

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

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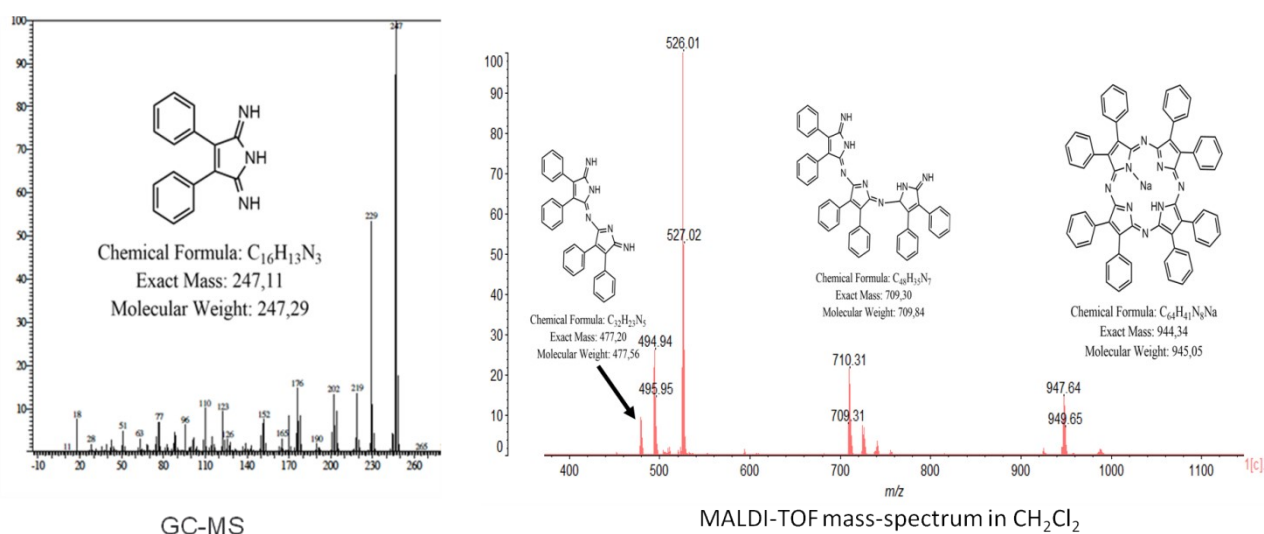


Figure S1. Chromato mass spectrum and MALDI TOF mass spectrum of the reaction mixture of diminoimide synthesis, illustrating the formation of its oligomerization.

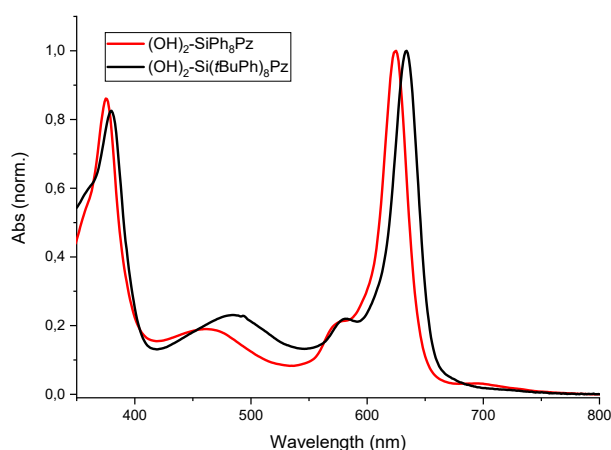


Figure S2. UV-vis spectra of the dihydroxy silicon octaarylporphyrazines in CH₂Cl₂.

