{-1}$
1	247 (16 500)	305, 316	10.9 ^[e]	0.18 ^[f]	0.017	0.075	0.37
2-C	254 (20 500)	323	14.2 ^[g]	0.32 ^[h]	0.023	0.048	0.49
3-C	254 (26 100)	322	13.6 ^[e]	0.33 ^[h]	0.024	0.049	0.54
3-Si ^[i]	263 (29 500)	314	6.3 ^[e]	0.78 ^[f]	0.124	0.035	0.66

^[a] Determined from single exponential decay fits of fluorescence kinetic traces. ^[b] $k_f = \Phi_f \tau_S^{-1}$. ^[c] $k_{nr} = (1 - \Phi_f) \tau_S^{-1}$. ^[d] Determined from Strickler-Berg equation. ^[e] $\lambda_{exc} = 255$ nm. ^[f] $\lambda_{exc} = 280$ nm. ^[g] $\lambda_{exc} = 300$ nm ^[h] $\lambda_{exc} = 260$ nm. ^[i] Data taken from ref. ^[1] except k_f (S-B).



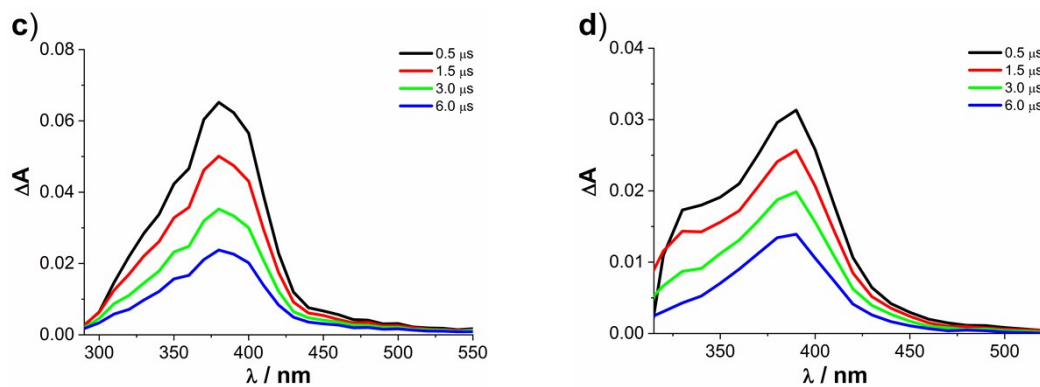


Figure S2. T-T absorption spectra of the compounds 1 (a), 2-C (b), 3-C (c) and 3-Si (d) in acetonitrile, $\lambda_{\text{exc}} = 266$ nm.

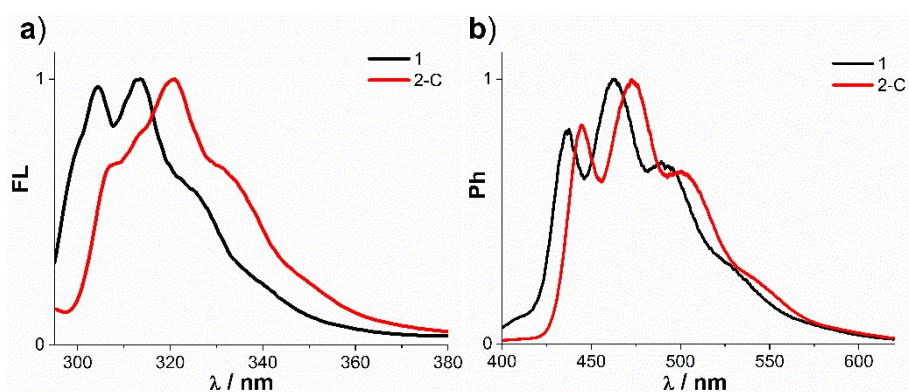


Figure S3. Normalized (a) fluorescence ($\lambda_{\text{exc}} = 280$ nm for 1 and $\lambda_{\text{exc}} = 285$ nm for 2-C) and (b) phosphorescence ($\lambda_{\text{exc}} = 290$ nm) spectra of 1 and 2-C in DCM:MeOH (1:1) at 77 K.

