### **Supporting Materials for**

# Silicon(IV) complexes of octaaryl substituted porphyrazines and corrolazines: Influence of the macrocycle contraction on spectral-luminescence, acid-base and redox properties

Ekaterina D. Rychikhina, Svetlana S. Ivanova, Veronika Novakova, Pavel A. Stuzhin

<sup>a.</sup> Research Institute of Macroheterocycles, Ivanovo State University of Chemistry and Technology, RF-153000 Ivanovo, Russia. <sup>b.</sup> Faculty of Pharmacy in Hradec Kralove, Charles University, 500 05 Hradec Kralove, Czech Republic



**Figure S1.** Chromato mass spectrum and MALDI TOF mass spectrum of the reaction mixture of diminoimide synthesis, illustrating the formation of its oligomerization.



Figure S2. UV-vis spectra of the dihydroxy silicon octaarylporphyrazines in CH<sub>2</sub>Cl<sub>2</sub>.



Figure S3. The mass spectra of compound 3a (Si octaphenylporphyrazine) and presumably its pentapyrrolic derivative, contained in the purple fraction.



Figure S4. The absorption spectra of  $(Pr_3SiO)SiCz(^{t}BuPh)_8$  (5b) and its porphyrazine precursor  $(Pr_3SiO)_2SiPz(^{t}BuPh)_8$  (4b) in  $CH_2Cl_2$ .



**Figure S5.** MALDI-TOF mass spectra of  $(Pr_3SiO)_2SiP_2Ph_8$  (**4a**) (green line),  $(Pr_3SiO)_2SiP_2('BuPh)_8$  (**4b**) (red line) and  $(Pr_3SiO)SiC_2Ph_8$  (**5a**) (black line).



Figure S6,A. The IR spectra of the dihydroxy silicon octaarylporphyrazines 3a,b.



**Figure S6,B.** IR spectra of  $(Pr_3SiO)_2SiPzPh_8$  (4a) (green line),  $(Pr_3SiO)_2SiPz(^tBuPh)_8$  (4b) (red line) and  $(Pr_3SiO)SiCzPh_8$  (5a) (black line) (KBr pellet)

### IR spectra of the SiPz and SiCz complexes



Figure S7,A. <sup>1</sup>H NMR spectrum of (Pr<sub>3</sub>SiO)<sub>2</sub>SiPzPh<sub>8</sub> (4a) in CDCl<sub>3</sub>.



Figure S7,B. <sup>1</sup>H NMR spectrum of (Pr<sub>3</sub>SiO)<sub>2</sub>SiPz(<sup>*t*</sup>BuPh)<sub>8</sub> (4b) in C<sub>6</sub>D<sub>6</sub>.



Figure S7,C. <sup>1</sup>H NMR spectrum of (Pr<sub>3</sub>SiO)SiCzPh<sub>8</sub> (5a) in CDCl<sub>3</sub>.



Figure S7,D. <sup>13</sup>C NMR spectrum of (Pr<sub>3</sub>SiO)SiCzPh<sub>8</sub> (6a) in CDCl<sub>3</sub>.



Photopysical properties of the SiPz and SiCz complexes

**Figure S8,A**. Absorption (black line), emission (red line) and excitation (green line) of  $(HO)_2SiPzPh_8$  (**3a**) in THF and DMF, and  $(Pr_3SiO)_2SiPz(^tBuPh)_8$  (**4b**) in DMF ( $\lambda_{ex} = 590$  nm,  $\lambda_{em} = 660$  nm).



**Figure S8,B**. Fluorescence decay for  $(Pr_3SiO)_2SiPzPh_8$  (4a) and  $(Pr_3SiO)SiCzPh_8$  (5a) in DMF. Excitation wavelength  $\lambda_{ex} = 600$  nm.

#### 1200 1,2 -1000 1,0 y = 6,6417x y = 3,6795x R<sup>2</sup> = 0,9992 1000 800 R<sup>2</sup> = 0,9991 800 In(A<sub>0</sub>/A<sub>1</sub>) 1,0 600 In(A<sub>n</sub>/A<sub>t</sub>) 600 0,8 400 400 0,8 200 200 0<del>4</del> 0 Abs 0,6 50 150 time, s 200 250 100 sqe 0,6 0 <del>|</del> 20 40 60 80 100 120 140 160 180 (OH)<sub>2</sub>-SiPh<sub>8</sub>Pz in DMF time, s (OSiPr<sub>3</sub>)<sub>2</sub>-SiPh<sub>8</sub>Pz 0,4 0 s 0,4 -0s 50 s 120 s 40 s 0,2 - 180 s - 240 s 80 s 0,2 120 s 160 s 0.0 0,0 700 400 400 600 Wavelenght, nm 500 600 700 800 800 500 Wavelength, nm 1,2 2500 y = 36,411x R<sup>2</sup> = 0,999 100 y = 12,908x 1,0 2000 R<sup>2</sup> = 0,9971 1,0 · 800 In(A<sub>0</sub>/A<sub>1</sub>) (<sup>1</sup>4/<sup>0</sup>4) 1000 UI 600 0.8 0,8 400 200 500 sqe Vps SqP 0,6 0 20 40 50 90 0 10 60 70 80 time, s Pr<sub>3</sub>SiO-SiPh<sub>8</sub>Cz 10 20 time, s (Pr<sub>3</sub>SiO)<sub>2</sub>-Si(*t*BuPh<sub>8</sub>)Pz 0,4 0,4 0 s 0 s 15 s 20 s 0,2 30 s 0.2 40 s 45 s 60 s 60 s 80 s 0,0 0,0 400 500 700 400 500 600 700 800 600 800 Wavelength, nm Wavelength, nm

## Photochemical properties of the SiPz and SiCz complexes

**Figure S9.** The changes of absorption spectra upon irradiation time in air saturated DMF solution containing DPBF and the photosensitizer (Si complex). Insets: logarithmic dependencies of absorbance on irradiation time at 415 nm.



**Figure S10,A**. Cyclic voltamograms of  $(Pr_3SiO)_2SiPzPh_8$  (4a) (black line) and  $(Pr_3SiO)SiCzPh_8$  (5a) (green line) in pyridine with ferrocene. Sweep rate was 25 mV/s.



**Figure S10,B.** Cyclic voltamograms of  $(Pr_3SiO)_2SiPzPh_8$  (4a) (green line) and  $(Pr_3SiO)SiCzPh_8$  (5a) (black line) in CH<sub>2</sub>Cl<sub>2</sub> with ferrocene. Sweep rate was 25 mV/s.



Figure S10,C. Cyclic voltamograms of  $(Pr_3SiO)SiCzPh_8$  (5a) in DMF (left) and in DMF with ferrocene (right). Sweep rate was 25 mV/s.