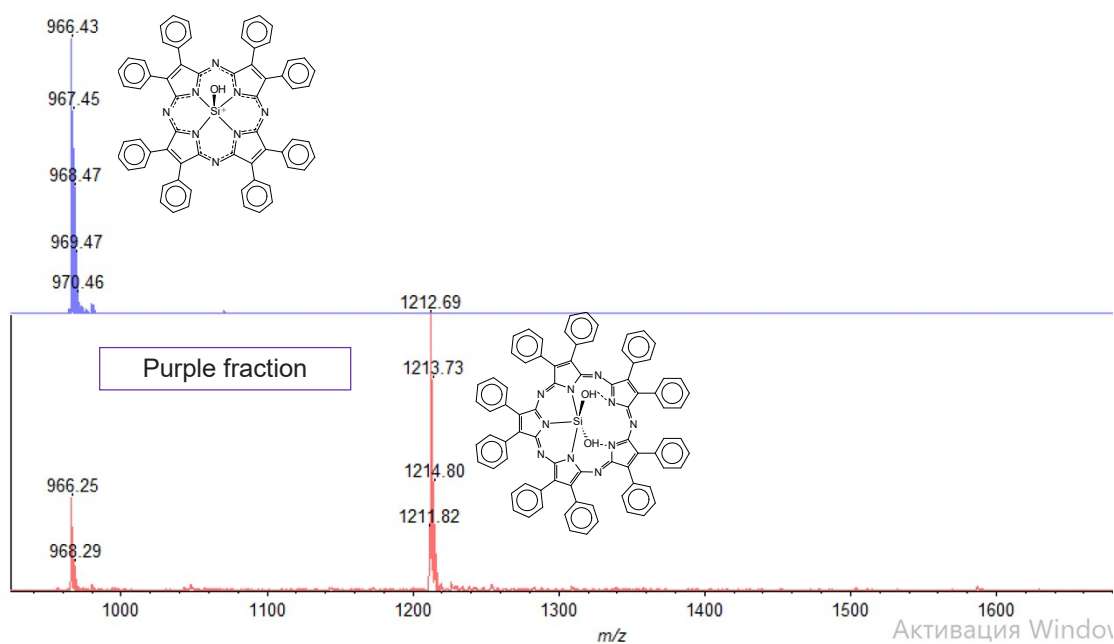


Figure S3. The mass spectra of compound **3a** (Si octaphenylporphyrazine) and presumably its pentapyrrolic derivative, contained in the purple fraction.

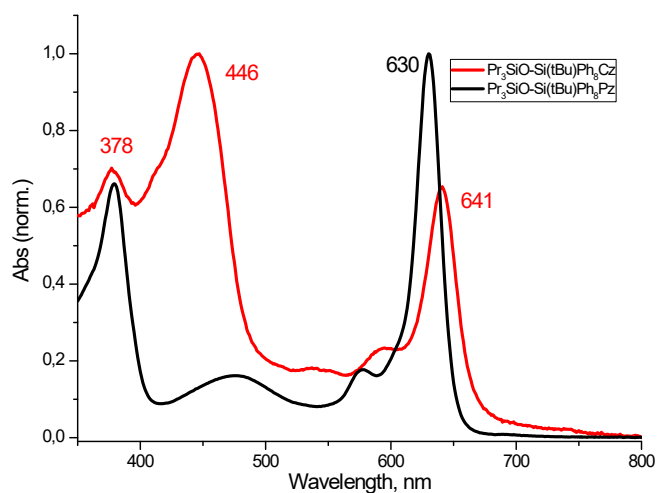


Figure S4. The absorption spectra of $(\text{Pr}_3\text{SiO})\text{SiCz}(\text{tBuPh})_8$ (**5b**) and its porphyrazine precursor $(\text{Pr}_3\text{SiO})_2\text{SiPz}(\text{tBuPh})_8$ (**4b**) in CH_2Cl_2 .

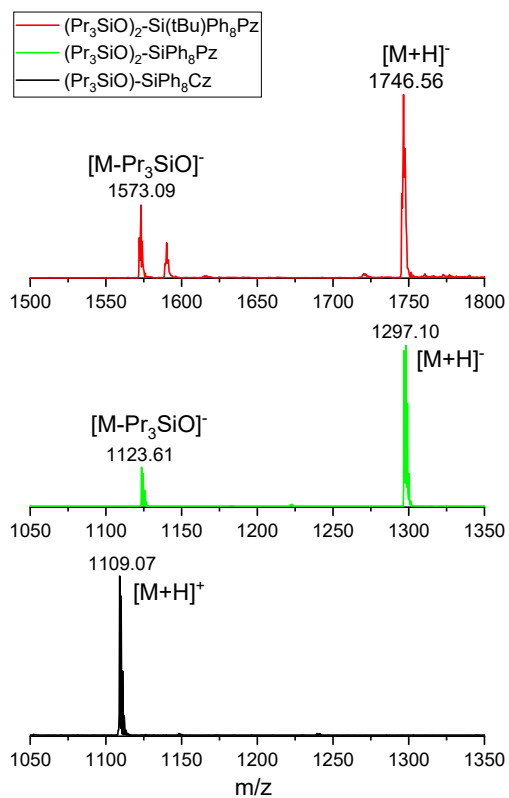


Figure S5. MALDI-TOF mass spectra of (Pr₃SiO)₂SiPzPh₈ (**4a**) (green line), (Pr₃SiO)₂SiPz(*t*BuPh)₈ (**4b**) (red line) and (Pr₃SiO)SiCzPh₈ (**5a**) (black line).