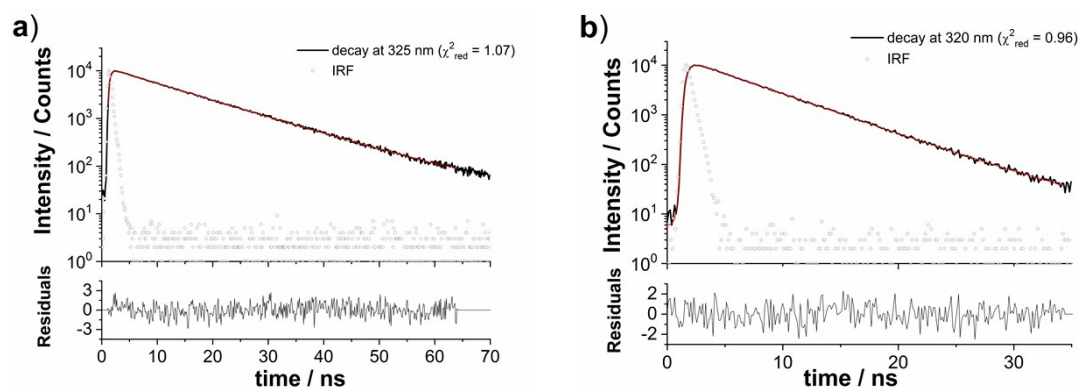


Figure S4. Fluorescence decays of 3-C (a) and 3-Si (b) in acetonitrile, $\lambda_{\text{exc}} = 255$ nm.

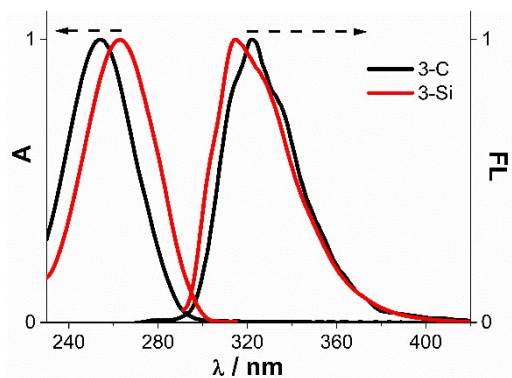


Figure S5. Stokes shift of 3-C and 3-Si in *n*-hexane.

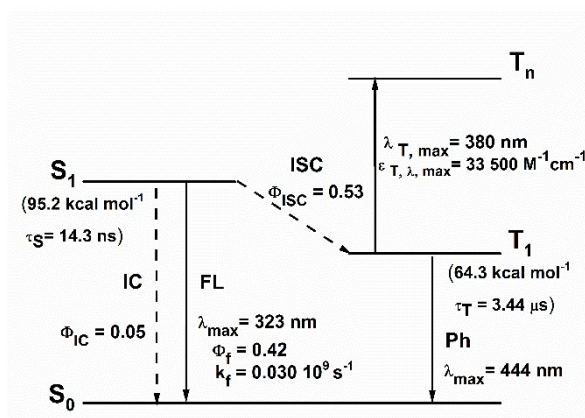


Figure S6. Deactivation processes of compound 2-C in acetonitrile.