IR spectra of the SiPz and SiCz complexes

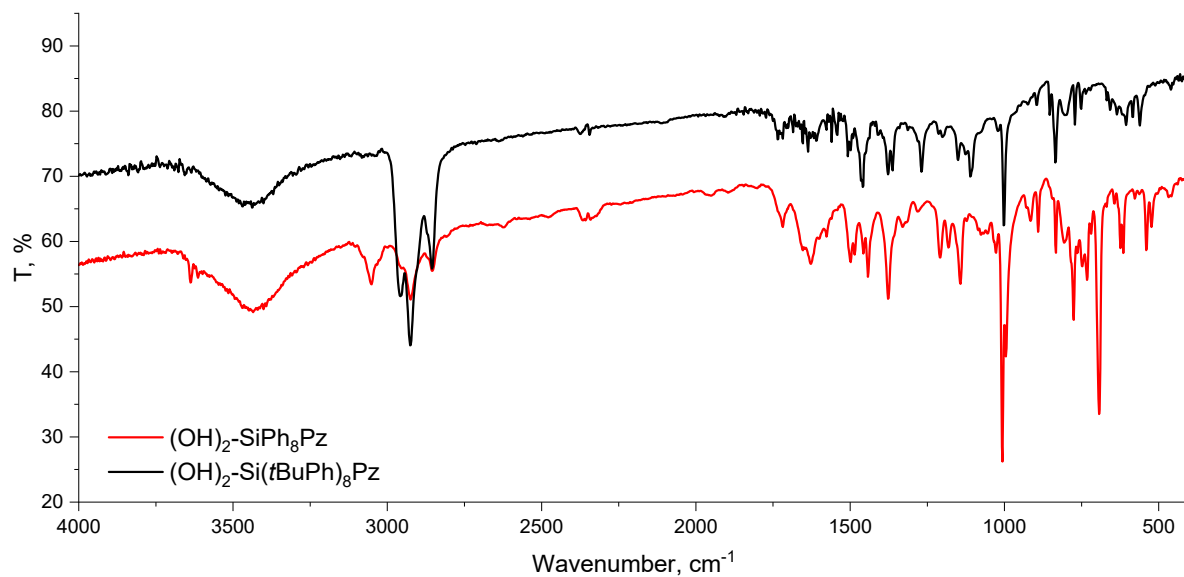


Figure S6,A. The IR spectra of the dihydroxy silicon octaarylporphyrazines **3a,b**.

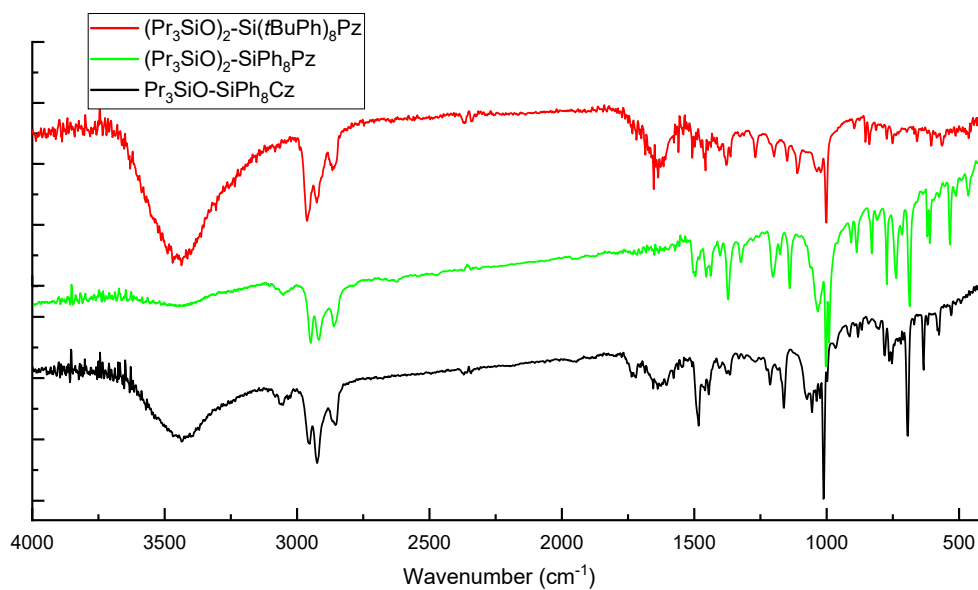


Figure S6,B. IR spectra of (Pr₃SiO)₂SiPzPh₈ (**4a**) (green line), (Pr₃SiO)₂SiPz(*t*BuPh)₈ (**4b**) (red line) and (Pr₃SiO)SiCzPh₈ (**5a**) (black line) (KBr pellet)

NMR spectra of the SiPz and SiCz complexes

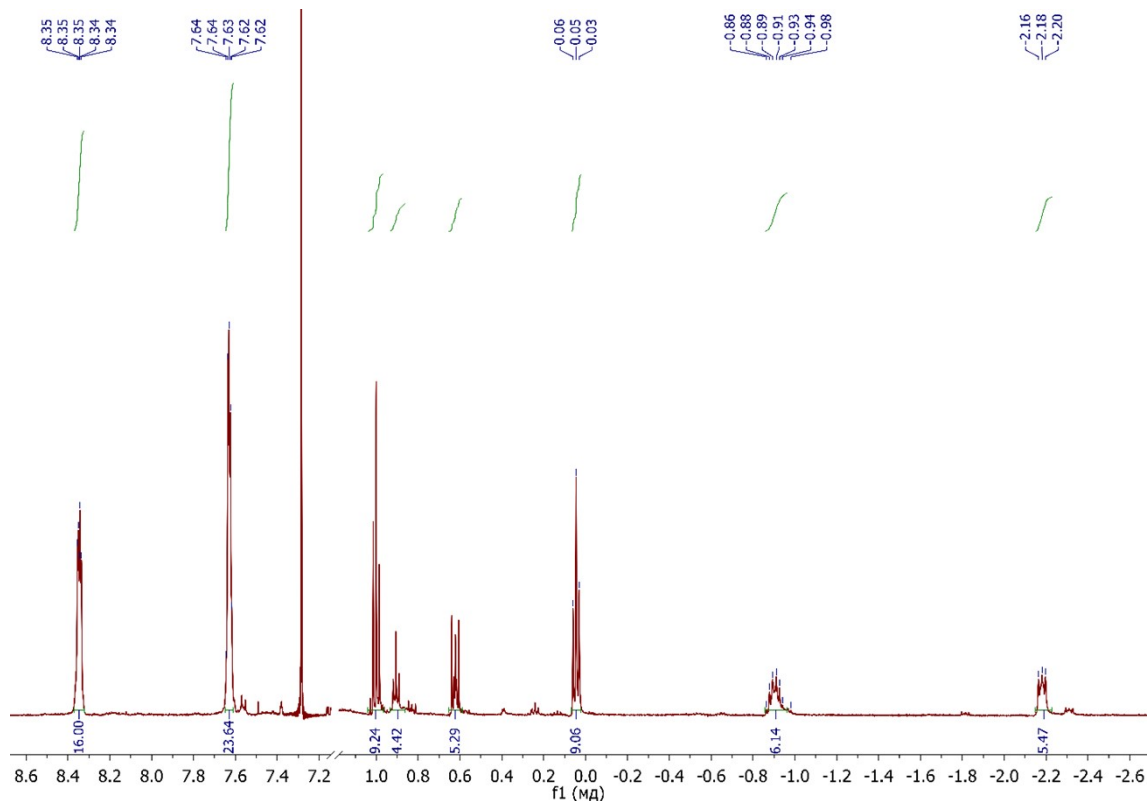


Figure S7.A. ^1H NMR spectrum of $(\text{Pr}_3\text{SiO})_2\text{SiPzPh}_8$ (**4a**) in CDCl_3 .