Justification for comparing ratio of oscillator strength to ratio of radiative rates

The radiative rate constant for emission from the 0 vibrational level of the excited electronic state u to all the vibronic levels, l , in the electronic ground state l , standing for 'upper' and 'lower', respectively, can be expressed as^[2]

$$k_f = \frac{1}{\tau_0} \equiv A_{u0 \rightarrow l} \quad \text{Eq. (1)}$$

equation 20 in ref.^[2] is

$$A_{u0 \rightarrow l} = \sum_a A_{u0 \rightarrow la} = \frac{8\pi h n^3}{c^3} K |\mu_{lu}(0)|^2 \sum_a v_{u0 \rightarrow la}^3 \left| \int \Phi_{la}^* \Phi_{ub} dQ \right|^2 \quad \text{Eq. (2)}$$

using the identity

$$\sum_a \left| \int \Phi_{la}^* \Phi_{ub} dQ \right|^2 = 1 \quad \text{Eq. (3)}$$

it can be written that

$$\sum_a v_{u0 \rightarrow la}^3 \left| \int \Phi_{la}^* \Phi_{ub} dQ \right|^2 = \frac{\sum_a v_{u0 \rightarrow la}^3 \left| \int \Phi_{la}^* \Phi_{ub} dQ \right|^2}{\sum_a \left| \int \Phi_{la}^* \Phi_{ub} dQ \right|^2} \quad \text{Eq. (4)}$$

which approximately is equal to

$$\sum_a \nu_{u0 \rightarrow la}^3 \left| \int \Phi_{la}^* \Phi_{ub} dQ \right|^2 \approx \langle \nu_f^{-3} \rangle_{Av}^{-1} \quad \text{Eq. (5)}$$

and

$$k_f = A_{u0 \rightarrow l} = \frac{8\pi h n^3}{c^3} K |\mu_{lu}(0)|^2 \langle \nu_f^{-3} \rangle_{Av}^{-1} \quad \text{Eq. (6)}$$

Making the approximations that both K and $\langle \nu_f^{-3} \rangle_{Av}^{-1}$ are respectively the same in 3-Si and 3-C, the ratio of radiative rates is

$$\frac{k_f^{3Si}}{k_f^{3C}} = \frac{|\mu_{lu}(0)|^{23Si}}{|\mu_{lu}(0)|^{23C}} \quad \text{Eq. (7)}$$

The assumption that

$$\langle \nu_f^{-3} \rangle_{Av}^{-13Si} \approx \langle \nu_f^{-3} \rangle_{Av}^{-13C} \quad \text{Eq. (8)}$$

seems to hold in the case of 3-Si and 3-C because their fluorescence spectral shapes and positions are similar.

If the oscillator strength and the transition moment squared are in the following relationship

$$f = \frac{2m}{\hbar^2} (E_u - E_l) |\mu_{lu}(0)|^2 \quad \text{Eq. (9)}$$

then it can be written that

$$\frac{f^{2Si}}{f^{2C}} = \frac{|\mu_{lu}(0)|^{22Si}}{|\mu_{lu}(0)|^{22C}} \quad \text{Eq. (10)}$$

and finally we end up with

$$\frac{k_f^{3Si}}{k_f^{3C}} \approx \frac{f^{2Si}}{f^{2C}} \quad \text{Eq. (11)}$$

as long as we can expect the transition moments squared of 3-Si and 2-Si to be similar and likewise for 3-C and 2-C.

Based on the results presented in Table 1 from the current work

$$\frac{k_f^{3Si}}{k_f^{3C}} = \frac{0.112 \times 10^9}{0.035 \times 10^9} = 3.2 \quad \text{Eq. (12)}$$

and

$$\frac{f^{2Si}}{f^{2C}} = \frac{0.006}{0.003} = 2 \quad \text{Eq. (13)}$$

these numbers are in a good agreement given all the approximations above. This leads to the conclusion that the difference in the transition moments squared are the reason that the radiative rate is larger in 3-Si than the radiative rate in 3-C.

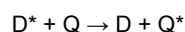
Direct and sensitized laser flash photolysis, determination of ϵ_T and Φ_{ISC}

The triplet-triplet (T-T) molar absorption coefficients ϵ_T of the investigated compounds 1, 2-C, 3-C and 3-Si were determined in the sensitized laser flash photolysis experiment using energy-transfer method.^[3] Benzophenone (BP) and xanthone (Xn) were used as triplet sensitizers (energy donors, D). The measurements with Xn and BP were performed using excimer ($\lambda_{exc} = 308$ nm) and YAG ($\lambda_{exc} = 355$ nm) lasers, respectively.