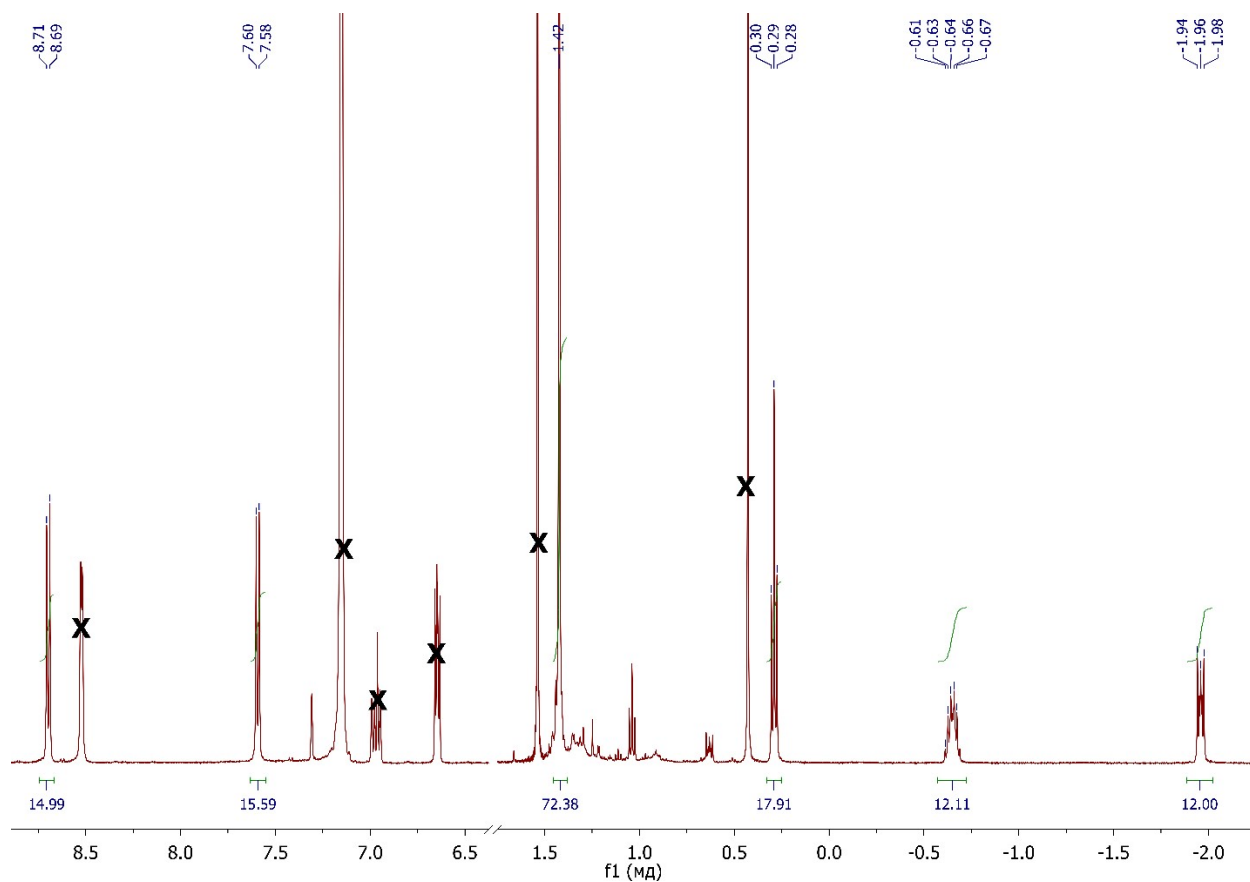


Figure S7.B. ^1H NMR spectrum of $(\text{Pr}_3\text{SiO})_2\text{SiPz}(t\text{BuPh})_8$ (**4b**) in C_6D_6 .

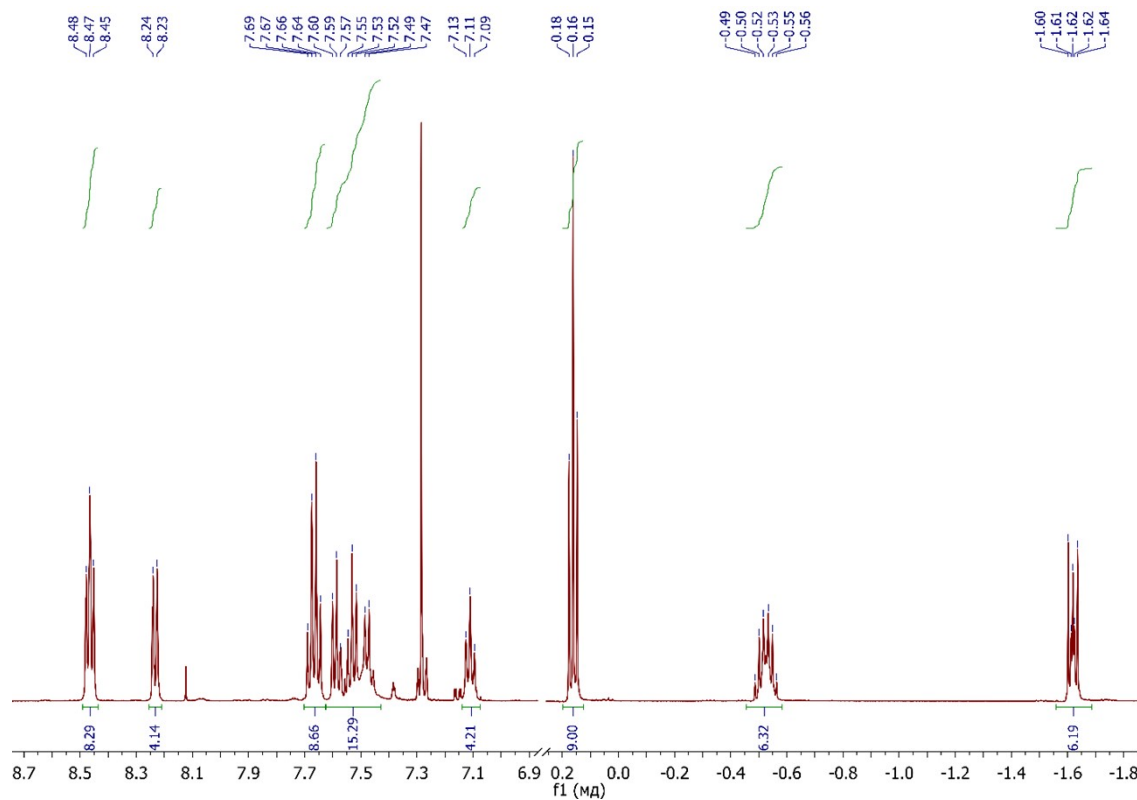


Figure S7,C. ^1H NMR spectrum of $(\text{Pr}_3\text{SiO})\text{SiCzPh}_8$ (**5a**) in CDCl_3 .

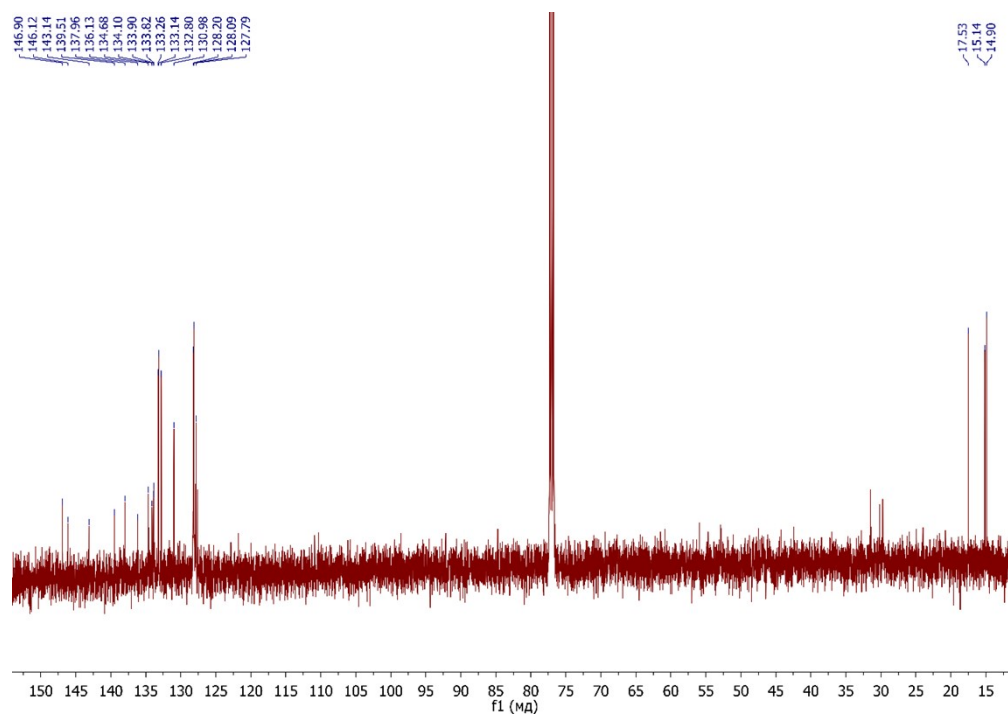


Figure S7,D. ^{13}C NMR spectrum of $(\text{Pr}_3\text{SiO})\text{SiCzPh}_8$ (**6a**) in CDCl_3 .