The molar triplet absorption coefficients of the quenchers (Q = 1, 2-C, 3-C and 3-Si) were determined based on the known values of the ϵ_T for the sensitizers. The molar absorption coefficients ϵ_T for BP in acetonitrile was taken to be $\epsilon_{520} = 6\,500 \text{ M}^{-1} \text{ cm}^{-1}$ ^[4] and for the Xn it was $\epsilon_{620} = 15\,750 \text{ M}^{-1} \text{ cm}^{-1}$ in acetonitrile.

The ϵ_{620} of Xn was determined using the relative actinometry method (see Eq. (16)) and 4-carboxybenzophenone (4-CB) as actinometer ($\epsilon_{535}(4\text{-CB})= 6\ 250\ \text{M}^{-1}\ \text{cm}^{-1}$ [5] $\Phi_{ISC}(4\text{-CB})= 1$ and $\Phi_{ISC}(\text{Xn})= 0.97$ [6])

To determine ϵ_T of compounds 1 and 3-Si xanthone was used as the energy donor and to determine ϵ_T of compounds 2-C and 3-C benzophenone was the energy donor



$$\epsilon_Q = \epsilon_D \frac{\Delta A_Q}{\Delta A_D \cdot P_{tr}} \quad \text{Eq. (14)}$$

$$P_{tr} = \frac{k_q[Q]}{k_q[Q] + k_d} \quad \text{Eq. (15)}$$

where

ϵ_D - T-T molar absorption coefficient of the energy donor (Xn or BP)

ϵ_Q - T-T molar triplet absorption coefficient of the quenchers Q (1, 2-C, 3-C, 3-Si)

ΔA_D - absorbance of Xn or BP measured at the maximum of T-T absorption spectra, i.e. 620 nm and 520 nm, respectively

ΔA_Q - absorbance of the investigated compounds 1, 2-C, 3-C, 3-Si measured at the maximum of T-T absorption spectra, i.e. at 360 nm, 380 nm, 380 nm, 370 nm, respectively

P_{tr} - probability of the energy transfer

k_q - quenching rate constant (energy transfer rate constant), determined from Stern-Volmer equation

[Q]- concentration of quencher (investigated compound)

k_d - deactivation rate constant without quencher ($D^* \rightarrow D$)

Intersystem crossing quantum yield of the investigated compounds (X) were calculated in the direct flash photolysis experiment using the relative actinometry method. Compound used as an actinometer for all investigated compounds was benzophenone. Excitation source was YAG laser, $\lambda_{exc}= 266\ \text{nm}$.

$$\Phi_{ISC}^X = \frac{\Delta A_X(\lambda_1) \cdot \epsilon_R(\lambda_2)}{\Delta A_R(\lambda_2) \cdot \epsilon_X(\lambda_1)} \cdot \Phi_{ISC}^R \quad \text{Eq. (16)}$$

where

$A_{266}(X)= A_{266}(\text{BP})$

X – investigated compound (1, 2-C, 3-C and 3-Si)

R- relative actinometer

Φ_{ISC}^R - quantum yield of intersystem crossing for actinometer ($\Phi_{ISC}^{BP} = 1$ [7])

$\Delta A_X(\lambda_1)$ - absorbance of the investigated compound X measured at the maximum of its T-T absorption spectra

$\Delta A_R(\lambda_2)$ - absorbance of the actinometer measured at the maximum of the T-T absorption spectra ($\lambda_2= 520\ \text{nm}$)

$\epsilon_X(\lambda_1)$ - the T-T molar absorption coefficients of the investigated compounds at the maximum of their T-T absorption spectra

$\epsilon_R(\lambda_2)$ - the T-T molar absorption coefficients of the actinometer at the maximum of T-T absorption spectra (520 nm), which is $\epsilon_{520}= 6\ 500\ \text{M}^{-1}\ \text{cm}^{-1}$ [4]

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