Photophysical properties of the SiPz and SiCz complexes

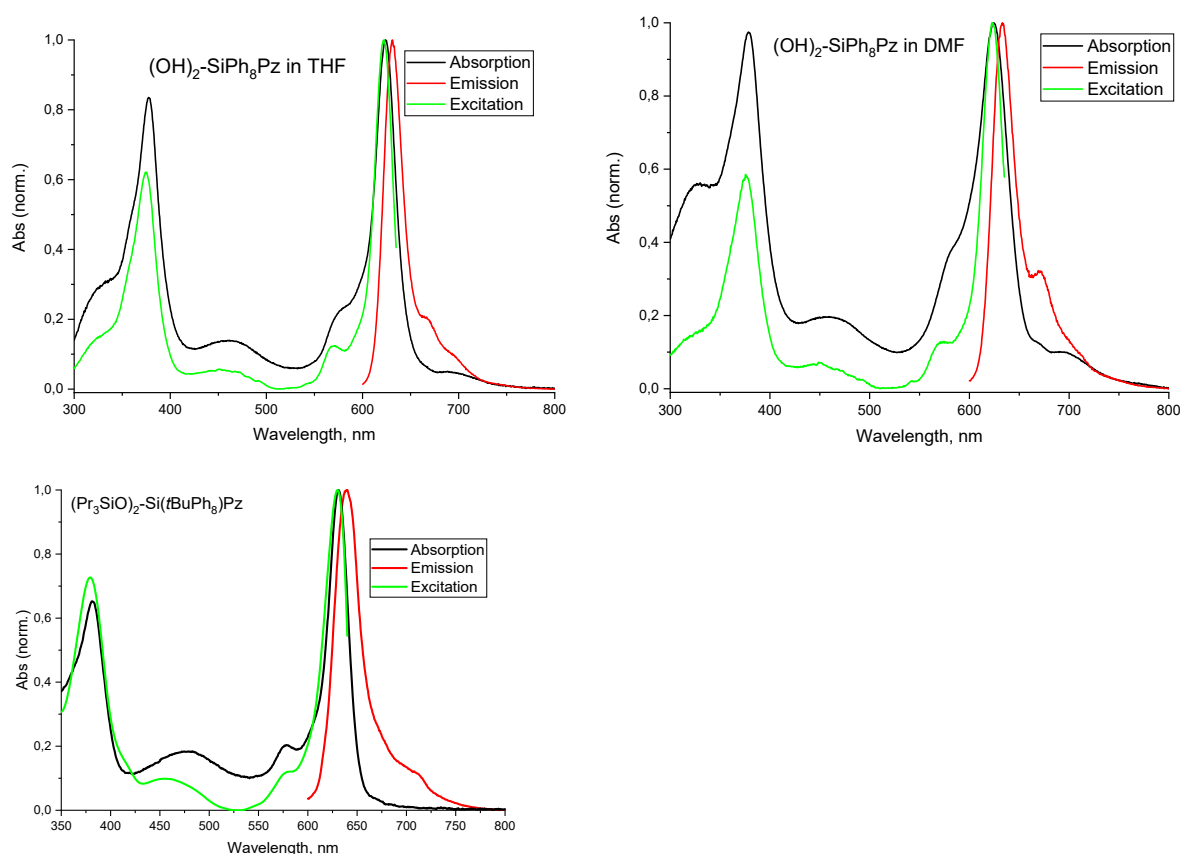


Figure S8,A. Absorption (black line), emission (red line) and excitation (green line) of $(\text{HO})_2\text{SiPzPh}_8$ (**3a**) in THF and DMF, and $(\text{Pr}_3\text{SiO})_2\text{SiPz}(t\text{BuPh}_8)_8$ (**4b**) in DMF ($\lambda_{\text{ex}} = 590$ nm, $\lambda_{\text{em}} = 660$ nm).

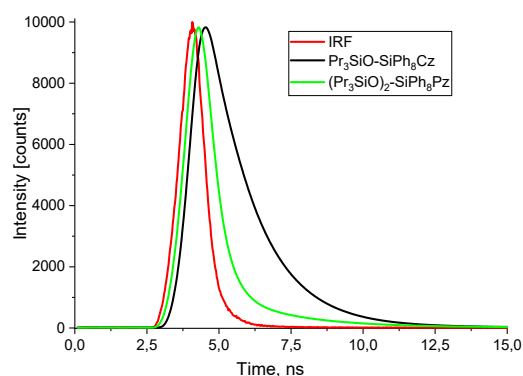


Figure S8,B. Fluorescence decay for $(\text{Pr}_3\text{SiO})_2\text{SiPzPh}_8$ (**4a**) and $(\text{Pr}_3\text{SiO})\text{SiCzPh}_8$ (**5a**) in DMF. Excitation wavelength $\lambda_{\text{ex}} = 600$ nm.

Photochemical properties of the SiPz and SiCz complexes

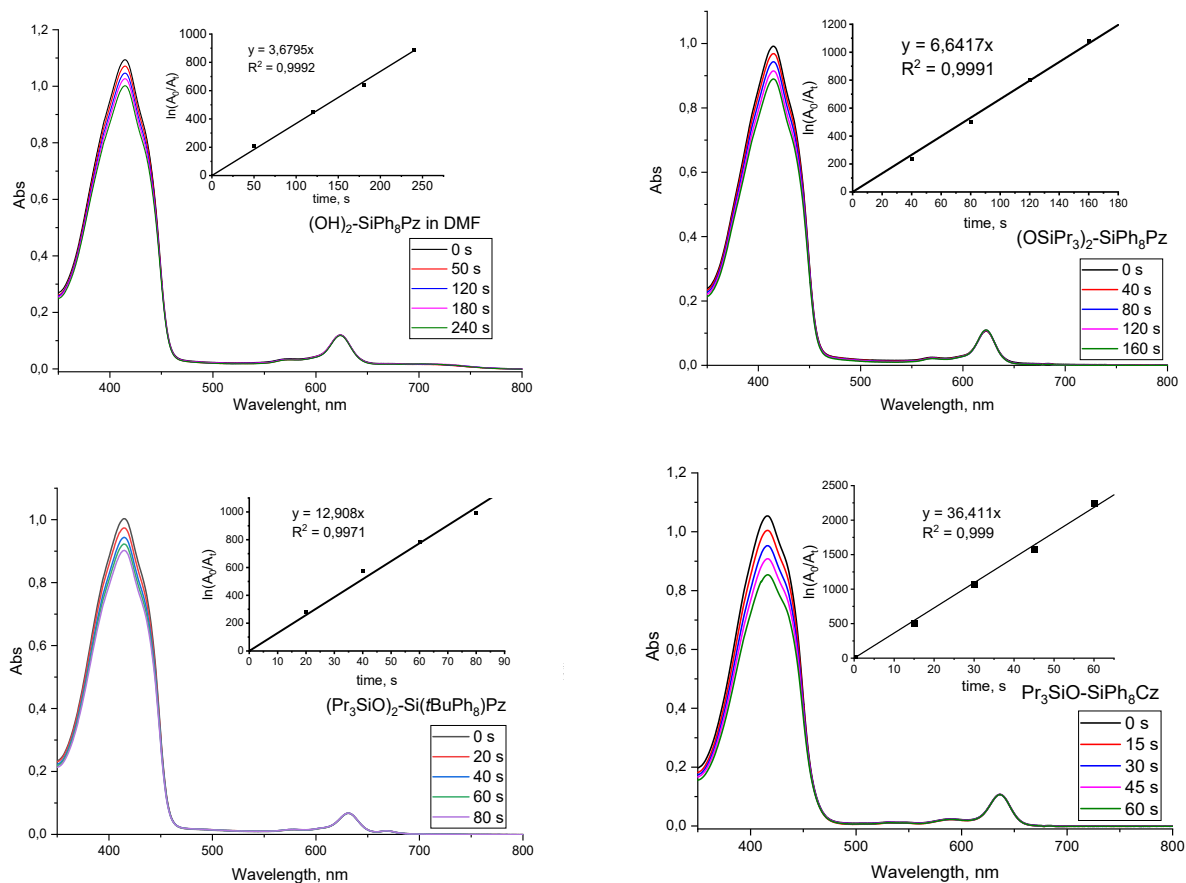


Figure S9. The changes of absorption spectra upon irradiation time in air saturated DMF solution containing DPBF and the photosensitizer (Si complex). Insets: logarithmic dependencies of absorbance on irradiation time at 415 nm.

Electrochemical properties of the SiPz and SiCz complexes

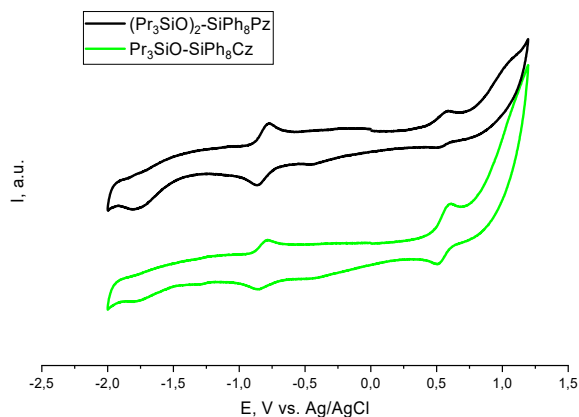


Figure S10,A. Cyclic voltamograms of $(\text{Pr}_3\text{SiO})_2\text{SiPzPh}_8$ (**4a**) (black line) and $(\text{Pr}_3\text{SiO})\text{SiCzPh}_8$ (**5a**) (green line) in pyridine with ferrocene. Sweep rate was 25 mV/s.

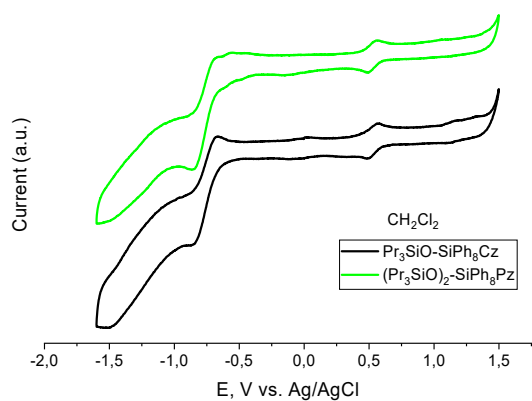


Figure S10,B. Cyclic voltamograms of $(\text{Pr}_3\text{SiO})_2\text{SiPzPh}_8$ (**4a**) (green line) and $(\text{Pr}_3\text{SiO})\text{SiCzPh}_8$ (**5a**) (black line) in CH_2Cl_2 with ferrocene. Sweep rate was 25 mV/s.

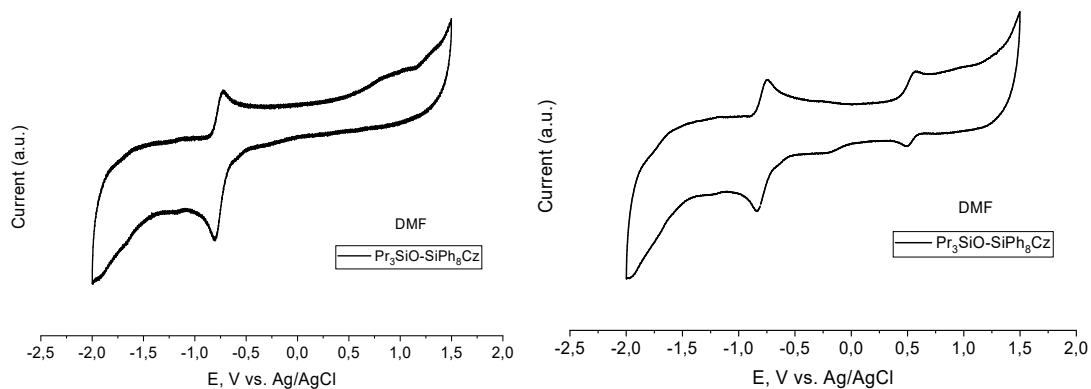


Figure S10,C. Cyclic voltamograms of $(\text{Pr}_3\text{SiO})\text{SiCzPh}_8$ (**5a**) in DMF (left) and in DMF with ferrocene (right). Sweep rate was 25 mV/s.